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# An Evaluation of Supercritical Water Oxidation Technology

by

David Neil Kupferer

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Submitted to the Department of Materials Science and Engineering
in Partial Fulfillment of the Requirements for the Degree of

Master of Engineering in Materials Science and Engineering
at the
Massachusetts Institute of Technology

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Signature of Author: ..........................................................................................
Department of Materials Science and Engineering
May 10, 2002

Certified by: ..........................................................................................
Ronald M. Latanision
Professor of Materials Science and Engineering
Professor of Nuclear Engineering
Thesis Supervisor

Accepted by: ..........................................................................................
Harry L. Tuller
Professor of Ceramics and Electronic Materials
Chair, Departmental Committee on Graduate Students

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## Abstract

Water exists in a supercritical state above its supercritical temperature, 374.2 °C, and pressure, 22.1 MPa. When organic waste is placed in a reactor with supercritical water, the vaporization, oxidation, and destruction of the organic compounds is achievable in a short time span, typically less than one minute. This process has come to be known as Supercritical Water Oxidation (SCWO). Potential applications for this developing technology include: military wastes, such as chemical agents and munitions, shipboard waste, industrial wastes, such as paper mill effluent and pharmaceutical waste, and municipal waste. It is a common belief among those involved in the development of SCWO that other niche applications will surface with time.

Many SCWO reactor designs have been developed to meet the needs of these varied applications. The two basic designs are the tubular and vessel design, to which many technical augmentations have been made to develop reactor designs such as the "transpiring wall reactor" and the "deep-well" reactor. The primary challenges that are inhibiting the rapid commercialization of SCWO include both engineering issues, such as corrosion, solids handling and scaling, and non-engineering issues, such as economics and public perception.

Many competitive technologies exist for the treatment of hazardous wastes. The two oldest technologies that are currently utilized in the majority of waste management applications are landfilling and incineration. Other technologies being developed and improved alongside of SCWO include: bio-treatment, wet air oxidation, plasma arc treatment, and adsorption. The international market for waste management and disposal is large, and as the policies and laws of the world become more environmentally protective, the development of alternative waste destruction technologies will become imperative. This paper explores the potential of SCWO to stake a claim in the future of daily waste management practices.

Thesis Supervisor: Ronald M. Latanision
Title: Professor of Materials Science and Engineering

## Biography

David Kupferer was born in Oak Park, Illinois on July 23, 1979. He was raised in Farmington Hills, Michigan from the age of 5 until he left for the University of Michigan in 1997. During the summer of 1999, David worked as a project engineer for North American Lighting, an automotive lighting design and manufacturing company. He then graduated from the University of Michigan with a Bachelor of Science degree in Mechanical Engineering in June of 2000. In August of 2000 David began working at, and continues to work for, the Defense Nuclear Facilities Safety Board (Board) in Washington DC. The Board is an agency in the executive branch of the government and is responsible for the oversight of the Department of Energy's defense nuclear facilities. In June of 2001, David began studying at the Massachusetts Institute of Technology to earn a Masters of Engineering degree in Materials Science and Engineering. He plans to graduate in June of 2002. Upon graduation David will begin a one-year position with Packer Engineering, a failure analysis consulting firm located in Naperville, Illinois.

# Acknowledgements

Without the contributions of many individuals, I would not be walking in the upcoming commencement ceremony on June 7th. I would first like to thank those who have been there for the long haul. My family has always been a very important part of my life and their unending support has been pivotal in my past and current successes. I love you guys.

My friends are the best. Zig, Bosker, Dilland, Alexa, Andrea, Higgins, Koby, Tommy O, Meade, Webs, Mac, Gabers, Sweet P, the Kennels, Hambone, Kristin, Kay, Gail, Hanna, Malon, Duncan, and all those I don't have the space to mention. My friends have been a cornerstone in my life, and I treasure the memories we have shared.

MIT is a wonderful place due primarily to the student body it is able to attract. Nowhere have I been introduced to so many intelligent, talented, and remarkable individuals. Most excel not only in academics, but also excel in all they choose to pursue. I have developed many new friendships in my time at MIT, and I hope many of them continue. Larry, Allison, Abel, Aleks, Nate, Grace, Robert, GJ, Amanda, Jeremy, and the list goes on and on. I wish them all nothing but the best, but know that luck will not be necessary in their inevitable success in academia, industry, and most importantly, life.

I want to thank the Professors at MIT who have taught me much about the art of engineering (my experience at MIT has demonstrated that engineering is not all science). Professors Lupis, Allen, Fitzgerald, Ballinger, Tuller, and many others help make the MIT community the most enlightening and exciting academic environment to which I have been witness. I would especially like to thank my advisor, Professor Latanision, for taking me on and introducing me to the world of SCWO.

And I always save the best for last. My fiancé. Her love and support has been the most important part of my life over the past three years. I love you Shan.

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## 1.0 Introduction

This thesis was written in the hope of achieving two objectives. The first objective is to bring together all the elements important to the commercialization of SCWO in a way the author hadn't seen after extensive literature and periodical research. Most technical writings on SCWO focus on either an account of the potential utilization of SCWO for a very specific application, such as destruction of military waste or shipboard waste treatment, or a review of a specific engineering problem SCWO development faces, such as corrosion or solids handling. The author hopes that this thesis will serve as a high-level survey of the majority of the elements important to the commercialization of SCWO technology. The second objective is to provide a basic analysis of the potential for SCWO commercialization in the area of municipal waste. The purpose of this objective is not for the author to feign omniscience and predict the future of SCWO technology, but more so to provide an extensive analysis of a hypothetical example of the commercial possibilities that exist for SCWO under the constrictive umbrella of today's base of knowledge.

## 2.0 Historical Perspective

### 2.1 History of Supercritical Fluids

Cagniard de la Tour discovered the phenomenon of supercritical fluids in 1822. It was another 60 years before Hannay and Hogarth learned that supercritical fluids possessed a unique power of extreme solubility. Research in the supercritical fluids area continued and in 1936, Pilat and Godlewicz filed the first U.S. patents that claimed the use of supercritical gases for separating molecular mixtures. German researcher Zosel explored the application of supercritical carbon dioxide science to extraction technology in the 1960's which led to one of the first commercial uses of supercritical fluids in producing hops extract that could be used for brewing beer in Germany.[18] This string of achievements led to the first international symposium focused on supercritical fluids which took place in 1978. The advancement of this technology still continues today, 180 years after the original discovery. B 1999 almost 1,800 patents had been filed worldwide related to supercritical fluid technology. The most commonly used supercritical fluids in today's industries are carbon dioxide, propane, butane, and fluoroform.[17] Other current commercial uses for supercritical fluid technology include: extraction of flavors from herbs and spices, production of low-nicotine tobacco, and decaffeination of both coffee and tea.[18]

## 2.2 History of Supercritical Water

Supercritical water was initially not a popular research topic for one major reason: water's critical temperature and pressure are much greater than those of the chemicals originally used in supercritical research and applications. For example, the critical temperature and pressure of water compared to carbon dioxide are 374 °C versus 31 °C and 22.1 MPa versus 7.4 MPa respectively. But finally, in 1966, a new branch of supercritical fluid research began when John Connolly published that hydrocarbons and water are completely miscible in all proportions in high temperature, high pressure water.[21] Wet Air Oxidation (WAO), the older cousin of supercritical water oxidation (SCWO), utilized this principle and was aggressively researched around the time of Connolly's publishing. Natural research instinct led researches to the idea of operating WAO reactors at even higher temperatures than was necessary to achieve WAO. Above water's supercritical temperature, it was discovered that organics could be oxidized and destroyed rapidly and efficiently. This discovery led to the first wave of patents regarding SCWO technology. In 1979, Thiel filed the first US patent that utilized supercritical water for oxidation.[19]

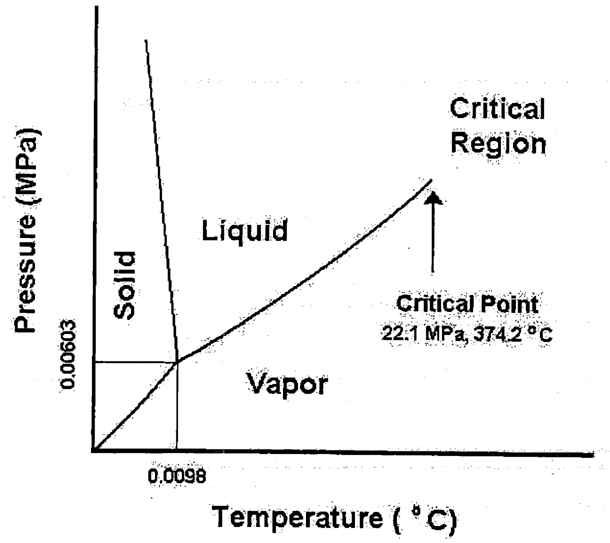

Figure 1. Pressure versus temperature diagram of water that illustrates the critical point and region

## 3.0 Properties of Supercritical Water

As can be seen in Figure 1, the vapor-liquid critical point of water exists at a

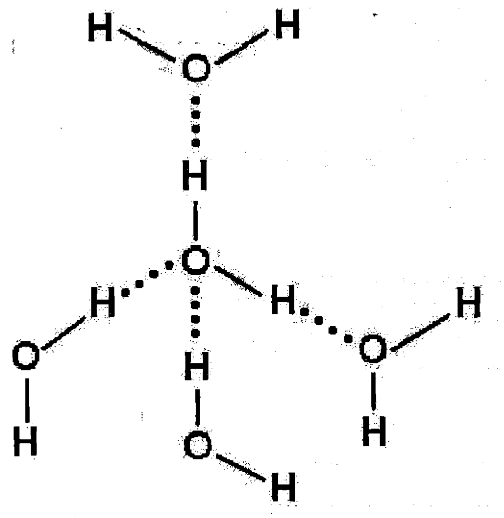

Figure 2. Diagram that illustrates the hydrogen bonds (the dotted lines) in liquid water at ambient conditions

temperature of 374.2 °C and a pressure 22.1 MPa.[6] Above this critical point, the hydrogen bonding (see Figure 2) in water molecules is almost entirely disrupted, so that the water molecules lose the ordering responsible for many of liquid water's characteristic properties.[7] These changes in water's characteristic properties include supercritical water behaving as a nonpolar rather than polar solvent. This is indicated by a decrease in the dielectric constant of water from 80 at ambient conditions to less than 5 above its critical point.[8] Other properties of water that change as the critical regime is approached and exceeded are diffusivity, ion mobility, density, and specific heat capacity. Specifically, as water approaches its critical point, the diffusivity and ion mobility in the water increase, the specific heat capacity of the water approaches infinity, and the water's density varies significantly with even small changes in temperature and pressure.[6] The density of supercritical water at 650 °C and 23.5 MPa is only one tenth that of liquid water.[7] The ionic dissociation constant in water decreases from $10^{-14}$ at room temperature to $10^{-23}$ at supercritical temperatures.[1] Figure 3 shows the effect of water approaching and exceeding the supercritical state on density, dielectric constant, hydrocarbon solubility, and organic solubility.

The reactions that occur between supercritical water and a wide variety of chemicals varies dramatically from the reactions that occur between liquid water at subcritical temperatures and those same chemicals. Under supercritical conditions, water generally has both the gaseous properties of being able to penetrate anything, while at the same time maintaining the liquid properties capable of dissolving materials into their various components.[9] Water solubility behavior in supercritical conditions is closer to that of high-pressure steam than that of liquid water.[7] For example, gases, including oxygen, nitrogen, and carbon dioxide, are completely miscible in the fluid.[4, 10] Also, nonpolar organic compounds with relatively high volatility will

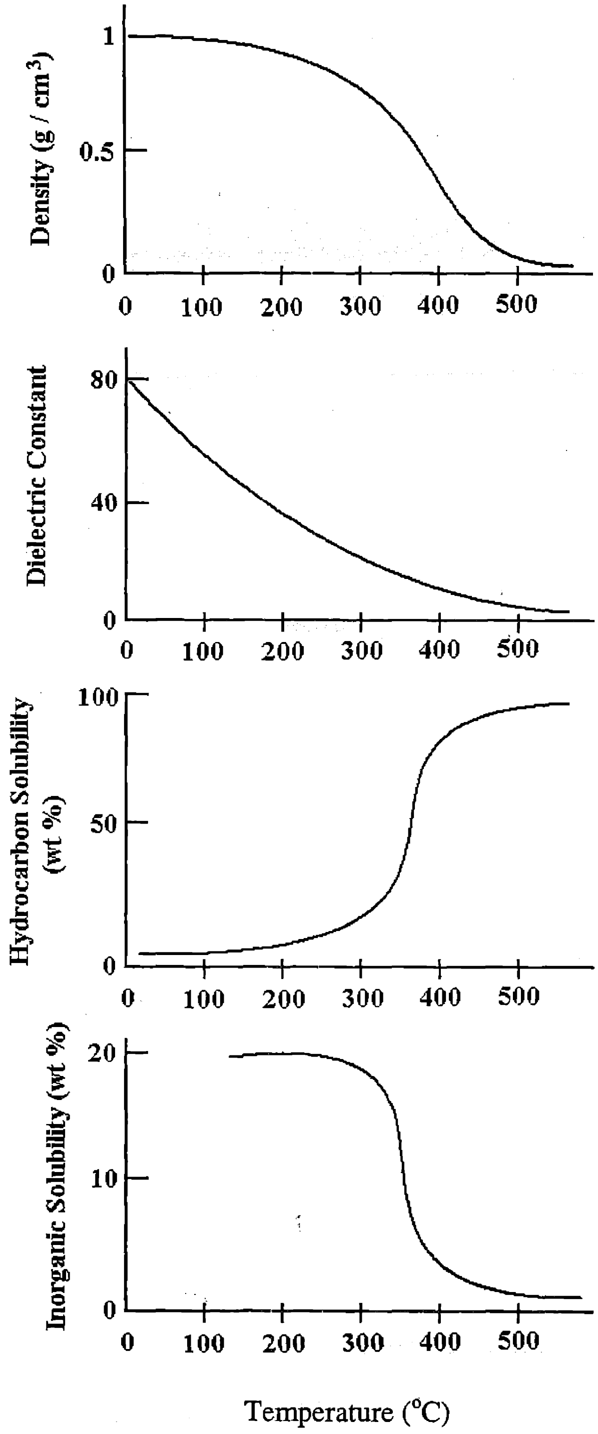

Figure 3. Graphical representations of water's characteristic properties graphed versus temperature. (plots assume supercritical pressure)

exist as vapors at typical supercritical water conditions, and hence will also be completely miscible with supercritical water.[7] The general rule is that in supercritical water conditions, organics are highly soluble while inorganics, including salts and metallic oxides, are highly insoluble.[11]

## 4.0 Supercritical Water Oxidation Theory

Supercritical water oxidation has also been known as hydrothermal oxidation to avoid any association with nuclear reactions. The term critical in supercritical water oxidation is meant to imply the notion that the water in the reactor is heated and pressurized to the supercritical regime as opposed to the potential implication that the water undergoes critical nuclear reactions.

Within the combination of supercritical water and an oxidant, the complete destruction of complex organic molecules is readily achievable.[6] Using the SCWO process, hazardous or toxic organic contaminants in aqueous wastes are rapidly oxidized at temperatures of about 600 °C, pressures of 24 to 30 MPa, a pH range of 2 to 12, and oxygen concentration levels ranging from parts-per-million up to whole percentage levels.[10] In this range of conditions, operating water densities can very significantly from 0.15 to 0.2 g / cm$^3$.[11] The ability to control high temperatures and pressures inside of a reactor vessel are widely understood, but monitoring and controlling the pH level in such an environment is relatively new territory. It is believed that the pH in the reactor and auxiliary equipment can be controlled though chemical additions, with chemicals such as sodium sulphate.

Since supercritical water is miscible in all proportions with oxygen, a homogeneous single phase results when organic compounds and oxygen are dissolved in supercritical water.[4] This single phase ensures intimate contact of the organic compound, oxygen molecules, and water molecules.[12] Due to this phenomenon, organic oxidation reaction rates are limited by reaction kinetics rather than by mass transfer. Therefore, very high waste conversion rates are possible within relatively short residence times. Typically in less than one minute, the organics are efficiently oxidized predominantly to carbon dioxide and water.[5] An example of the organic destruction sequence is shown in equations 1 and 2.

$$CH_4\ (g) + \tfrac{1}{2}\, O_2\ (g) <=> CO\ (g) + 2\ H_2\ (g) \qquad (1)$$

$$CO\ (g) + H_2O <=> CO_2\ (g) + H_2\ (g) \qquad (2)$$

## 5.0 The Supercritical Water Oxidation Process (see Figure 4)

Before reaching the reactor, aqueous organic waste, which may be combined with either a caustic solution or fuel, is pressurized and heated from ambient conditions to a pressure and temperature resembling that of the reactor vessel, typically about 500 to 600 °C and 24 to 30 MPa. The heated and pressurized waste stream is then mixed with an oxidant such as air or oxygen, or even possibly hydrogen peroxide despite its relatively high cost.[1] The incoming waste stream is limited to a specific range of potential heating value by either mixing waste streams of high and low organic content or diluting the waste stream with water. Fuel can also be added to the waste stream if the organic content of the stream is too low to sustain the energy required to operate the reactor.

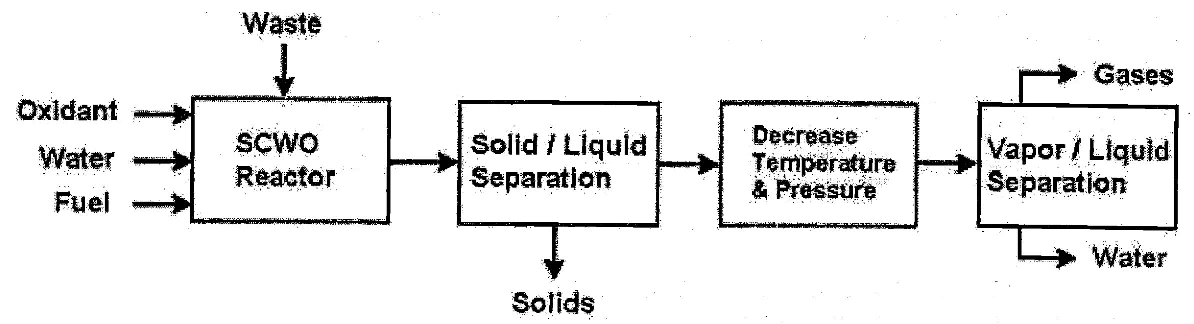

Figure 4. An illustration of the supercritical water oxidation process

Next, the stream flows into the reactor vessel and the organics in the stream spontaneously oxidize. Heat is released from the oxidation reaction, and the reactor vessel is capable reaching temperatures as high as 650 °C. The residence time required to achieve even very high destruction percentages (above 99.9%) is typically less than one minute. The majority of salts precipitate as quickly as the oxidation reactions occur due to their low solubility in supercritical water. Inorganic compounds such as metallic oxides or ash will not be substantially effected by the conversion to supercritical pressures and temperatures.

The waste stream leaves the reactor and is lowered to a subcritical temperature and pressure. The lowering of temperature and pressure causes the supercritical steam composition to separate to gases and liquids from the remaining solution.[1] The gaseous phase consists primarily of carbon dioxide and oxygen (nitrogen as well if air is used as the oxidant). The salts can be either redesolved into the supercritical water or removed as solids while the reactor is supercritical. It would be practically impossible to remove 100 percent of the salts during the supercritical treatment as the salts still retain some solubility in the supercritical vapor. Residuals such as heat, water, hydrochloric acid, sulfuric acid, carbon dioxide, oxygen, nitrogen, inorganic ionic species or salts, metallic oxides, and oxidized ash are either recoverable or environmentally acceptable.[5, 6] Since the process is run at relatively low temperatures compared to other thermal waste treatments, the temperatures are too low for the formation of $NO_x$ and $SO_x$, and therefore environmentally harmful gas production is minimized.[9]

The exothermic oxidation reactions that occur while the waste stream is in the reactor vessel produce heat that is recoverable in the form of steam. One possible immediate energetic use of the steam produced is to preheat the incoming feed stream through the use of heat exchangers.[12] It has been demonstrated that over 45% of the sludge heating value can be recovered as steam.[12] Another possible use of the hot steam that is generated would be the use of the steam in power generation.[22]

## 6.0 Supercritical Water Oxidation Applications

Hypothetically, any substance that can be fed into a stream and pumped to a high pressure can be treated by SCWO. The SCWO process is best suited, in terms of destruction efficiency and cost, for treating large volumes of dilute aqueous wastes, in the range of 1 - 20 mass percent organic composition, including waste contaminated with volatile organics.[1, 13] Realistically, due to the current state of the solids handling technology in typical SCWO systems, treatment of solids requires significant solids size reduction to about 0.004 inches or less.[5] That is not to say that solid wastes have been ruled out as a potential candidates for treatment through SCWO. This leaves an extremely wide base of mixtures and compounds that can be treated through the use of SCWO such as aqueous waste streams, sludges, and contaminated soils. Streams treated with SCWO may consist of acrylonitrile wastewater, cyanide, pesticide, PCB's, halogenated aliphatics and aromatics, aromatic hydrocarbons, spent caustic wastewaters containing phenolic compounds, MEK and organic nitrogen compounds. SCWO can treat municipal and industry sludges such as biological sludges, industrial organic chemicals, synthetics, paints, industrial organics, agricultural chemicals, explosives, petroleum and coal products, rubber, and plastic products.[24, 29]

With the broad range of potential treatment candidates there is an equally broad range of real-world applications for SCWO. The potential applications can be divided into three distinct categories based on their end user. These categories are: government applications, commercial applications, and applications that could be pertinent to both government and commercial use.

It is important to note that government environmental policy plays a very important role in the use of SCWO as a waste treatment method. Environmental laws and policies are the driving force behind the great majority of the companies and governments seeking to develop new technologies for cleaner waste disposal. After all, landfilling or incineration, both of which are currently cheaper than SCWO technology, could easily dispose of most waste streams. It is easy to see the common thread of environmental protection in the applications that are currently being aggressively pursued by the stakeholders of SCWO.

## 6.1 Government Applications

### 6.1.1 Military Applications

There are over 23,000 tons of chemical agents stored by the US government inside the continental United States. In January of 1993, the United States was one of 130 countries that signed the Chemical Weapons Convention. The Chemical Weapons Convention calls for the complete elimination of chemical weapons, both in storage and production, shortly after the turn of the century. Supercritical water oxidation has been shown to treat such chemical agents as VX, GB (sarin), and HD (mustard), and energetic materials such as TNT and Comp B. SCWO, therefore, could prove to be a critical technology in the timely destruction of such legacy military materials.[3]

### 6.1.2 Space Applications

NASA has explored the use of SCWO in the destruction of biomass and human metabolic waste created during long-term space flight. As missions in space increase in length, the timely remediation and treatment of the waste created while in space is a growing concern due to the importance of the weight and size of mission payloads. Conventional methods of storage will become more costly both quantitatively and qualitatively in the near future.

### 6.1.3 Department of Energy and Nuclear Applications

SCWO treatment may be utilized in the necessary volumetric reduction of radioactive waste through the destruction of the organic components of the wastes. This could potentially apply to both medical and research facilities, as well as nuclear facilities.[19] It is hoped that SCWO systems could decompose organic wastes such as gloves, plastic bottles and cation exchange resins.[10] The Department of Energy has made substantial investment of resources to research SCWO as an option for removing the organic components of mixed low-level radioactive wastes stored at several US DOE sites.[2]

### 6.1.4 Superfund Sites

There are at least 36,000 sites in the United States that are seriously contaminated by hazardous waste, the worst of which are often referred to as the Superfund Sites. It has been demonstrated that SCWO could be used to treat contaminated soil although important issues still need to be resolved on how to handle the solid soils in the reactor Although questions exist on handling solids soils in SCWO reactors, it has been demonstrated that SCWO can treat contaminated soils. One of the biggest problems associated with cleaning up the Superfund sites is answering the question "how clean is clean?" SCWO's high destruction efficiency, above 99 percent, could help to answer this question.

## 6.2 Commercial Applications

### 6.2.1 Paper Mill Effluent

The volume of paper mill waste produced in the US is enormous. In the 1980s, each ton of pulp produced about 25,000 gallons of contaminated wastewater from the chlorine-bleaching process.[32] 73 million tons of paper products were produced in 1986, which equates to an equivalent total waste flow of 219 cubic meters per second. This flow is larger than some major rivers including the Merrimack in Massachusetts whose flow is 205 cubic meters per second.[33] Paper mill effluent contains between 250 and 300 chemicals, including dissolved organics, methanol, turpenes, acetone, fatty acids, cellulose decomposition products, lignins and tannins, sulphides, mercaptans, resin-acids, soaps, chlorine, and caustic soda.[31] Given the large variety of organic waste found in paper mill effluent, SCWO is a great waste treatment candidate if and when restrictions tighten on the dumping and storage of these types of hazardous wastes.

### 6.2.2 Pharmaceutical Waste

Pharmaceutical waste includes expired or discarded medical drugs and waste materials generated during the manufacturing of pharmaceuticals. The wide range of waste that is produced includes a variety of hazardous organic compounds. Treatment of this waste is a necessary and final step in the production of pharmaceuticals. As in the case of paper mill effluent treatment, the driving force behind SCWO treatment is its high destruction efficiency. The question will be raised in the years and decades to come, "is the high destruction efficiency necessary?"

### 6.2.3 Other Potential Commercial Applications

Overall, industrial waste is a good candidate for SCWO treatment due the variety of industrial waste composition and methods of production worldwide. The two examples described above are just that, examples. A time goes on, industrial waste treatment and destruction will become a bigger priority as environmental restrictions become more stringent.

## 6.3 Applications Pertinent to Both Government and Commercial Waste Treatment

### 6.3.1 Shipboard Waste

The United States Navy has begun to research the possibility of treating shipboard waste using SCWO systems as part of their "environmentally sound ships" program.[21] Examples of shipboard waste include black water (sewage), gray water (sinks and showers), paints, solvents, contaminated fuel, oil, etc.[21] Currently, the Navy is focusing its SCWO research for application to aircraft carrier use. Commercial cruise liners are very environmentally aware with respect to their onboard waste destruction and treatment capabilities. Unfortunately, due to the lax international restrictions on dumping shipboard waste into the world's oceans, there is currently little incentive for cruise liners to use their onboard treatment capabilities. But the companies that operate these luxury vacation vessels understand that some day soon these international policies may change.

### 6.3.2 Municipal Sludge and Water Treatment

The treatment of municipal sludge with SCWO technology is readily achievable. Pilot reactors have been operated successfully in the destruction of organic waste from municipal sludge with a treatment capacity of 10 dry tons per day. This is a huge validation to the long-term waste disposal potential that SCWO technology possesses. While the pilot plant for treating the sludge was a success, questions still exist on the economic feasibility of the reactors especially related to the scalability and the throughput of the units.

### 6.3.3 Power Generation

The exothermic oxidation reactions that take place during supercritical water oxidation might allow for clean, environmentally friendly power generation on a large scale in the future. This is especially true in the processing of low-grade fuels and oils that have been declared waste.[26] Another potential power application for supercritical water may be the use of supercritical water as a coolant in nuclear reactors. Nuclear reactors primarily operate at lower temperatures and pressures than that of supercritical water, but increasing the reactor temperature and pressure to the supercritical region would increase the power conversion efficiency of the reactor. Although the use of supercritical water as a coolant in nuclear reactors does not directly employ SCWO technology, research in the area of nuclear power could lead to further developments and discoveries that could be utilized in the area of supercritical water oxidation.

## 7.0 Supercritical Water Oxidation System Designs

### 7.1 Reliance on Waste Stream Chemistry

In the mid-90's it became apparent that both the fundamental and technical aspects of SCWO process design and commercial-scale development needed to be addressed. Despite research completed since that time, much design and development work is still necessary. In particular, design models for special wastes need to be developed.[14] The reason for this is that the SCWO environment can be very hostile. The level of hostility inside the reactor is inherently very dependent on the feeding waste stream and its chemistry. Treatment of water run-off from showering requires very different capabilities than treatment of topsoil contaminated with pesticides.

One of the most difficult and complex SCWO applications is the treatment of military refuse. Government and military wastes consisting of chemical agents, munitions, energetics, smokes, and dyes are typically high in corrosive content, salts, inorganics, organics, ions, halogens, and halides. These potential waste stream components and their reaction products substantially increase the likelihood of corrosion and solids handling issues. Highly specialized, robust reactor designs will be necessary for this type of application.

More easily characterized streams from applications such as human waste and biomass in space and contaminated soil wastes such as those at Superfund sites tend to be less harsh in stream form than the military wastes in the previous category. Despite the overall reduction in waste stream complexity with these specialized applications, specialized reactor issues need to be addressed before these applications can be realized.

Commercial waste such as municipal sludge and specialized industrial wastes such as pharmaceutical wastes are produced in large quantities yearly and therefore have long-term SCWO treatment possibilities. These wastes are found in large quantities and are moderate in the context of corrosion and solids deposition; two characteristics ideally suited for SCWO treatment.

There is clearly a wide range of wastes that have the potential to be processed with a SCWO system, and as mentioned earlier, the hostility of the SCWO reactor environment is dependent on the feeding waste stream. Therefore, the SCWO reactor system design is very dependent on the intended application of the design. Depending on the application of the SCWO technology, very different system designs are required.

6.2 Tubular Reactor

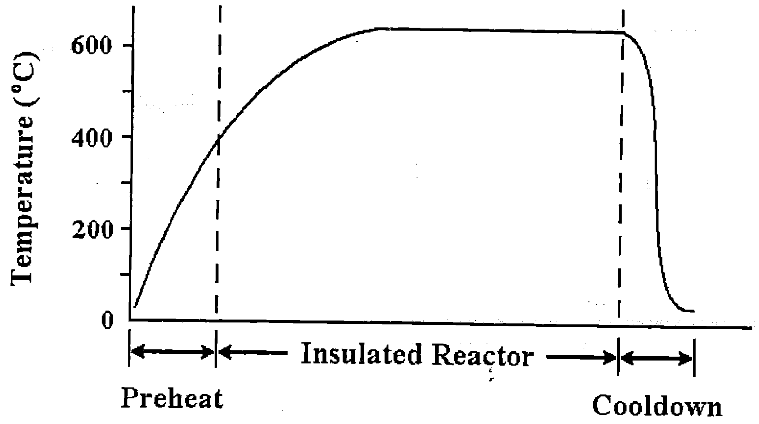

Figure 5. An example temperature profile of a tubular reactor.

The tubular reactor is also known as a pipe reactor, one example of which is the plug-flow reactor. Due to its simple design and operation, the tubular reactor is currently the most common test and research reactor.[21] The tubular reactor has the shape of a long cylindrical tube with a small diameter. The waste stream constantly flows through the length of the reactor and remains at supercritical temperatures and pressures for a period of time great enough to oxidize the organics, typically less than a minute. Figure 5 in a graph of a typical temperature profile of the tubular reactor design.

6.3 Vessel Reactor

The vessel reactor, one example of which is the continuously fed, stirred-tank reactor, is a short and stout cylindrical vessel designed to handle waste streams containing a large amount of inorganic components. The vessel reactor generally has two temperature zones for treating the waste. The upper portion of the reactor is kept above supercritical temperatures, 450 to 650 °C. Due to its supercritical state, this upper region of the reactor is the area in which the majority of the oxidation reactions take place. Solids will precipitate to the lower portion of the reactor, which is kept at a temperature in the sub-critical regime. Many of the salts will be soluble in the subcritical water while other insoluble compounds will settle on the bottom of the reactor as brine and be removed periodically. It is important to note that there is no physical barrier between the two temperature regions of the reactor vessel.

### 6.4 Specialty SCWO Reactor Designs

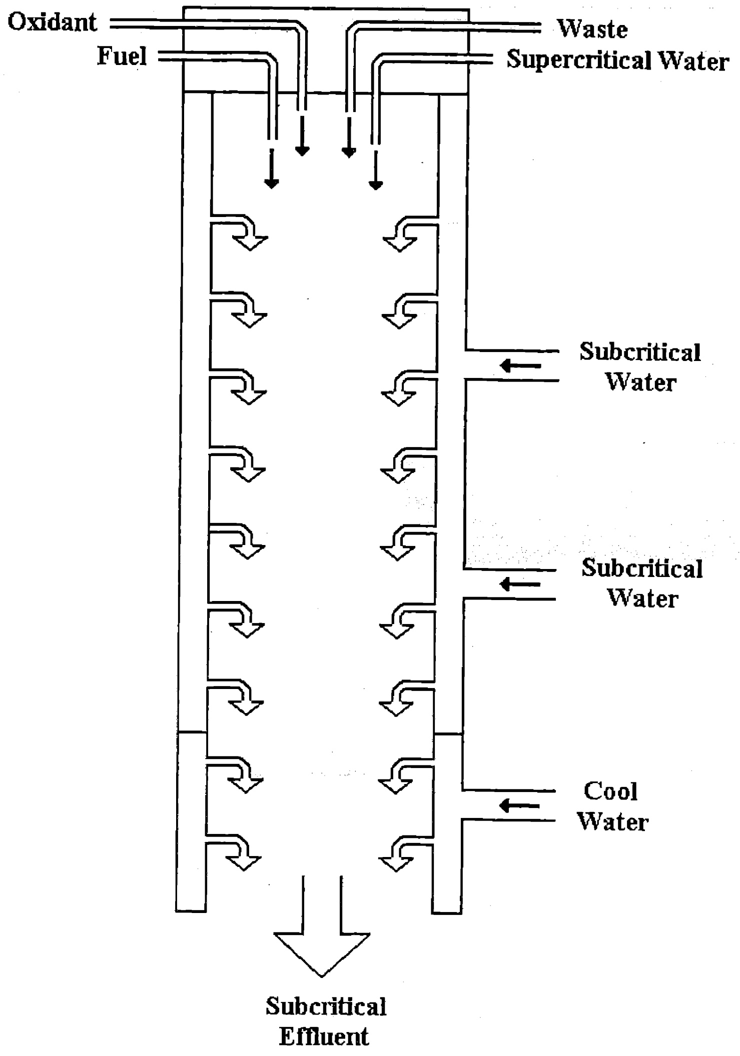

Figure 6. A diagram showing the workings of the transpiring wall reactor (TWR).

The most discussed SCWO reactor design that has been developed is the transpiring wall reactor (TWR). The TWR was developed from technology utilized in the gas turbine industry and is a modification of the previously described tubular reactor.[21] Foster Wheeler and GenCorp Aerojet developed the TWR design. Figure 6 shows a simple schematic diagram of a TWR. The TWR design includes a dual shell consisting of an outer shell that acts as a pressure boundary and an inner shell that acts as a temperature boundary. The region between the inner and outer shell is kept at sub-critical temperatures and the region inside the inner shell is kept at supercritical temperatures. The backbone of the reactor is the use of the inner shell as a porous liner within the reactor pressure boundary. Clean water from the outer subcritical region of the reactor flows through the porous liner to the supercritical portion of the reactor.[3] Through this complex perspiration system, the porous liner is said to protect the reactor against corrosion and salt deposition. The TWR was developed to eliminate concerns about pressure vessel susceptibility to stress corrosion cracking as well as general corrosion, assuming the theory that the vessel's wall are never directly exposed to the reacting materials.[16]

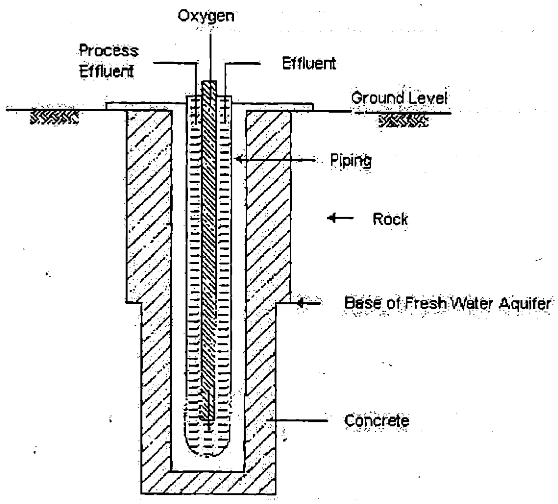

Figure 7. An illustration of the flow path and encasement of the deep-well reactor design

Another SCWO reactor design utilized a deep-well construction within conventionally drilled and cased wells to exploit gravity to build the pressures necessary for SCWO operation. Typical design depths ranged from 1,500 meters to over 3,500 meters.[38] The flow of the deep well design (see Figure 7) involved transferring effluent down one reactor pipe, adding an oxidant at a sufficient depth at which supercritical water pressures are achieved and oxidation can occur, then transporting the treated effluent up another reactor pipe. The deep-well reactor boasted a compact, underground SCWO reactor design. A major concern with this reactor design in recent years has been the extreme heat loss to the surroundings over such extreme depths.

Another specialized SCWO reactor design developed for a very specific purpose is located at Los Alamos.[21] The Los Alamos reactor incorporates a reactor vessel itself is made of quartz (glass) and is designed to process wastes that contain chlorinated solvents. This reactor showcases the diverse possibilities for materials of construction, a topic that is discussed in greater detail in the following section.

# 8.0 Supercritical Water Oxidation Development Challenges

## 8.1 Engineering Challenges

### 8.1.1 Corrosion

The extremely aggressive environment created during the SCWO process can potentially cause severe corrosion problems to both the system tubing and the reactor vessel itself. It has been generally noted that the worst corrosion in SCWO systems occurs in the heat exchangers, where the fluid is hot but subcritical and can sustain ionic reactions. In the heat exchanger tubing the dominant form of corrosion observed is localized corrosion, typically Stress Corrosion Cracking (SCC).[2] The reactor walls are also slowly uniformly corroded so that the reactor can not be reliably run for extended periods of time. Severe metal corrosion will typically occur most in these systems when the hazardous waste include halogens and nitrates.[15] Some ions, such as sodium, hydrogen, chlorine, fluorine, and ammonia, have also been known to accelerate corrosion in the systems.[23] Corrosion is also an issue along the walls of the reactor vessel where salt deposits have collected at sub-critical temperatures.

The corrosion of SCWO systems is both a chemical and materials engineering issue, or more specifically, the interaction of those two sciences. The degree of corrosion occurring in the aforementioned reactor designs will be dependent on both the application, which represents the feeding waste stream, and the materials of construction. For applications whose waste streams contain few corrosion agents, there is wide range of potential materials of construction. For application with very harsh and corrosive waste streams, it is possible that no material combination exists that will "solve" the problems of corrosion. In such cases, the goal of corrosion minimization and long-term reactor reliability will be paramount. In reality, each application and design combination needs to be taken on a case-by-case basis and fundamentally explored to form the basis for materials selection. General trends exist for the serviceability of materials used with specific waste streams but these trends may be taken with a grain of salt.

Iron-base alloys are currently found to be insufficient in corrosion resistance for highly corrosive waste streams. Many research observations have shown that iron-alloys in SCWO systems are more corrosive at subcritical temperatures, around 300 °C, that at the supercritical temperature, around 400 °C. It has also been demonstrated that corrosion rates generally increase with temperature in the supercritical regime, above 375 °C. The corrosion is also shown to be inversely correlated to feed steam pH level, so that the corrosion rate is much greater in a feed stream with a pH of 2 than a feed stream with a pH of 8. It has been found that in chloride steams the corrosion rate of 316-L stainless steel can be greater than 50 mils per year.[1] Many iron-base alloys have also been tested. Alloy 20 CB 3 demonstrated a high susceptibility to pitting. Alloy 2205 demonstrated a weakness to crevice corrosion, especially at joints. Ferralium 255 was also tested and non-uniform corrosion was observed, specifically anisotropic degradation which was more pronounced in the ferrite phase.[1]

Nickel-Base alloys have a good reputation for use in severe service applications and have been used in the fabrication of bench scale and pilot plant SCWO reactors. There is evidence that suggests these materials may not be the solution for handling very aggressive SCWO feed steams. Nickel-Base alloys have demonstrated significant uniform corrosion and localized effects such as pitting, stress corrosion cracking and dealloying under testing conditions that attempt to replicate actual SCWO service.[1] Similar to iron-base alloys, nickel-base alloys have been shown to corrode at a higher rate just above the supercritical temperature and at lower pH levels. Many nickel-base alloys have been tested for use in SCWO systems. It has been seen that while alloy 625 forms a protective film after extended use, minor pit development and grain boundary carbide formation have been observed in the material over time. Nickel-base alloy HR-160 show signs of severe grain boundary corrosion when exposed to a highly chlorinated feed at a high temperatures.[1] In general, when tested in acidic chemical agent simulant feeds, corrosion of the tested nickel alloys (C-22, C-276, 625, 825 and HR-160) was found too severe to be considered for primary use in the SCWO systems. Dealloying was also present in the nickel alloys. Chromium was sacrificed in the non-chlorinated feeds while the nickel was sacrificed in the chlorinated feeds. Although a great deal of further testing and research of nickel-base alloy

G-30 is needed, it may be acceptable to use as a primary strength material for the outer shell of the reactor vessel.[1]

One possible solution to the severe corrosion problems in SCWO systems utilized in processing complex and harsh waste streams could be the use of noble metals or their alloys in the construction of the system.[1] It is generally thought that noble alloys could make a substantial contribution to corrosion resistance as a liner in the reactor vessel. Research has been discussed for noble metals, such as titanium, platinum, and gold, to explore this possibility. Given platinum's general resistance to corrosion, it would obviously be a good selection for a corrosion resistance liner, the largest drawback of platinum being its high cost. But even platinum, along with the other noble metals, has shown unusually high corrosion rates in environments replicating those of a SCWO system designed for treatment of harsh organic waste. The use of noble liners has also been seen to accelerate the affects of stress corrosion cracking in tubing systems that replicated the SCWO environment.[1]

### 8.1.2 Solids Handling

The difficulty of handling solids inside of a SCWO reactor, similar to other engineereing issues related to SCWO reactors, is dependent on the feed stream chemistry. A good example of an aqueous waste stream that consists of a variety of solids is sewage sludge. The inorganic solids in the waste stream will be oxidized in the reactor, so that the problematic solids that remain will consist primarily of inorganics and insoluble salts. Examples of chemicals that will remain in the solid state in both subcritical and supercritical water include: calcium carbonate, iron (and its oxides), copper (and its oxides, etc). Salts, which consist of inorganic cations and anions, will dissolve and precipitate by several different processes. The ions that are bound to biomass waste will precipitate as the biomass changes state, which occurs at temperatures of 150 to 250 °C.[35] Salts whose solubility decreases with increasing temperature, inverse solubility, will precipitate when the solubility limit (usually referring to temperature) of salt species is surpassed. The solubility limit of salts with inverse solubility is highly dependent on the salt concentration. Sodium chloride, table salt, is a good example of such a salt and will precipitate in the temperature range of 370 to 450 °C, which coincides with the lower supercritical regime of water.[35]

There are two standard types of solid deposition inside of the SCWO reactor systems. The first is settling. Settling occurs when inorganics and salts precipitate out of solution due to gravity. The second is scale formation. Scale formation occurs when the solution near the system walls are supersaturated, which leads to the deposition of solids on the wall surface. Scale formation tends to occur when waste streams contain solids similar to calcium.[36] Both methods of deposition are highly dependent on the velocity and turbulence, Reynolds Number, of the solution flow at the speculated point of precipitation.[35] It is generally the case that settled solids can be more easily removed by simple flushing or brushing while scale solid deposits require a greater frictional type force for removal and can even become baked on to the sides of some reactor system designs, especially tubular reactor designs.[36]

There have been many SCWO system designs that have been guided by the minimization of solids handling difficulty. Unfortunately, much of the research in this area and the majority of the reactor designs are proprietary and unknown to those outside of the companies pursuing SCWO technology. Published information is available and more can be learned from the patents that claim the rights to the mechanisms for controlling solids deposition in SCWO reactors. The simplest solution exists in the case of the tubular reactor, where solids deposition and handling is controlled through fluid velocity. It is believed, and to a degree proven in actual reactor operation, that if the waste stream is kept flowing above a critical velocity, significant salt deposition can be avoided. There is a ceiling on the concentration of solids where operation of a tubular reactor, in the normal sense, no longer becomes viable do to the solids handling issues that unavoidably develop. Comparatively, salt deposition and solids handling issues in vessel reactor designs have been shown to be manipulated by temperature differentiation. An example of this is the two zone reactor with a hot supercritical upper half and a cooler, subcritical lower half. The beauty of this design lies in controlling the region in which the precipitated solids exist to simplify their periodic removal.

### 8.1.3 Other Engineering Challenges

Other than corrosion and solids handling, the two most prominent engineering challenges that remain obstacles to the commercialization of SCWO are scaling and chemistry. Scaling, or increasing the reactor size by orders of magnitude, is a problem faced by SCWO systems with several origins. The first and most obvious is that, as with any high pressure system, increasing the size of a pressure vessel increases the probability of introducing defects to the pressure barrier. Scaling the reactors also increases the volume of waste that must flow through the pressure barrier. Simply put, the larger and more complex the system, the harder it becomes to control the system's environment. Another important origin of scaling debacle is that increasing the volume of waste throughput in a reactor comes at the cost of proportionally increasing the volume of inorganic solids and salts processed in that same system. Typically, an increase in complexity of a system results in an equivalent decrease in reliability, all else being equal. In order to maintain reliability, the chemical process must incorporate combinations of potential reaction catalyts, acid neutralizing agents, pH altering chemicals, oxidants, etc. that may increase the efficiency, reliability, and safety of SCWO reactors. Therefore, feed and reactor chemistry must also be researched further before complex waste streams will be able to be processed effectively in commercial SCWO systems.

### 8.1.4 Codependence of SCWO Engineering Issues

Many of SCWO's engineering issues are intertwined and dependent on one another in some form. This is particularly true of corrosion issues, solids handling issues, and scaling. Many of the acids that form during oxidation and other reactions that take place in the supercritical environment promote corrosion of the reactor vessel. These acids can be neutralized to form salts with simple chemical additions to the incoming waste stream. While the neutralization helps the corrosion and solids handling issue by lowering the corrosion effects and in turn the volume of inorganic corrosion products in the reactor, the inorganic salts that are formed through the neutralization process complicate the problem of solids handling. Meanwhile, scaling the reactor to treat a greater volume of waste causes a proportional increase in salts formed during processing, which also complicate the solids handling problem.

For Example, hydrochloric acid, HCl, can be neutralized in SCWO reactor systems with the addition of sodium hydroxide, NaOH, in the waste feed stream. The neutralization of the hydrochloric acid produces sodium chloride, NaCl which is similar to table salt, and water (see Equation 3). The sodium chloride is primarily insoluble in supercritical water and therefore would precipitate in a SCWO reactor.

$$HCl + NaOH \Leftrightarrow NaCl + H_2O \qquad (3)$$

## 8.2 Non-engineering Challenges

### 8.2.1 Public Perception

As discussed previously, one of the largest driving forces for the development of SCWO technology is the public's unwillingness to recognize the environmental consequences of current destruction technologies. On the other hand, one of the largest challenges SCWO faces before becoming commercially viable is to overcome public stigmatism of SCWO. Today's society has become particularly energy conscious and it is common belief that due to the high operating pressure and temperature of SCWO, this new technology will be very energy intensive. This is not entirely accurate. In any high temperature process, you need fuel to create heat. In the case of home appliances such as an oven or toaster, the fuel can be thought of as electricity. In the case of both incineration and SCWO, organics become a source of fuel. It therefore stands to reason that given a high enough concentration of organic content in the waste stream, SCWO will be self-sustaining. The general feeling is that SCWO can be self-sufficient if the waste stream consists of around 20 percent organic material, hence near that concentration SCWO will not be energy intensive. Above the hypothetical 20 percent organic concentration, as discussed above, SCWO may even be able to operate as an energy source. Hydroprocessing, Inc is currently successfully testing this hypothesis with a SCWO reactor operated in Texas.

Another public perception obstacle to the commercialization of SCWO is that SCWO is a relatively new destruction technology. While society generally loves new technological toys, there is always a risk that the commercialization of new technology will fail, which makes governments, and even more so privately held companies, hesitant to invest.

The most important public perception hurdle acts not only as an inhibitor of the commercialization of SCWO, but also acts as an important guidance mechanism to SCWO's development. This public perception hurdle is safety of operation. This problem has only one simple solution; SCWO systems must prove to be reliable and safe both in reality and in the public eye. This is achievable assuming the engineering hurdles to the commercialization of SCWO steadily diminish with consistent research advances.

### 8.2.2 Economics

The engineering challenge of increasing the size and throughput of SCWO reactors is likely going to be the factor that determines whether the comparative cost of SCWO technology will be competitive for treating moderate waste streams that have few corrosion and solids handling problems. Researchers optimistically believe that the issue of scaling SCWO reactor sizes can be resolved in the next few years. Economic competitiveness is less likely to occur in the near future for treatment of extremely harsh complex waste streams such as mixed radioactive waste.

Research, high temperature-high pressure environments, processing solids, and trial and error testing are all costly. Many of the respected researchers involved in the development of SCWO believe that the hurdle of operation economics is the largest hurdle still faced by SCWO. Admittedly, the high cost of the reactors is largely a result of the engineering hurdles still faced by the commercialization of SCWO.

## 9.0 Competitive Technology

### 9.1 Landfill

Using landfills to dispose of waste is a very old process that has been modernized over time. Landfills today have significant enclosures to ensure that liquids and gases in the waste can not seep out of their resting place to public water streams. Another method landfill operators utilize to control pollution is through layering dirt in the waste, this occurs to the point where 20 percent of the landfill consists of this preventive dirt. Rising land prices and shipping costs are constantly increasing the cost of landfills, meanwhile sites for landfills are becoming scarce, which leads to an exponentially escalating cost for landfilling waste. Landfill disposal is a feasible option for waste dispose but in the long run will likely prove to be untenable.

### 9.2 Incineration

While incineration is a tried and true permanent solution to many of the problems associated with hazardous wastes, it is not necessarily the best in terms of economics and environmental acceptability. There is a general feeling of distrust from the public about incineration. The American public has evolved into a more environmentally aware group and is becoming conscious of the emissions of all chemical processes including waste treatment. Incinerators, due to their high operating temperature of 800 to 1300 °C, emit several toxic gases including $NO_x$, $SO_x$, and CO. Incineration can be expensive due to the high cost of the equipment, and the equipment cost for incineration is steadily increasing as more stringent regulations emerge to restrict stack gas emissions to the atmosphere. Operating costs depend greatly on energy requirements that are in turn dependent on the organic content of the waste. For waste streams above 25 percent organic content, incinerators can sustain the incineration process. If the organic content of the waste drops below 25 percent, the fuel additions that are necessary to provide the destruction energy for the waste can become a significant cost. Unlike SCWO, a major safety benefit of incineration is that incinerators operate near atmospheric pressure. Currently, incineration is a reliable option to effectively dispose of the chemical agent stockpiles.

### 9.3 Wet Air Oxidation (WAO)

WAO technology is over 30 years old and hundreds of wet air oxidation reactors are currently in use. WAO reactors typically operate from 150 to 325 °C and at pressures of 2 to 20 MPa. Residence times for WAO treatment of organic waste is much longer than SCWO treatment, typically taking anywhere from 10 to 100 minutes to properly treat. WAO has more limited treatment possibilities than those of SCWO. For example, WAO is not effective in treating polychlorinated biphenyls (PCB) or dioxins.[27] On the other hand, WAO requires less power consumption. The fact that WAO has a lower destruction efficiency compared to SCWO is the most important and distinguishing characteristic between these two similar technologies.

### 9.4 Bio-treatment

Bio-treatment consists of utilizing microorganisms to absorb, accumulate, and destroy specific toxic compounds. There are many limitations to bio-treatment. One is that while bio-treatment is very efficient at destroying selective compounds, in applications where total destruction is the goal, this selectivity limitation is a significant drawback. Also, many bio-treatment methods are very time intensive, some taking years to complete. Such methods can also be difficult to monitor and control.[24] Bio-treatment methods are best suited for treatment of wastewaters with relatively low organic concentrations of less than one percent or less due to the increasing likelihood of the system becoming poisoned or inefficient with greater concentrations of organic content.[24] From a safety perspective, bio-treatment is a desirable treatment process since it operates at low temperatures and pressures.

### 9.5 Adsorption

Adsorption, such as activated carbon adsorption, is a method used to remove specific substances from a waste stream. Similar to bio-treatment, the optimal waste stream for treatment by adsorption is a waste stream that has low organic content, typically less than 1 percent. Unlike bio-treatment, the one percent ceiling for adsorption is an issue of cost as opposed to technological barriers. The primary cost of the carbon adsorption process is the cost of regenerating the carbon. It can therefore be shown that cost of carbon adsorption treatment is proportional to the organic content fraction of the waste, which becomes to great to be competitive for treating aqueous wastes above one percent organic content.[34]

### 9.6 Plasma Arc

Plasma arc can be thought of as a thermal treatment, but that is not entirely accurate. Plasma arc actually consists of creating and sustaining an electric arc by passing electrical current through a gas. Electrons are stripped from the gas by the arc which creates a plasma state, examples of which are lightning bolts, fluorescent gas in light bulbs, and the spark of an engine spark plug.[25] A major drawback of the using a plasma arc in waste destruction is that the waste stream must consist of a very small percentage of solids upon entering the arc. This would require advance filtration methods including the possibility of ion exchange or adsorption as pretreatment.

## 10.0 Benefits and Shortcomings of SCWO

Supercritical water oxidation has many benefits over the previously described competitive technologies in the destruction of organic waste. SCWO has a very high destruction efficiency of organic wastes that meets and exceeds those of the competitive technologies. SCWO's high destructive efficiency is particularly important in making comparisons to wet air oxidation due to the similarity of the technologies. SCWO has demonstrated destruction of hazardous organic chemicals at efficiencies in excess of 99.99%.[5] Another benefit of SCWO is that SCWO systems are being designed and tested as a completely enclosed system. Not only does this aid in controlling any undesired releases to the environment, but this compactness may also allow SCWO to be portable. When considering such applications as site remediation at the Superfund Sites, portability is a large benefit. In SCWO systems as opposed to most thermally activated systems, oxygen is carried by water as opposed to air. This allows SCWO systems to produce a fraction of the off-gas generated in high temperature thermally activated systems. For example, while $NO_x$ is a relatively toxic gas of large concern and is a prevalent off-gas in incineration systems, $NO_x$ is not produced as an off-gas in SCWO systems.[4] SCWO is also very flexible as to the composition of the waste streams that is meant to be processed, including many inorganic materials such as metals which are not as acceptable in other treatment processes such as adsorption and biological treatment.[24]

On the downside, the SCWO process must be carried out in a reactor capable of handling high temperatures, high pressures and a very aggressive, potentially acidic, environment.[1] Due to these extreme conditions, in its current test applications of destroying military and industrial wastes, SCWO has been plagued by reactor corrosion and salt deposition problems.[3] Hence, the issues of corrosion management and solids handling are the two primary concerns for dictating the future of SCWO technology treating harsh and complex wastes.[5]

Considering the high effectivity of the SCWO process and its correspondingly environmentally safe destruction of the chemical agents, the utilization of SCWO in the treatment of hazardous waste has the potential to change the entire concept of waste treatment, reuse, and environmental safety in a wide variety of industrial arenas.[6]

## 11.0 The Innovators and Developers of Supercritical Water Oxidation

There have been many individuals and companies who have staked a large claim on the development of SCWO and have gambled on its success. Over time larger companies are beginning to make their mark in the SCWO community. As mentioned earlier, the particular application each company is pursuing for the introduction of SCWO technology guides the SCWO reactor design. Also mentioned earlier, government policy and law is a driving force for pursuing particular SCWO applications. Therefore, it can be deduced that, worldwide, SCWO reactor design is dependent on the priorities of the governments across the globe and of international society.

The priorities of the United States government are constantly shifting. For example, the United States government has changed its priority from stockpiling chemical weapons to the destroying those stockpiles. Meanwhile, environmental conservation has become a greater priority of that same government. To those ends, the United States is currently pursuing the destruction of its chemical weapons stockpile and other hazardous wastes in an environmentally friendly manner. This environmental accountability has also led the Navy to look at methods for transforming its ships to produce less waste throughput to the world's oceans.

Many of the world's priorities outside of the United States differ greatly. One statistic that is important to the international developers of SCWO is that the population density of Europe and Japan are approximately twice and eleven times greater than that of the United States, respectively. Given the large number of people habiting such a small land area in both Japan and Europe, landfilling and incineration of hazardous waste are becoming less viable due to an all but unavoidable future land shortage, as well as the associated pollution control problems.

Due to the varying governmental priorities driving the production of SCWO technology worldwide, companies in the United States have different short-term and long-term goals for the development of SCWO technology than their competitors in other countries. The focus in the United States is the timely destruction of military waste for the simple reasons of economics. The United States government has a large checkbook with which to fill its needs. General Atomics and Foster Wheeler are two of the prominent companies involved in developing SCWO for the destruction of military wastes in the United States. It is note-worthy that General Atomics has participated with the US government applications such as the destruction of the Army's chemical weapon agents, the Air Force's energetic materials, and the Navy's shipboard waste. Hydroprocessing, Inc. is a Texas based company that is developing SCWO systems for use in municipal waste processing and is operating a pilot SCWO reactor in Austin, Texas with real world sludge from the City of Austin's Hornsby Bend Sludge Management facility.

Possibly the biggest player in the United States with respect to SCWO has been Modar, Inc. Modar, originally an MIT start-up company, played a large role conducting the fundamental research to develop SCWO technology. Proof of this can be found in Appendix A where it can be seen that Modar is the assignee of 7 patents related to SCWO, the last of which is October 1997 (Modar is registered for a total 10 patents with the USPTO). In 1995, General Atomics acquired Modar as part of its long-term plans to develop SCWO.

International companies involved in the development of SCWO technology include Chematur in Sweden and Organo in Japan. Both of these companies are pursuing SCWO to be used in the processing of municipal and industrial wastes. Many universities in Europe and Japan are also participating in fundamental research of SCWO reactor engineering issues such as solids handling, corrosion, and the chemistry both inside of the reactor and in the feed stream.

## 12.0 Intellectual Property of Supercritical Water Oxidation

There are 259 patents registered with the United States Patent and Trademark Office (USPTO) that involve "supercritical water". There are 1510 patents registered with the USPTO that include the term "wet air oxidation" or "wet oxidation", 114 that include "supercritical water oxidation", and 24 that include "hydrothermal oxidation". Of the 259 patents involving supercritical water, only 25 also include the terminology "waste treatment". Of the patents that involve wet air oxidation, supercritical water oxidation, and hydrothermal oxidation, those that also include the terminology "waste treatment" number 77, 32, and 2 respectively.

All this data tells us is that there many patents that cover just about any subject, including SCWO and SCWO related fields. To judge which of these patents are meaningful to the current development of SCWO technology, it is necessary to view each patent in its entirety paying particular attention to the patent's final section, the claims of the patent.

In January of 1954, a patent was issued to Frederick J. Zimmermann entitled waste disposal. In the claims of the patent, Zimmermann claimed the rights to the process of adding oxygen to "carbonaceous waste liquor" at a temperature between "at least 450 degrees Fahrenheit and the critical temperature of water". This process later became known as Wet Air Oxidation (WAO) and is the older cousin of SCWO. Over 37 years later, in 1979, Reinhard Thiel patented the design of a reactor to be operated at a temperature and pressure above the critical point of water in the application of oxidizing organic compounds. His patent was titled a "process for wet oxidation of organic substances". Norman L. Dickenson was awarded a patent for his invention entitled "Pollutant Free Low Temperature Slurry Combustion Process Utilizing the Supercritical State". In this October 1981 patent, Dickenson claimed the rights to the combustion of "fuel" at pressures and temperatures that exceed the supercritical state of water. This was the first patent that claimed the use of the "supercritical state" of water for destruction, but the patent is very vague in regards to the oxidation of organic compounds. Destruction of organic compounds in a supercritical environment was left to Michael Modell who patented the "Processing Methods for the Oxidation of Organics in Supercritical Water" in July of 1982, the first true patent to cover the fundamental science of SCWO in its entirety and emphasize the destruction of organic compounds.

The most troublesome step of patent analysis is judging which patents are the most important, that is, which patents best perform their job of protecting the idea or innovation of the patent's author. This type of high-quality patent is often referred to as *blocking* intellectual property. The generic literal definition of blocking intellectual property can be thought of as intellectual property, such as a patent, that is in the unique position of being able to legally prohibit the development or implementation of a commercial good or service. By this definition, any patent would qualify as blocking intellectual property given both the desire of an outside party to utilize any of the claims of the author's patent and the judicial systems acknowledgment to the validity of the patent. After all, that is the primary functionality of a registered patent. In general, the broader the patent's claims extend the better its ability to block the infringement of those claims.

In the case of SCWO's technological development, there have been over 20 years of innovation in the area. A table has been constructed of 89 patents that either marked important developments or improvements of SCWO technology (See Appendix A). Registration of a patent through the USPTO only protects the author's ownership to the claims of the patent for 20 years. After that 20 year time period, the author of the patent forgoes their legal rights to the ideas and innovations found in that patent. In the case of SCWO many of the original fundamental patents, such as Thiel's 1979 patent, Dickenson's 1981 patent, and Modell's 1982 patent, have surpassed their 20-year ownership window. Since these broad fundamental patents can no longer be considered blocking, current blocking patents are those that are design specific and are only protective to the development of specific SCWO reactor designs. And time is starting to wind down on their legal ownership as well.

In 1980, Edwin Matovich patented ideas that would lead to the development of the Transpiring Wall Reactor SCWO system design, which was later patented for SCWO application by Thomas McGuinness in 1995, and Daman in 1996 under the current name of TWR. In 1981, Jay McGrew patented what would later evolve into the deep well SCWO reactor design, which was patented for SCWO applications in 1986 by James Burleson. In 1989, Glenn Hong claimed the design of a SCWO reactor that utilized two-zones. These designs, with the exception of the deep well reactor, are still being actively pursued today, and new designs will continue to emerge. Table 1 shows the companies with the most patent holdings in SCWO technology along with a brief description of the specific areas their patents tend to cover.

It is apparent from glancing at Table 1 that Modar, Inc. has the greatest number of patents by a factor of 2. But the patent is only as robust as the assignee's willingness to risk sacrificing time and capital to protect the rights of that patent in the judicial system. Another important point is that patents licensed through the USPTO are only protective of the author's ideas and innovations inside of the United States. This clearly reduces the value of patents registered through the USPTO as SCWO is a technology that is being developed for global application. More important perhaps than the individual ownership of the rights to develop the technology is the know-how and knowledge behind the individuals at the forefront of SCWO technology. This qualitative workforce value is what will separate the companies the will fail from the companies that will succeed in the development of SCWO.

## 13.0 Expert Opinions on Supercritical Water Oxidation

There have been many articles written on the technological possibilities and problems of SCWO systems. The majority of the articles and papers written on the subject of SCWO lack a thorough discussion of potential applications of SCWO systems. In order to generate data on potential future applications of SCWO systems, that author generated a survey that was distributed to 45 researchers in industry and academia with a request to participate in the survey. 15 responses were received and many of those surveyed offered their personal opinions with regards to the future of SCWO technology. A summary of those responses is shown in Appendix B.

| Years Issued | Assignee | Number of SCWO Related Patents | Focused Area of SCWO Intellectual Property |
|---|---|---|---|
| 1982-97 | Modar, Inc. (MA, TX) | 8 | Wide range of patents |
| 1996-97 | Abitibi-Price Inc. (Mississauga, CA) | 4 | Tubular reactor designs and solids handling solutions |
| 1996-97 | Foster Wheeler Development Corporation (Livingston, NJ) | 3 | TWR design, corrosion and solids handling solutions |
| 1996-2001 | General Atomics (San Diego, CA) | 3 | Wide range of patents |
| 1993-2001 | Modell Development/Environmental Corporation (MA) | 3 | Tubular reactor designs with emphasis on paper mill effluent |
| 1996-97 | RPC Waste Management Services, Inc. (Austin, TX) | 3 | Double shell and tubular designs with an emphasis on corrosion solutions |
| 1981-83 | Dickinson; Norman L. (Lavallette, NJ) | 3 | Fundamental SCWO principles and power application |
| 1987-89 | VerTech Treatment Systems, Inc. (Denver, CO) | 3 | Wide range of SCWO designs |
| 1992-93 | ABB Lummus Crest Inc. (Bloomfield, NJ) | 2 | Both vessel and tubular reactor patents |
| 1986-97 | Kenox Corporation (Toronto, CA) | 2 | Original mixer design |
| 1988-92 | Nippon Shokubai Kagaku Kogyo Co., Ltd. (Osaka, JP) | 2 | WAO reactor systems |
| 1995-96 | McGuinness; Thomas G. (Aurora, IL) | 2 | Permeable wall SCWO reactor design |
| 1993 | Zimpro Passavant Environmental Systems, Inc. (Rothschild, WI) | 2 | Two stage reactor design and pH control |

Table 1. A table of people and companies with ownership rights to important patents involving SCWO technology.

When a technology is developed in a laboratory, there is usually a big push toward exploring that technology by entrepreneurs, companies, and sometimes, society at large. Once it is realized that the technology has large engineering problems yet to be solved, the novelty of the technology wears off and another innovative technology becomes the latest and greatest engineering fad. The fundamental theory behind SCWO technology has evolved over the past 40 years and SCWO itself is over 20 years old. SCWO can be thought of as a slowly developing technology, the major reason for which is economic viability in combination with the continuing appearance of new engineering hurdles, though decreasing in resolution difficulty from the original engineering hurdles faced by SCWO decades ago. Many of the researchers who responded to the survey have either observed or participated in the development of SCWO over the past decades. Over this lengthy development period, each researcher has had opportunities to reflect on the evolution of SCWO and make individual predictions for its future. Hence, the field of SCWO experts has become divided into the optimists, the survivors, and the discouraged. The discouraged consider SCWO technology to be impractical and overly expensive for everyday waste treatment but tend to concede that SCWO technology has ongoing potential for specialized, primarily government, applications where cost is not the foremost issue. The survivors tend to believe that SCWO's large economic hurdles are inherently coupled to the remaining engineering hurdles (corrosion, solids handling, and scalability), which will be whittled down for the decades to come. The survivors tend to agree with the discouraged that specialty applications will utilize SCWO in the near future, but the survivors also believe that in the long term, as hazardous waste is continually produced, SCWO will be become economically viable for everyday waste treatment. The optimists believe that breakthroughs in SCWO technology will continue to fall in place, and within the next two decades, SCWO systems will be used daily in a variety of waste treatment capacities, from municipal waste and water treatment to complex applications such as military munitions destruction.

## 14.0 Economic Analysis of Supercritical Water Oxidation Treatment of Municipal Waste

A true economic analysis of SCWO technology with regard to one particular application, in this case the treatment of municipal sludge, is extremely difficult to create. There are several reasons for this. The first reason stems from SCWO being used to destroy organic materials that have been classified as unwanted and even hazardous, making cost relatively inconsequential. Evolving government and social policy will continue to be the force that decides whether SCWO is a necessary technology, and future government and social policies are inherently unpredictable. The second reason a true economic analysis of SCWO is difficult is that an end market for SCWO is vague at best. That is, predicting an application in which SCWO will be utilized economically cannot be taken for granted. This causes ambiguity in the scale and peripheral costs of implementing consumer based SCWO units.

Given these difficulties, assumptions were made for even the most basic type of economic analysis of the commercialization of SCWO. Two large assumptions were made for this analysis to help subvert the aforementioned difficulties, but these assumptions came at the risk of the assumptions proving to be false. The first major assumption was that SCWO would be a significant player in the future of waste destruction. The second important assumption was that the destruction of municipal waste would be a viable application for SCWO in the near future. These assumptions are not unrealistic as is demonstrated by the survey results from academia and industry, which can be found in Appendix B.

To complete any cost analysis a large amount of data must be collected. The costs of development and operation must be evaluated. In the case of a new technology, SCWO, attempting to capture a current market, municipal waste treatment, SCWO must prove to be available at a competitive cost with improved performance over competing technology. The market must then be assessed to estimate the percentage of the market can be captured to predict potential revenue. The previous assumptions combined with the market estimate make it possible to speculate on the potential profit level.

It is known that three companies interested in the development of SCWO, Modell Development Corporation, Chematur, and Hydroprocessing, have compared projections for the costs associated with constructing, maintaining, and operating SCWO reactor systems. Hydroprocessing, as mentioned earlier, is operating a full-scale pilot reactor in Texas and therefore has unique knowledge of the construction costs for a full-scale system. The costs can be broken down into fixed costs and variable costs. The fixed costs are usually up-front and include the cost of the equipment, system design, construction, and miscellaneous permanent costs. The variable costs are generally ongoing and include the cost of operating materials, labor, maintenance, and miscellaneous reoccurring costs. Figure 8 shows the estimated cost breakdown for both fixed and variable costs. The variable costs in Figure 8 are annual costs.

Figure 8 shows that the estimated initial investment for a SCWO reactor ranges from $2,000,000 to $4,000,000 depending on the size or throughput of the reactor. Figure 8 also shows that the approximate annual operational cost of a SCWO reactor ranges from $700,000 to over $1,500,000, again depending on the size or throughput of the reactor. The assumed throughputs of the large and small reactors are 20 and 5 dry tons of aqueous waste per day, respectively. These figures equate to a cost range of $250 to $500 dollars per ton of waste processed, not including the initial investment.[41] This is comparable to the cost of incineration, which is

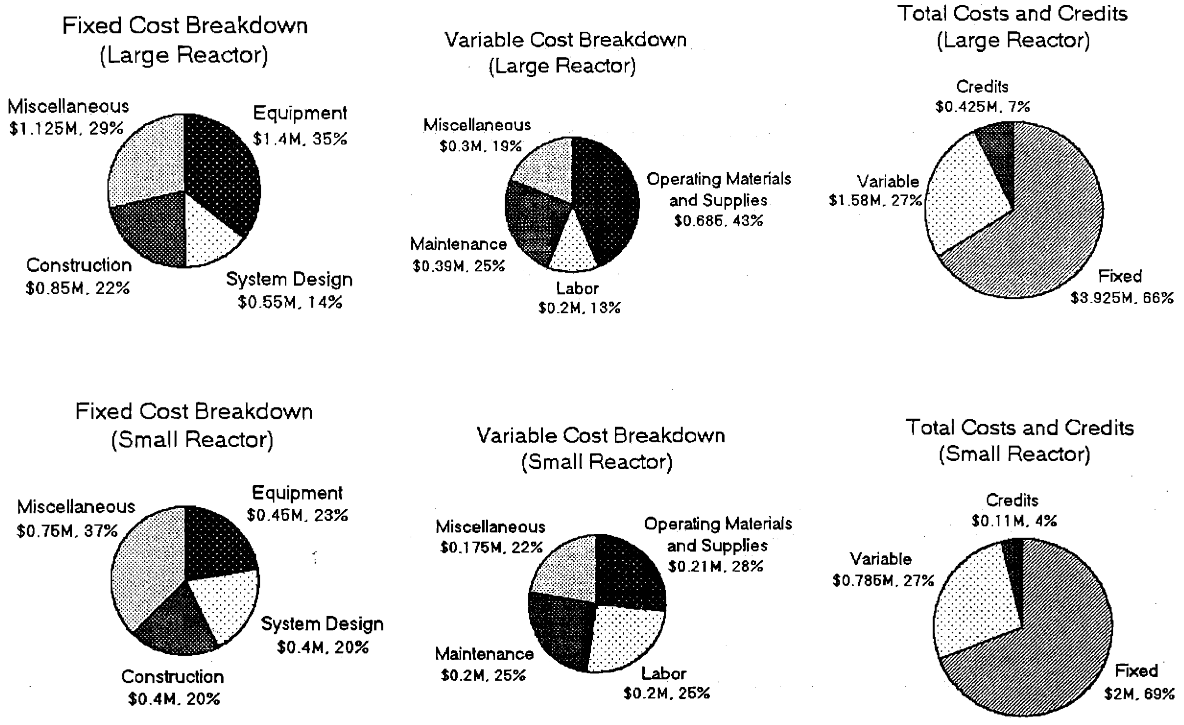

Figure 5. Pie charts breakdown of the fixed, variable, and total costs associated with constructing, operating, and maintaining a SCWO reactor.[41]

estimated to cost from $250 to $450 per dry ton of waste.[19, 38, 41] Therefore, the costs of SCWO can be competitive.

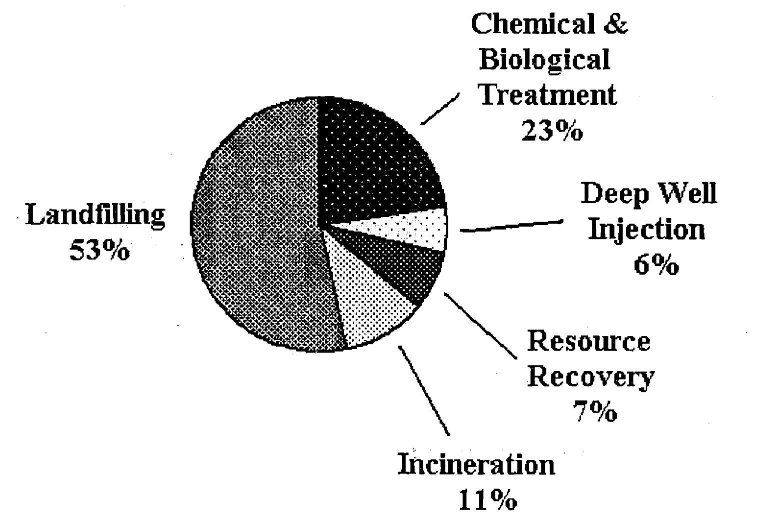

Figure 9. This pie chart illustrates the breakdown of waste treatment methods utilized in the US in 1987.[38]

There are over 260 million tons of hazardous waste produced in the United States every year.[38] Generally, a waste is classified as hazardous if it meets any one or more of the following criteria: fatal in low doses, toxic, carcinogenic, mutagenic, teratogenic, flashpoint less than 60 °C, corrosive, explosive, or highly reactive. Annual sludge production in the United States is estimated around 40 million dry tons per year, divided relatively evenly between industrial sludge and municipal sludge.[38] Incineration is used to treat approximately ten percent of the waste in America. Figure 9 shows the percentage of waste treated by six treatment methods. If SCWO can capture half of the incineration market in area of municipal sludge, SCWO would be used to treat one million dry tons of waste annually. This would require, very optimistically, 200 large SCWO reactors. At a cost of $2,000,000 each, the company that commercializes a SCWO reactor design for municipal sludge could make a profit of 40 million dollars in the United States assuming a profit margin of ten percent.

Fundamental research and design development costs required to launch commercial SCWO reactors have not been taken into account, and could prove to be very substantial. The development of SCWO reactors for government use, as in the destruction of military waste, may provide as important subsidy for improving and enhancing SCWO technology. Such government subsidy of fundamental SCWO technology could be a springboard to commercial applications. Overall, the development of SCWO technology will continue, and if commercialization becomes viable from the prospective of reliability and efficiency, profits can be made.

## 15.0 Summary and Future Research Considerations

### 15.1 Summary

Water in the supercritical state combined with hazardous waste, will result in the destruction of the organic compounds in the waste in a process known as supercritical water oxidation (SCWO). SCWO is ideal for treating waste streams containing 5 to 20 percent organic content. Many potential applications exist for this developing technology, including destruction of: military wastes, such as chemical agents and munitions; shipboard waste; industrial wastes, such as paper mill effluent and pharmaceutical waste; and municipal waste. It is a common belief among those involved in the development of SCWO that niche applications will proliferate with time.

Many SCWO reactor designs have been developed to meet the needs of these varied applications. The two basic designs are the tubular and vessel design, to which many technical augmentations have been made to develop reactor designs such as the "transpiring wall reactor" and the "deep-well" reactor. The primary challenges that are inhibiting the rapid commercialization of SCWO are engineering issues, such as corrosion, solids handling and scaling, and non-engineering issues, such as economics and public perception.

Many competitive technologies exist for the treatment of hazardous wastes. The two oldest technologies that are currently utilized in the majority of waste management applications are landfilling and incineration. Other technologies being developed and improved alongside of SCWO include: bio-treatment, wet air oxidation, and adsorption. Since the commercialization of SCWO is an international endeavor and the original patents covering SCWO technology are expiring or expired, the scientist who are knowledgeable and at the forefront of SCWO technology will be more important to a company's success in the commercialization of SCWO than the ownership of patent rights. Given the resolution of reliability and other engineering issues, SCWO technology has the potential to stake a claim in the waste management industry and to return a sufficient profit.

### 15.2 Future Research Considerations

It goes without saying that the future of SCWO is uncertain. We are currently in an era known by many as an information age. The focus of scientists, engineers, and technologists is often driven by the economics of research and commercialization, which has in recent history been very promising in the areas of electronics and nanotechnology. This focus will change. Waste management, and even more so, hazardous waste management, will continue to be a growing problem as the world's population steadily increases and monetary motivation continues to drive technology as opposed to environmental accountability. SCWO may be an important piece of the waste management puzzle even as alternate technologies are developed.

Research will continue in the area of SCWO's major engineering difficulties such as corrosion, reactor and feed stream chemistry, and solids handling to improve the reliability, safety and efficiency of SCWO reactor systems. It is likely that, in the decades to come, SCWO will be utilized initially in specialty applications where cost is not as important as destruction efficiency. Based upon these initial applications, the possibility exists that SCWO could eventually be used in everyday treatment of municipal waste.

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# Appendix A

| Patent Number | Issue Date | Inventor(s) | Title | Assignee | Abstract |
|---|---|---|---|---|---|
| 1440109 | Dec., 1922 | Schenck | Armored Container | | |
| 1986196 | Jan., 1935 | Grosse. | Apparatus for Conducting Reactions at Elevated Pressures | | |
| 2398546 | Apr., 1946 | Messmore. | Thermal Insulation of Vessels | | |
| 2665249 | Jan., 1954 | Zimmerman. | Waste Disposal | | |
| 2824058 | Feb., 1958 | Zimmerman. | Method for the Continuous Self-Sustaining Flameless Oxidation of Combustable Materials | | |
| 3207572 | Sep., 1965 | Saul. | Wet Combustion of Waste Liquors | | |
| 3282459 | Nov., 1966 | Wilson. | Pressure Vessel Havning Concentric Casings | | |
| 3449247 | Jun., 1969 | Bauer. | Process for Wet Oxidation of Combustable Waste Materials | | |
| 3472632 | Oct., 1969 | Hervert et al. | Internally Lined Reactor for High Temperatures and Pressures and Leakage Monitoring Means Therefor | | |
| 3515520 | Jun., 1970 | Hervert. | Reactor with Internal Protective Sleeve for Corrosive Systems | | |
| 3716474 | Feb., 1973 | Hess et al. | High pressure thermal treatment of waste oil-containing sludges | | |
| 3804756 | Apr., 1974 | Callahan et al. | Environmentally safe disposal of organic pollutants | | |
| 3852192 | Dec., 1974 | Fassell et al. | Reactor for wet oxidation of organic matter | | |
| 3876497 | Apr., 1975 | Hoffman | Paper mill waste sludge oxidation and product recovery | | |
| 3876536 | Apr., 1975 | Pradt et al. | Waste Oxidation Process | | |
| 3920548 | Nov., 1975 | Fassell et al. | Wet Oxidation Process for Waste Material | | |
| 4017421 | Apr., 1977 | Othmer | Wet combustion process | Self, Othmer; Donald F. (333 Jay St., Brooklyn, NY 11201) | Aqueous solutions and suspensions of solid particles, even those containing less than one percent of organic materials, may be combusted with air, oxygen, or their mixtures in a process which provides for preheating in countercurrent batches of the raw original liquid by either open (direct contact) or closed (heat transfer surface) condensation of steam generated by multiple flash evaporations which cool earlier batches of hot liquid after the wet combustion. Excess heat may often be withdrawn from the process for power generation or other use as high pressure steam, with or without combustion gases and other non-condensibles. No pumps are necessary, liquid batches are pressurized by steam generated in the flash evaporations for which only one pressure vessel is required instead of the many in the continuous processes. Waste liquids as sewage sludges and black liquors from wood pulping may have their organic constituents, as measured by BOD or COD, so reduced that the final, spent liquid may be discharged directly to a receiving body of water. |
| 4100730 | Jul., 1978 | Pradt | Regulation of a wet air oxidation unit for production of useful energy | Sterling Drug, Inc. (New York, NY) | A wet oxidation apparatus comprising a reactor vessel, means for continuously introducing combustible material, water, and oxygen containing gas, into the reactor; the heat of combustion in the reactor being sufficient to evaporate the water supplied to said reactor, means controlling the quantity of water fed to the reactor, thereby maintaining the liquid level in the reactor, and a gas and water vapor outlet for the reactor; gas and water vapor discharging from the reactor being passed through a turbine or similar device to produce mechanical power. The air supplied to the reactor is controlled to be insufficient to oxidize all of the fuel supplied to the reactor, or alternately, the reactor is operated in a way to enrich the gas and water vapor stream discharging from the reactor with organic matter, said enriched stream being subjected to vapor phase oxidation creating a superheated stream improving the efficiency of the power producing cycle. |
| 4113446 | Sep., 1978 | Modell et al. | Gasification process | Massachusetts Institute of Technology (Cambridge, MA) | Solid or liquid organic materials are converted to high BTU gas with little or no undesirable char formation by reaction with water at or above the critical temperature of water and at or above the critical pressure of water to achieve the critical density of water. The reaction can be conducted either in the presence or in the absence of a catalyst. |
| 4141829 | Feb., 1979 | Thiel et al. | Process for wet oxidation of organic substances | Bayer Aktiengesellschaft (Leverkusen, DE) | A process has been developed for the oxidation of organic substances, dissolved or dispersed in an aqueous system, with a gas containing molecular oxygen at elevated temperature and under elevated pressure chiefly to carbon dioxide and water, with subsequent phase separation of the reaction mixture into a gaseous phase substantially containing inert gas, carbon dioxide, steam and organic constituents and a liquid phase substantially containing water, characterized in that the pressure is adjusted, at the given temperature, so that by evaporation of water from the aqueous system, more steam than the exothermicity of the oxidation reaction gives rise to, goes into the gaseous phase, which is fed to a heat exchanger in which the amount of heat required to maintain the oxidation temperature is completely or partially transferred to a mixture of water and a gas containing molecular oxygen, which mixture flows in on the other side of the heat exchanger and is subsequently fed to the reactor. A particular advantage of the process of the invention is that, in addition to the oxidation of organic substances, it is possible to feed inorganic constituents, after the oxidative degrad |
| 4174280 | Nov., 1979 | Pradt et al. | Oxidation process | Sterling Drug Inc. (New York, NY) | A process for wet air oxidation of liquid or solid combustible materials which are insoluble, immiscible and difficult to suspend in water which comprises injecting said materials directly into the wet air oxidation reactor, thereby producing a regular, safe and trouble-free reaction. |

| Patent Number | Issue Date | Inventor(s) | Title | Assignee | Abstract |
|---|---|---|---|---|---|
| 4199545 | Apr., 1980 | Matovich | Fluid-wall reactor for high temperature chemical reaction processes | Thagard Technology Company (Irvine, CA) | A fluid-wall reactor for high temperature chemical reactions is described, the reactor comprising (A) a porous reactor tube, at least a portion of the interior of which defines a reaction zone, the tube being made of a fabric of a fibrous refractory material; (B) a pressure vessel enclosing the reactor tube to define an inert fluid plenum, the pressure vessel having at least one inlet for admitting the inert fluid which is directed under pressure through the porous tube wall to provide a protective blanket for the inside surface of the reactor tube; (C) means for introducing at least one reactant into the reaction zone, the reactants being directed in a predetermined path axially of the reactor tube and being confined by the protective blanket substantially centrally within the reaction zone; (D) means disposed within the plenum for heating the reactor tube to the temperature level at which it emits sufficient radiant energy to initiate and sustain the desired chemical reaction, the radiant energy being directed into the reaction zone to coincide with at least a portion of the path of the reactants; and (E) a heat sh |
| 4217218 | Aug. 1980 | Bauer | Removal of solids from a wet oxidation reactor | Sterling Durg Inc. (New York, NY) | A cleaning and washing system for a reactor utilizing a by-pass, normally closed, to be opened while the normal flow of sludge is closed, for washing out unwanted solid particles in the reactor. |
| 4229296 | Oct., 1980 | Wheaton , et al. | Wet oxidation system employing phase separating reactor | Whirlpool Corporation (Benton Harbor, MI) | Processes are provided for accomplishing wet oxidation using a reaction zone wherein the gas phase (oxygen) is allowed to pass therethrough at a flow rate independent of the liquid phase (waste water) flow rate so that more oxygen can be supplied to a given volume of waste water than is possible for a conventional reactor of the equivalent size. A high efficiency wet oxidation is provided by which the process technology can be practiced either in a single stage or multistage. The reactor is directed to operate at temperatures ranging from about 350.degree. to 600.degree. F. at pressures ranging from about 800 to 2200 psig and the reactor provides a gas phase/liquid phase separation feature. |
| 4241722 | Dec., 1980 | Dickinson | Pollutant-free low temperature combustion process having carbonaceous fuel suspended in alkaline aqueous solution | Self, Dickinson; Norman L. (Box 211, Lavallette, NJ 08735) | A continuous process for the combustion of carbonaceous fuels under conditions such that oxides of nitrogen are not formed and oxides of sulfur and particles of ash are effectively prevented from contaminating the gaseous products released to the atmosphere. Fuel is charged as a slurry in alkaline aqueous solution and contacted with combustion air so that the catalytic properties of both water and alkali operate to permit rapid and complete combustion at unusually low temperatures. Useful heat is extracted from the heated mixture. At the low combustion temperatures, sulfur in the fuel oxidizes to the trioxide which dissolves completely in the alkaline liquid phase which also retains particles of ash and unburned fuel. |
| 4272383 | Jun., 1981 | McGrew | Method and apparatus for effecting subsurface, controlled, accelerated chemical reactions | McGrew; Jay L. (12213 Maxwell Hill Rd., Littleton, CO 80120) | A method and apparatus is disclosed for effecting accelerated chemical reactions between reactants at elevated temperatures and pressures including the wet oxidation of materials in waste streams. A reactor has a through pipe that extends down into a cased hole in the earth and back up independent of the hole. A controlled flow of influent fluid with reactants is flowed down the pipe to form a hydrostatic column of fluid that is of sufficient depth to exert a pressure and provide a temperature sufficient to cause reactants to react at an accelerated reaction rate and to achieve the necessary retention time to substantially complete the reaction. Heat is released in the reaction zone to heat the fluid, and the heated fluid is then flowed back up in heat exchange relation to the downflowing fluid. The temperature of the fluid is controlled in the reaction zone by adding heat for start-up and selectively adding or removing heat to maximize the reaction rate and to prevent boiling of the fluid. When a gas is used as a reactant, enlarged gas bubbles are formed at approximately the ground surface level and are pumped down with the influent fluid to cause intense mixing, contacting, and a c |
| 4292953 | Oct., 1981 | Dickinson | Pollutant-free low temperature slurry combustion process utilizing the super-critical state | Self, Dickinson; Norman L. (Box 211, Lavallette, NJ 08735) | A continuous process for the combustion of solid fuels in the presence of an aqueous liquid phase under conditions such that oxides of nitrogen are not formed and oxides of sulfur and particles of ash are effectively prevented from contaminating the gaseous products released to the atmosphere. Fuel is charged as a slurry in alkaline aqueous solution and contacted with combustion air so that the catalytic properties of both water and alkali operate to permit rapid and complete combustion at comparatively low temperatures. Temperatures in the adiabatic reactor are, however, permitted to exceed the critical temperature of the liquid phase. Under the conditions of the process, formation of nitrogen oxides is negligible, sulfur in the fuel goes to sulfur trioxide which dissolves completely in the alkaline liquid phase which also retains particles of ash and unburned fuel. The resulting flue gas is essentially free from objectionable pollutants. Heat is made available at a temperature high enough to generate and superheat steam. |
| 4338199 | Jul., 1982 | Modell | Processing methods for the oxidation of organics in supercritical water | Modar, Inc. (Natick, MA) | Organic materials are oxidized in supercritical water to obtain useful energy and/or resultant materials. In one embodiment, conventional fuels are oxidized with high efficiency to obtain useful energy for power generation and/or process heat. In another embodiment toxic or waste materials are converted to useful energy for power and heat and/or to non-toxic resultant materials. The method is also useful to permit use of a wide range of organic materials as a fuel in the desalination of seawater and brine or the removal of certain inorganic salts from water. |
| 4380960 | Apr., 1983 | Dickinson. | Pollution-free low temperature slurry combustion process utilizing the super-critical state | Self, Dickinson; Norman L. (16230 Greenwood LA., Monte Sereno, CA 95030) | A continuous process for the combustion of solid fuels under conditions such that flue gas is essentially free of particulates and oxides of sulfur and nitrogen. Fuel is charged as an aqueous slurry and additional water condensed from the flue gas may be recycled to the pressurized combustion zone. Combustion is promoted both by water vapor and alkali added with the fuel slurry, while the alkali serves also to neutralize and remove sulfur in completely oxidized, or sulfate, form. Heat of combustion raises the temperature of the reactants above the critical temperature of water, forming a hot fluid from which useful heat is transferred. Under the pressure of the system, heat recovery results in condensation of water, retaining and slurry product ash and providing recycle water, which helps to control reaction temperature as well as to promote the combustion. |
| 4543190 | Sep., 1985 | Modell | Processing methods for the oxidation of organics in supercritical water | Modar, Inc. (Natick, MA) | A method of oxidizing an organic material in an oxidizer includes forming a mixture of the organic material with water and a fluid including oxygen under conditions near supercritical pressure. At the inlet of the oxidizer, the mixture is caused to undergo reaction under supercritical conditions for water, characterized by a temperature of at least about 400.degree. C. and a pressure of at least about 220 atmospheres in the oxidizer. |
| 4564458 | Jan., 1986 | Burleson | Method and apparatus for disposal of a broad spectrum of waste featuring oxidation of waste | Self, Burleson; James C. (374 Dawn Hill, Friendswood, TX 77546) | In the preferred and illustrated embodiment, a deep well is utilized to form a reaction chamber for combustible waste in water. A stream of water borne combustible waste is delivered into a deep well, sufficiently deep to obtain a pressure and temperature in a bottom located reaction chamber at which the water becomes supercritical, there being a pipe for delivering oxygen under pressure for combusting oxygen dissolved in the supercritical water with the waste materials. The reaction is exothermic to sustain itself. It is started preferably by electric current flow to initially raise the temperature in the reaction chamber. The preferred structure is a cased abandoned well having a surrounding cement bond to the formation thereby retarding heat loss into the formation, the bottom located reaction chamber sustaining supercritical conditions. |

| Patent Number | Issue Date | Inventor(s) | Title | Assignee | Abstract |
|---|---|---|---|---|---|
| 4594164 | Jun., 1986 | Titmas. | Method and apparatus for conducting chemical reactions at supercritical conditions | Self, Titmas; James A. (4380 Norona Dr., Stow, OH 44224) | Continuously flowing water contaminated with organic and inorganic materials is treated by being fed to the top of a downdraft column (25) of a hydraulic column reactor (10) and conducted to the bottom thereof to a reaction chamber (18). The pressure and temperature conditions in the reaction chamber (18) are maintained at approximately the necessary pressure and temperature to create supercritical water conditions to thereby treat the water and its lower specific gravity. The treated water can then be separated in the reaction chamber (18) into a particulate and precipitate enriched portion and a particulate and precipitate depleted portion, which portions are conducted upwardly in separate updraft columns (29, 30) and continuously removed therefrom. |
| 4604215 | Aug., 1986 | McCorquodale | Wet oxidation system | Kenox Corporation (Toronto, CA) | A process for oxidizing an aqueous suspension of organic matter at elevated temperature and pressure includes exposing the organic matter to an oxygen-containing gas in a reactor for a period sufficient to reduce chemical oxygen demand of the organic matter to a predetermined desired level. An aqueous suspension of organic matter and bubbles of oxygen containing gas is split, rearranged and combined by an arrangement of vanes within the reactor core. |
| 4692252 | Sep., 1987 | Atwood et al. | Method of removing scale from wet oxidation treatment apparatus | VerTech Treatment Systems, Inc. (Denver, CO) | A method of removing scale from the surfaces of a fluid treatment apparatus by directing a base solution and an acid solution through the fluid treatment apparatus. The fluid treatment apparatus cleaned by the method of the present invention is a vertical tube wet oxidation treatment apparatus in which an aqueous slurry of organic materials is oxidized in a tube which extends deep into the surface of the earth. Water rinses are performed between the steps of circulating the aqueous base solution, circulating the aqueous acid solution, and operating the fluid treatment apparatus. The water used for separating the sequential steps is preferably buffered water. The aqueous acid solution is preferably a mineral acid and most preferably nitric acid. The aqueous base solution is preferably potassium hydroxide or sodium hydroxide. The method also contemplates a sectional wash of the apparatus by directing a base or acid solution partially into the apparatus. |
| 4713177 | Dec., 1987 | Atwood et al. | Process for mitigating scale formation in tube reaction apparatus | VerTech Treatment Systems, Inc. (Denver, CO) | A process for reducing calcium, magnesium and aluminum salt scale build-up in continuous flow or plug flow tube reactors in which a fluid waste undergoes a chemical reaction under heat and pressure to form more environmentally desirable compounds. The process includes the injection of a precipitating reagent into the influent path of a fluid waste stream in a tube reactor to preferentially precipitate calcium, magnesium and aluminum ions which are then carried through and out of the reaction apparatus in a non-scale forming suspension. |
| 4751005 | Jun., 1988 | Mitsui , et al. | Method for treatment of waste water | Nippon Shokubai Kagaku Kogyo Co., Ltd. (Osaka, JP) | Efficient treatment of waste water is accomplished by subjecting the waste water to wet oxidation under continued supply of an oxygen containing gas at a temperature of not more than 370.degree. C. under a pressure enough for the waste water to retain the liquid phase thereof intact, in the presence of a catalyst containing a composite oxide of at least two metals selected from the group consisting of Ti, Si, and Zr and at least one metal selected from the group consisting of Mn, Fe, Co, Ni, W, Cu, Ce, Ag, Pt, Pd, Rh, Ru, and Ir or a compound of the one metal mentioned above. |
| 4767543 | Aug., 1988 | Chornet , et al. | Oxidation of wastewaters | Universite de Sherbrooke (Sherbrooke, CA) | The present invention relates to an improved process for the wet oxidation of water soluble organic pollutants or of an aqueous suspension of organic pollutants. In the contacting of an oxidizing gas and a polluted aqueous phase, the improvement comprises forming a fine mist of the polluted aqueous phase in the presence of the oxidizing gas, thereby increasing the interfacial area between the gas and the polluted aqueous phase. Then the formed mist is introduced into a heated reaction chamber under pressure, thereby enhancing the rate of the destructive oxidation of the organic pollutant by the increase in mass transfer between the gaseous phase and the aqueous mist, the reaction temperature being selected to favor rapid destruction of the pollutant without the formation of stable intermediate reaction products. After destruction of the pollutants, the reaction mixture is allowed to flash off at a pressure lower than the reaction pressure. |
| 4792408 | Dec., 1988 | Titmas. | Method and apparatus for enhancing chemical reactions at supercritical conditions | James A. Titmas Associates Incorporated (Akron, OH) | A continuously flowing fluid is processed by being fed to the top of a hydraulic downdraft column (17) which is of a height such that the pressure at the bottom thereof will approximately be at the pressure necessary to create supercritical water conditions. The fluid is conducted to the bottom of the column (17) and received in a reaction chamber (21) in which the majority of the fluid is recirculated around an annular baffle plate (24). The material in the reaction chamber (21) is heated to a temperature above that necessary to create supercritical water conditions by an independent reaction taking place in a heating chamber (32). The result is that the fluid will undergo chemical reactions at the supercritical temperature and pressure range and will be of a lower specific gravity than the unprocessed fluid. The material not being recirculated in the chamber (21) is fed to one of two updraft columns (30, 31), a start-up column (30) used to preheat the material in the downdraft column (17) during initiation of the process, and a second column ( 31) isolated from the downdraft column (17) so as not to transmit any heat thereto during normal operation of the process. The tempe |
| 4822497 | Apr., 1989 | Hong et al. | Method for solids separation in a wet oxidation type process | Modar, Inc. (Houston, TX) | The present invention relates to a novel aqueous-phase oxidizer and solids separator reactor. More particularly, the invention relates to a two zone pressure vessel in which precipitates and other solids fall or are sprayed from a supercritical temperature super zone into a lower temperature sub zone. The feed material may consist of various waste products which are subsequently oxidized in the super zone of the pressure vessel. The resultant brine or slurry which is found at the lower temperature sub zone of the vessel is removed via a pipe and disposed of accordingly. |
| 4853136 | Aug., 1989 | Roussel , et al. | Process for oxidizing substances dissolved or in suspension in an aqueous solution | L'Air Liquide (Paris, FR) | The process comprises injecting into the inlet of a polyphase tubular reactor (6), on one hand, the aqueous solution at such temperature that the oxidation reaction occurs at a temperature between 50.degree. C. and 370.degree. C. and at an absolute pressure Pe of between 2 bars and 210 bars, and, on the other hand, gaseous oxygen at a pressure slightly higher than said pressure Pe. The invention is applicable to the treatment of effluents for the chemical destruction of pollutants. |
| 4861497 | Aug., 1989 | Welch et al. | Method for the processing of organic compounds | Self, Welch; James F. (P.O. Box 1235, Boulder, CO 80306-1235); Siegwarth; James D. (85 S. 35th St., Boulder, CO 80303) | This invention provides a method for the detoxification of aqueous solutions of organic compounds utilizing a liquid-phase oxidant such as hydrogen peroxide (aq) or ozone (aq). The aqueous solutions of organic compounds and the liquid-phase oxidant are mixed, then compressed and heated to bring the mixture into a supercritical phase. The oxidation reaction proceeds in the supercritical phase. |

| Patent Number | Issue Date | Inventor(s) | Title | Assignee | Abstract |
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| 4869833 | Sep., 1989 | Binning et al. | Method and apparatus for controlled chemical reactions | VerTech Treatment Systems, Inc. (Denver, CO) | A method and apparatus for effecting accelerated chemical reactions at elevated temperatures and pressures including wet oxidation of materials in waste streams. An influent waste stream or first reactant is directed through a long tubular coil within a containment vessel with a second reactant being added to the influent. The flow rates for the gas and liquid components of the waste stream are set to cause plug or slug flow of the waste stream through the tubular coil. The curvature of the coil tends to induce a secondary flow in the liquid such that the liquid tends to travel in a spiral thereby providing more intimate mixing of the reactants; and the containment vessel may be partitioned to form a series of successive compartments to permit different temperature gradients to be applied to successive sections of the tubing coil across its length. Alternatively, a tube in tube construction for the tubular coil permits counter current heat exchange betwen the waste stream within the inner tube and the returning stream. Multiple injection and extraction points are provided along the path of the tubular coil to permit gas, liquid or solid reactants to be added or extracted as desired. The tubular coi |
| 4898107 | Feb., 1990 | Dickinson. | Pressurized wet combustion of wastes in the vapor phase | Dipac Associates (Monte Sereno, CA) | Liquid wastes and solid wastes, which can be put into slurry form, have combustible constituents burned from them at supercritical temperature and subcritical pressure, with respect to water, resulting in purified water and, with the more concentrated wastes, recovery of valuable energy. Pressure makes possible the recovery of latent heat so that the dry heating value of the waste is made available. Consequently, relatively dilute wastes can be "incinerated" without the consumption of auxiliary fuel. |
| 5053142 | Oct., 1991 | Sorensen et al. | Method for treating polluted material | NKT A/S (Brondby, DK); Forskningscenter Riso (Roskilde, DK) | A method for treating polluted material such as industrial waste water or polluted water from other sources, sewage or sewage sludge or other forms of sludge, or polluted soil, to degrade oxidizable substances therein, comprising subjecting the polluted material to a wet oxidation process in a reactor so as to decompose and/or modify oxidizable substances therein and optionally improve the filterability of solids when present in the material; the material may optionally be pretreated so as to facilitate the wet oxidation process. Solid polluted material is preferably in the form of a liquid suspension, such as an aqueous suspension, when subjected to wet oxidation. The wet oxidation process is performed to such an extent, optionally with subsequent substantial removal of heavy metals, that the decomposed and/or modified substances remaining after the wet oxidation and the optional removal of heavy metals are substantially biodegradable. |
| 5057220 | Oct., 1991 | Harada , et al. | Process for treating waste water | Osaka Gas Company Limited (Osaka, JP) | The invention provides processes for treating waste water comprising subjecting waste water to liquid phase oxidation without catalyst, liquid phase oxidation with catalyst and anaerobic digestion and/or aerobic treatment. |
| 5075017 | Dec., 1991 | Hossain , et al. | Method for removing polychlorinated dibenzodioxins and polychlorinated dibenzofurans from paper mill sludge | Kimberly-Clark Corporation (Neenah, WI) | A process for removing PCDD's and PCDF's from paper mill sludge is provided. The process comprises combining the sludge with an oxidant and then oxidizing the sludge under supercritical or near supercritical conditions to destroy the PCDD's and PCDF's. Using this process, destruction efficiencies of greater than 98% have been achieved for 2,3,7,8-TCDD, which is reportedly the most toxic of the dioxins. |
| 5100560 | Mar., 1992 | Huang. | Apparatus and method for supercritical water oxidation | ABB Lummus Crest Inc. (Bloomfield, NJ) | A pressurized feed material (30) in aqueous suspension is oxidized in a supercritical temperature reaction zone (20) in an upper region of a vertically elongated, cyclindrical walled, closed pressure vessel (10) to form an oxidized super fluid phase (46) which is removed from the upper region of the vessel and a brine (44) containing precipitates and other solids which are collected in and removed from a subcritical temperature zone (16) in the lower region of the vessel. The wall (12) of the cylindrical pressure vessel (10) is scraped by rotatable scraper means (60) which upon rotation will dislodge precipitated solids from the wall (12). |
| 5106513 | Apr., 1992 | Hong. | Process for oxidation of materials in water at supercritical temperatures and subcritical pressures | Modar, Inc. (Houston, TX) | Disclosed is a method of oxidizing materials in the presence of an oxidant and water at supercritical temperatures to obtain useful energy and/or more desirable materials. Pressures between 25 and 220 bar are employed. The use of appropriately high temperatures results in a single fluid phase reactor, rapid reaction rates, high efficiency oxidation, and precipitation of inorganic materials. |
| 5133877 | Jul., 1992 | Rofer et al. | Conversion of hazardous materials using supercritical water oxidation | The United States of America as represented by the United States (Washington, DC) | A process for destruction of hazardous materials in a medium of supercritical water without the addition of an oxidant material. The harzardous material is converted to simple compounds which are relatively benign or easily treatable to yield materials which can be discharged into the environment. Treatment agents may be added to the reactants in order to bind certain materials, such as chlorine, in the form of salts or to otherwise facilitate the destruction reactions. |
| 5158689 | Oct., 1992 | Ishii et al. | Method for purification of waste water | Nippon Shokubai Kagaku Kogyo Co., Ltd. (Osaka, JP) | A method for the purification of waste water by the use of a heat-exchanger type reaction vessel composed of a plurality of inner tubes and a shell defining jointly with the outer peripheries of the inner tubes a passage for the flow of a heat transfer medium, which method comprises passing said waste water through said inner tubes and, at the same time, feeding a molecular oxygen-containing gas to the flow of said waste water thereby establishing contact between said waste water and said feed gas and consequently effecting wet oxidation of the impurities present in said waste water. |
| 5192453 | Mar., 1993 | Keckler et al. | Wet oxidation process for ACN waste streams | The Standard Oil Company (Cleveland, OH) | A process is disclosed which limits the corrosion of the materials of construction of a wet oxidation system treating wastewaters. The process is particularly useful in the wet oxidation treatment of ammonium sulfate containing wastes such as acrylonitrile wastewaters. The wastewater is mixed with an oxygen containing gas such that a substantial residual oxygen gas concentration is maintained from before the stream-gas mixture is heated for wet oxidation until after the oxidized stream-gas mixture is cooled and separated. Preferably, in the treatment of acrylonitrile waste water the shutdown procedure comprises cooling said waste stream by introducing an aqueous liquid substantially free of organic impurities and containing a basic material. |
| 5200093 | Apr., 1993 | Barner et al. | Supercritical water oxidation with overhead effluent quenching | ABB Lummus Crest Inc. (Bloomfield, NJ) | In a supercritical oxidation process, the oxidized supercritical fluid effluent (46) discharged from the upper region of the reactor vessel (10) is contacted with a cold quench liquid (66) so as to produce a relatively solids free vapor stream (53) and a liquid stream (51) containing the bulk of the precipitates and other solids carried over in the oxidized supercritical fluid effluent (46). The temperature of the resultant liquid stream (51) is maintained at a temperature below the solids solubility inversion temperature, typically below 600.degree. F., so as to dissolve a substantial portion of the precipitates and other solids collected therein. |

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| 5230810 | Jul., 1993 | Clark , et al. | Corrosion control for wet oxidation systems | Zimpro Passavant Environmental Systems, Inc. (Rothschild, WI) | A process for controlling corrosion in a wet oxidation system by controlling the operating pH range within the system is described. A pH operating range is selected within which corrosion to the wet oxidation system is minimized. The pH within the wet oxidation system is monitored and a pH adjusting material is added to the waste material being treated to maintain the system pH within the selected pH operating range, thus minimizing corrosion. |
| 5232604 | Aug., 1993 | Swallow et al. | Process for the oxidation of materials in water at supercritical temperatures utilizing reaction rate enhancers | Modar, Inc. (Houston, TX) | Disclosed is a method of substantially completely oxidizing material in an aqueous phase at supercritical temperatures and sub- or supercritical pressures by initiating the oxidation in the presence of small amounts of strong oxidizing agents that function to increase the initial reaction rate for the oxidation. The strong oxidizing agents suitable for use in the present invention comprise at least one selected from the group consisting of ozone (O.sub.3), hydrogen peroxide (H.sub.2 O.sub.2), salts containing persulfate (S.sub.2 O.sub.8.sup.2-), salts containing permanganate (MnO.sub.4.sup.-), nitric acid (HNO.sub.3), salts containing nitrate (NO.sub.3.sup.-), oxyacids of chlorine and their corresponding salts, hypochlorous acid (HOCl), salts containing hypochlorite (OCl.sup.-), chlorous acid (HOClO), salts containing chlorite (ClO.sub.2.sup.-), chloric acid (HOClO.sub.2), salts containing chlorate (ClO.sub.3.sup.), perchloric acid (HOClO.sub.3), and salts containing perchlorate (ClO.sub.4.sup.-). |
| 5240619 | Aug., 1993 | Copa et al. | Two-stage subcritical-supercritical wet oxidation | Zimpro Passavant Environmental Systems, Inc. (Rothschild, WI) | A two-stage wet oxidation process for COD removal from high strength wastewater is disclosed. The wastewater stream is treated in a first stage subcritical wet oxidation zone at temperatures between about 250.degree. and 374.degree. C. to remove a substantial portion of the COD. Subsequently, all or a portion of the first stage oxidized waste stream is treated in a second stage supercritical wet oxidation zone at temperatures of 374.degree. to about 600.degree. C. to remove any remaining COD content. Both stages of wet oxidation treatment are carried out at essentially the same system pressure. |
| 5250193 | Oct., 1993 | Sawicki et al. | Wet oxidation of aqueous streams | Air Products and Chemicals, Inc. (Allentown, PA) | This invention relates to improved wet oxidation process for the destruction of organic components in a wastewater stream contaminated with inorganic salts. In wet oxidation, the wastewater stream is contacted with an oxygen-containing water stream at elevated temperatures and pressures. The improvement for treating aqueous wastewater streams contaminated with inorganic salts wherein the organic contaminants are present in an amount from about 0.5 to 2% by weight resides in oxidizing the organic components in a tubular reactor at a temperature ranging from 325.degree. C. to not more than 370.degree. C. and a pressure ranging from 220 to 345 bar. The oxidation reaction is carried out in a reaction time of 5 minutes or less |
| 5252224 | Oct., 1993 | Modell et al. | Supercritical water oxidation process of organics with inorganics | Modell Development Corporation (Framingham, MA) | A method and apparatus is disclosed for oxidation of aqueous mixtures of organic material, including toxic material in the presence of inorganic materials, by reaction of said material with water and oxygen at supercritical conditions. Oxygen and the aqueous mixture are separately pressurized to greater than about 218 atmospheres, combined to form a reaction mixture and then directed through a tubular reactor having a substantially constant internal diameter. The velocity of the reaction mixture is sufficient to prevent settling of a substantial portion of solids initially present in the reaction mixture and of solids which form during passage through the reactor. The mixture is heated to temperature above about 374.degree. C. in the tubular reactor. A substantial portion of the organic material in the reaction mixture is oxidized in the tubular reactor to thereby form an effluent mixture. Inorganic salts in the effluent mixture, which are insoluble at conditions of supercritical temperature and pressure for water, are dissolved in a liquid water phase during cooldown of the effluent mixture at an outlet end of |
| 5339621 | Aug., 1994 | Tolman | Waste treatment system and method utilizing pressurized fluid | Environmental Energy Systems, Inc. (Santa Fe, NM) | The invention comprises an apparatus and method for high pressure treatment of wastes without the addition of excess oxygen and without interference by corrosive deposits. Waste materials are suspended or dissolved in a processing fluid. The pressure of the fluid is raised to a pressure in the range of from about 70 psig to about 5,000 psig. A boiler is then used to heat the high pressure fluid to temperatures above the critical temperature. Solids within the boiler participate in fluidized bed particle scrubbing technology in order to minimize the fouling and corrosion occurring within the boilers during heating. From at least a portion of the vapors produced by the heating in the boiler, net energy output is produced. Useful byproducts can be produced from the vapors. |
| 5358645 | Oct., 1994 | Hong et al. | Zirconium oxide ceramics for surfaces exposed to high temperature water oxidation environments | Modar, Inc. (Houston, TX) | Disclosed is an apparatus and a process for high temperature water oxidation of combustibles in which during at least a part of the oxidation, corrosive material is present and makes contact with at least a portion of the apparatus over a contact area on the apparatus, wherein at least a portion of the contact surface area comprises a zirconia based ceramic, with the temperature of the oxidation process in excess of about 300.degree. C. and the pressure of the oxidation process is in excess of about 27.5 bar (400 psi). |
| 5358646 | Oct., 1994 | Gloyna et al. | Method and apparatus for multiple-stage and recycle wet oxidation | Board of Regents, The University of Texas System (Austin, TX) | An organic or inorganic feed compound can be treated in two or more zones to progressively oxidize the compound. The first zone oxidizes the compound to an intermediate product which includes a first intermediate compound which is intermediate the feed compound and end product. The second zone further oxidizes the intermediate product to an end product or a second intermediate compound which is intermediate the first intermediate compound and an end product. One or both zones may operate catalytically and/or at supercritical conditions for water to oxidize the compounds. |
| 5372725 | Dec., 1994 | Halff , et al. | Method for separation and removal of impurities from liquids | Self, Halff; Albert H. (3514 Rock Creek Dr., Dallas, TX 75225); Reid; Allen F. (4736 Reservoir Rd., Geneseo, NY 11454) | A mechanism for converting impurities or contaminants in a fluid to a non-hazardous or less hazardous condition by raising the fluid to a supercritical state. This is accomplished by a rotatable mechanism having a reaction chamber adapted to receive the fluid and by rotating the rotatable mechanism at a high speed and by heating the fluid to cause the temperature and pressure of the fluid in the reaction chamber to reach the supercritical state. |
| 5384051 | Jan., 1995 | McGinness | Supercritical oxidation reactor | Self, McGinness; Thomas G. (500 N. Guadalupe St., #G-5, Sante Fe, NM 87501) | The invention relates to an improved apparatus and method for initiating and sustaining an oxidation reaction. A fuel, such as natural gas or hazardous waste, is introduced into a reaction zone within a pressurized containment vessel. A permeable liner is placed within the containment vessel and around the reaction zone. An oxidizer, preferably oxygen, is mixed with a carrier fluid, such as water, and the mixture is heated and pressurized to supercritical conditions of temperature and pressure. The supercritical oxidizer-carrier mix is introduced to the reaction zone gradually and uniformly, over a comparatively large area, by forcing it radially inward through the permeable liner and toward the reaction zone. A means and method for cooling the exhausted by-products and using them as a cleansing rinse are disclosed. |

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| 5417937 | May., 1995 | Voigt et al. | Apparatus for wet oxidation | Ciba-Geigy Corporation (Ardsley, NY) | The apparatus (1) for wet oxidation is pre-assembled with its individual units, namely a high-pressure pump (2), a heat exchanger (3), a reactor (4) for the actual wet oxidation and a compressor (5) for feeding an oxygen/gas mixture, in one or two supporting flames and is accommodated in such a manner that its dimensions and its overall weight allow it to be transported on a road and/or rail vehicle, there advantageously being provided two such supporting flames in the form of standard containers (8 and 9), of which one may contain the reactor (4), divided into individual tube sections (6), and the heat exchanger (3), and the other may contain the remaining units, so that the entire apparatus can be pre-assembled into virtually operational condition and the two containers simply have to be set up, joined together and connected on site. Wet oxidation can thus be carried out even where relatively small quantities of medium are to be purified. |
| 5425883 | Jun,. 1995 | Reid , et al. | Method for separation and removal of impurities from liquids | Self, Reid; Allen F. (4736 Reservoir Rd., Geneseo, NY 11454); Halff; Albert H. (3514 Rock Creek Dr., Dallas, TX 75225) | The method of separating impurities from an aqueous solution by means of rotating tile aqueous solution at high speeds until a high pressure and a high temperature is reached. At that time the impurities are separated from the solution. The aqueous solution is kept at high temperatures and pressures until the impurities are separated from the liquid. Preferably, a device providing a centrifugal force, such as a centrifuge, is used to achieve the high temperatures and pressures which should preferably be no lower than 705.4.degree. F. and 3,208 psi, respectively. |
| 5427764 | Jun., 1995 | Barber. | Methods of controlling flow of fluids reacting at supercritical conditions | RPC Waste Management Services, Inc. (Austin, TX) | High temperature reactions are conducted within a high pressure reaction vessel. The interior surfaces of the high pressure containment vessel are protected from the high temperature and corrosive effects of the reaction by causing the reactants to converge in a vortex which contains the highest reaction temperature within the central portions of the reactor. A toroidal reaction vessel is disclosed in which the reactants are directed into a vortex at the axis of origin of the torus by flow guides. |
| 5461648 | .Oct., 1995 | Nauflett , et al. | Supercritical water oxidation reactor with a corrosion-resistant lining | The United States of America as represented by the Secretary of the Navy (Washington, DC) | A supercritical water oxidation reactor includes a vessel with an interior urface, two cooling sections, a heat exchanger, an oxygenating section, a pump, and a trap. The interior surface of the vessel has a corrosion-resistant, artificial ceramic or diamond-like coating. The artificial diamond coating is thin and crystal-like in structure. The heat exchanger is located between the two cooling sections. The heat exchanger and the two cooling sections surround the exterior of the vessel. The oxygenating section comprises a porous cylindrical baffle positioned within the vessel. The porous baffle transfers oxygen, hydrogen peroxide, or other oxygenating substances to an aqueous hazardous waste introduced into the reactor. In accordance with another aspect of the invention, the oxygenating section includes a shaft having a helical extension. The shaft has a corrosion-resistant, artificial diamond or diamond-like coating on its outer surface. The shaft rotates the helical extension to assist in removing solids from the aqueous hazardous waste. |
| 5470481 | Nov., 1995 | Modell , et al. | Method and apparatus for recovering wash water from pulp and paper mill effluent | Modell Environmental Corporation (Waltham, MA) | A method and apparatus for recovering wash water from effluent generated by a pulp and paper mill. The method includes filtering at least a portion of the effluent to form a filtrate stream and an organic solids feed stream. The organic solids feed stream is exposed to a temperature and a pressure which are supercritical for water to cause a substantial portion of the organic component to oxidize and form a product stream that, when cooled, includes a gaseous component, an inorganic solids component, and a liquid wash water component. The wash water component is separated from the gaseous and inorganic solids components, thereby recovering wash water. |
| 5501799 | Mar., 1996 | Bond et al. | Method to remove inorganic scale from a supercritical water oxidation reactor | Abitibi-Price, Inc. (Mississauga, CA); General Atomics (San Diego, CA) | A supercritical water oxidation reactor is alternately supplied with a feed stream and a flushing stream. The feed stream contains organic and inorganic materials. The organic materials are oxidized under supercritical conditions in the reactor and the inorganic materials precipitate out of solution under the same conditions. The flushing stream is a solution in which the inorganic material is soluble. More than one supercritical water oxidation reactor may be connected so that the feed stream is alternately supplied to each reactor. During the period when the feed stream is being supplied to a reactor the effluent from the reactor is cooled to a temperature at which inorganic precipitates are soluble and is then supplied as a flushing stream to one or more of the remaining connected supercritical water oxidation reactors. |
| 5543057 | Aug., 1996 | Whiting et al. | Supercritical water oxidation of organics using a mobile surface | Abitibi-Price, Inc. (Mississauga, CA) | A method for oxidizing organic material in an aqueous stream containing one or more inorganic salts, inorganic salt precursors or mixtures thereof, comprising oxidizing said organic material under supercritical conditions in the presence of an oxidant and a mobile surface of particles to which inorganic salts insoluble under the reaction conditions can adhere. |
| 5545337 | Aug., 1996 | Hong. | Ceramic coating-system or water oxidation environments | Modar, Inc. (Natick, MA) | A process for water oxidation of combustible materials in which during at least a part of the oxidation corrosive material is present and makes contact with at least a portion of the apparatus over a contact area on the apparatus. At least a portion of the contact surface area comprises titanium dioxide coated onto a titanium metal substrate. Such ceramic composites have been found to be highly resistant to environments encountered in the process of supercritical water oxidation. Such environments typically contain greater than 50 mole percent water, together with oxygen, carbon dioxide, and a wide range of acids, bases, and salts. Pressures are typically about 27.5 to about 1000 bar while temperatures range as high as 700.degree. C. The ceramic composites are also resistant to degradation mechanisms caused by thermal stresses. |
| 5552039 | Sep., 1996 | McBrayer, Jr. et al. | Turbulent flow cold-wall reactor | RPC Waste Management Services, Inc. (Austin, TX) | A high pressure and high temperature reactor, especially operating under supercritical water conditions combined with corrosive atmosphere. The reactor comprises a reaction chamber and a pressure vessel, which surrounds the reaction chamber. It has high integrity since it has only one penetration in the pressure vessel, and its size is minimized due to induced turbulent flow of the ignited reaction mixture. |
| 5558783 | Sep., 1996 | McGuinness. | Supercritical oxidation reactor | Self, McGuinness; Thomas G. (2990 Middlebury Ct. West, Aurora, IL 60504) | The invention relates to an improved apparatus and method for initiating and sustaining an oxidation reaction. A fuel, such as natural gas or hazardous waste, is introduced into a reaction zone within a pressurized containment vessel. A permeable liner is placed within the containment vessel and around the reaction zone. An oxidizer, preferably oxygen, is mixed with a carrier fluid, such as water, and the mixture is heated and pressurized to supercritical conditions of temperature and pressure. The supercritical oxidizer-carrier mix is introduced to the reaction zone gradually and uniformly, over a comparatively large area, by forcing it radially inward through the permeable liner and toward the reaction zone. A means and method for cooling the exhausted by-products and using them as a cleansing rinse are disclosed. |

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| 5560822 | Oct., 1996 | Bond et al. | Apparatus to remove inorganic scale from a supercritical water oxidation reactor | Self, Bond; Luke D. (20 Hardwick Court, Etobicoke, Ontario, M9C 4G5, CA); Mills; Charles C. (3445 NightHawk Trail, Mississauga, Ontario, L5M 6G4, CA); Whiting; Philip (R.R.#3, Milton, Ontario, L9T 2X7, CA); Koutz; Stanley L. (4449 Yerba Santa Dr., San Diego, CA 92115); Hazlebeck; David A. (486 Live Oak Dr., El Cajon, CA 92020); Downey; Kevin W. (6526 Malcolm Dr., San Diego, CA 92115) | A supercritical water oxidation reactor is alternately supplied with a feed stream and a flushing stream. The feed stream contains organic and inorganic materials. The organic materials are oxidized under supercritical conditions in the reactor and the inorganic materials precipitate out of solution under the same conditions. The flushing stream is a solution in which the inorganic material is soluble. More than one supercritical water oxidation reactor may be connected so that the feed stream is alternately supplied to each reactor. During the period when the feed stream is being supplied to a reactor the effluent from the reactor is cooled to a temperature at which inorganic precipitates are soluble and is then supplied as a flushing stream to one or more of the remaining connected supercritical water oxidation reactors. |
| 5560823 | Oct., 1996 | Whiting. | Reversible flow supercritical reactor and method for operating same | Abitibi-Price, Inc. (Mississauga, CA) | A supercritical water oxidation reactor is described having first and second reaction zones connected in series and through which an aqueous feed stream to be oxidized can be passed in either direction. A self-contained heat exchange fluid system allows supercritical and subcritical temperatures to be maintained in either reaction zone. When supercritical water oxidation is occuring in one reaction zone the effluent is being cooled to a subcritical temperature and used to flush the second reaction zone to remove inorganic scale. |
| 5571423 | Nov., 1996 | Daman. | Process and apparatus for supercritical water oxidation | Foster Wheeler Development Corporation (Livingston, NJ) | An improved process and apparatus are disclosed for the supercritical water oxidation of organic waste materials which avoids or at least substantially reduces the corrosion and solids deposition problems associated with prior art techniques. According to this invention, externally heated supercritical water is fed to a platelet tube reactor to both protectively coat its inner surface and heat the waste stream to oxidation reaction conditions. Higher reaction temperatures can be used as compared to prior art processes, which significantly improves the reaction rate and permits smaller reactors to be used. The protective film of water on the reactor inner surface, coupled with the elimination of preheating of the waste material, substantially reduces solids deposition and corrosion. |
| 5571424 | Nov., 1996 | Ahluwalia. | Internal platelet heat source and method of use in a supercritical water oxidation reactor | Foster Wheeler Development Corporation (Livingston, NJ) | A process and apparatus for the supercritical water oxidation of organic waste materials which avoids or at least substantially reduces the corrosion and solids deposition problems associated with prior art techniques and which provides for efficient heating of the waste material to reaction conditions. Externally heated supercritical water is fed to a compound platelet tube reactor. The compound reactor includes a reaction zone and inner (smaller) and outer (larger) concentric platelet tubes supported concentrically within a shell. The water fed to the reactor both protectively coats surfaces of the inner and outer platelet tubes facing the reaction zone and heats the waste stream to oxidation reaction conditions. Higher reaction temperatures can be used as compared to prior art processes, which significantly improves the reaction rate and permits smaller reactors to be used. The protective films of water on the surfaces of the platelet tubes, coupled with the elimination of preheating of the waste material, substantially reduces solids deposition and corrosion. |
| 5591415 | Jan., 1997 | Dassel et al. | Reactor for supercritical water oxidation of waste | RPC Waste Management Services, Inc. (Austin, TX) | A reactor enclosed in a pressure vessel in a manner that the walls of the pressure vessel are thermally insulated and chemically isolated from the harsh environment of the reaction zone in the reactor. This allows the pressure vessel to handle the high pressures involved, since it is maintained at a reasonably low temperature range. Simultaneously, it allows the reactor to handle the high temperatures involved, since the pressure differentials around it are only minimal. |
| 5614087 | Mar., 1997 | Le | Wet oxidation system | Kenox Corporation (CA) | An apparatus is provided for oxidizing an aqueous suspension of organic matter at elevated pressure. The apparatus has a reactor and an inlet for the aqueous suspension which is introduced to an upstream end of the reactor. A device for circulating the aqueous suspension through the reactor. An inlet for an oxygen containing gas introduced to the aqueous suspension. An outlet for removing treated aqueous suspension from a downstream end of the reactor and a static mixer vane arrangement for splitting, rearranging and combining the aqueous suspension as the circulating device circulates the aqueous suspension through the reactor. The improvement comprises withdrawing the treated aqueous suspension from the downstream end of the reactor and combining a major portion thereof with fresh incoming aqueous suspension. The circulating device returns the combined aqueous suspension to the reactor via the inlet for the aqueous suspension. A minor portion of the withdrawn aqueous suspension is disposed of while at the uppermost region of the reactor, spent gases are removed therefrom as separated from the aqueous mixture. |
| 5620606 | Apr., 1997 | McBrayer, Jr. et al. | Method and apparatus for reacting oxidizable matter with particles | RPC Waste Management Services, Inc. (Austin, TX) | Method/system of adding solid particles to inhibit or prevent plugging in a reactor at conditions such that the temperature and pressure are at least in the vicinity of supercritical conditions for water. Particles may be added in conjunction with a pH-adjusting material, thereby inhibiting plugging in the reactor caused by addition of the pH-adjusting material. Reactor pressure may be reduced by flowing the stream through a static restriction device. |
| 5667698 | Sep., 1997 | Whiting. | Reversible flow supercritical reactor and method for operating same | Abitibi-Price Inc. (Mississauga, CA) | A supercritical water oxidation reactor is described having first and second reaction zones connected in series and through which an aqueous feed stream to be oxidized can be passed in either direction. A self-contained heat exchange fluid system allows supercritical and subcritical temperatures to be maintained in either reaction zone. When supercritical water oxidation is occuring in one reaction zone the effluent is being cooled to a subcritical temperature and used to flush the second reaction zone to remove inorganic scale. |
| 5670040 | Sep., 1997 | Ahluwalia. | Internal platelet heat source and method of use in a supercritical water oxidation reactor | Foster Wheeler Development Corporation (Livingston, NJ) | A process and apparatus for the supercritical water oxidation of organic waste materials which avoids or at least substantially reduces the corrosion and solids deposition problems associated with prior art techniques and which provides for efficient heating of the waste material to reaction conditions. Externally heated supercritical water is fed to a compound platelet tube reactor. The compound reactor includes a reaction zone and inner (smaller) and outer (larger) concentric platelet tubes supported concentrically within a shell. The water fed to the reactor both protectively coats surfaces of the inner and outer platelet tubes facing the reaction zone and heats the waste stream to oxidation reaction conditions. Higher reaction temperatures can be used as compared to prior art processes, which significantly improves the reaction rate and permits smaller reactors to be used. The protective films of water on the surfaces of the platelet tubes, coupled with the elimination of preheating of the waste material, substantially reduces solids deposition and corrosion. |

| Patent Number | Issue Date | Inventor(s) | Title | Assignee | Abstract |
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| 5674405 | Oct., 1997 | Bourhis et al. | Method for hydrothermal oxidation | Modar, Inc. (Natick, MA) | A method of continuous flow hydrothermal oxidation which provides for a low cost means of reaction *initiation and propagation.* The aqueous-organic feedstock and oxidant are introduced to a small reaction chamber and allowed to mix with the hot, partially reacted contents thereof. This backmixing serves to initiate the reaction of the incoming feedstock. Optionally, the contents of the chamber then pass to a second reactor located downstream, in order to allow for completion of the oxidation reaction. |
| 5683587 | Nov., 1997 | Ferrara et al. | Process for treating industrial wastes | Ferrara; Marcello (via Marco Polo, 73, Messina, IT); Scopelliti; Maria Gabriella (via Marco Polo, 73, Messina, IT) | Water to be utilized is reacted with soda ash and lime to produce a less corrosive and foulant water. Reaction sludges are fed to a desulfurization unit, where SO.sub.x, NO.sub.x and CO.sub.2 abatement occurs; other industrial waste sludges and/or waters and/or gases can also be utilized in such connection. *FIG. 1 is one of the possible process schemes of the present invention.* |
| 5755974 | May., 1998 | McBrayer, Jr. et al. | Method and apparatus for reacting oxidizable matter with a salt | RPC Waste Management Services, Inc. (Austin, TX) | Method and apparatus for inhibiting plugging in a reactor that operates at a temperature and a pressure that are at least in the vicinity of supercritical condition for water. One or more salts are preferably added, in a controlled manner, to a stream containing a first salt, in order to allow a eutectic, molten blend with the first salt to be formed. *The blend may have a melting point below the* temperature of the reactor. The stream is introduced into the reactor and preferably at least a portion of the blend is in a molten state. Plugging in the reactor may thus be inhibited or prevented. |
| 5941184 | Aug., 1999 | Casacia et al. | Controlled thermal oxidation process for organic wastes | Eco Waste Solutions Inc. (Ontario, CA) | A controlled thermal oxidation process for solid combustible waste. The process comprises a first combustion stage wherein the waste is burned in a *downward direction from top to bottom. A first,* fixed air flow of predetermined volume is passed from bottom to top of the waste. A second, modulated air flow of predetermined lesser volume is passed over the waste and through the combustion flame. The process further comprises a second combustion stage wherein products of combustion from the first stage are exposed to high temperature conditions for a short period of time under 135% to 200% overall stoichiometric air conditions. |
| 6054057 | Apr., 2000 | Hazlebeck , et al. | Downflow hydrothermal treatment | General Atomics (San Diego, CA) | A system and method for treatment of a feed material includes a reactor chamber in a reactor vessel. The reactor vessel has a longitudinal axis which is vertically oriented so that gravitational forces act generally in a direction along the axis between a top and a bottom of the vessel. A feed material is introduced by a nozzle into the reactor chamber as a jet stream through the top end of the vessel. This jet stream causes back-mixing in the reactor chamber, contributing to rapid initiation of *reaction and general down flow of material through the reactor chamber. The material in the reactor* chamber can be quenched to dissolve sticky solids in the effluent before the effluent is discharged from the lower end of the vessel. Further, the reactor vessel can include a plug flow section to carry out additional reaction of the feed material. |
| 6238568 | May., 2001 | Hazlebeck | Hydrothermal processing with phosphate additive | General Atomics (San Diego, CA) | A system (10) and method for hydrothermal treatment of a feed material (11) includes a reaction chamber (14) in a reactor (12). Importantly, an additive (16) is added with the feed material (11) to the reaction chamber (14). The additive (16) causes a reaction medium (18) in the reaction chamber (14) to include phosphate compounds. The phosphate compounds allow precipitating salts to be *transported through the reactor (12) without plugging and inhibiting the build-up of precipitating salts* in the reaction chamber (14). |
| 6171509 | Jan., 2001 | McBrayer, Jr. , et al. | Method and apparatus for treating salt streams | Chematur Engineering AB (Karlskoga, SE) | A method for avoiding the precipitation of salts from a salt containing water stream prior to the stream reaching a supercritical water reactor is presented. The salt containing water stream is preferably kept at temperatures below supercritical conditions as the stream is transferred to the reactor. After the salt stream reaches the reactor the temperature of the salt stream is preferably raised to the appropriate temperature by mixing the salt stream, within the reactor, with a second stream that has been heated above the supercritical temperature of water. Alternatively, a method for preventing the clogging of the conduits upstream from the reactor may involve the mixing of two subcritical waste streams. One stream may include salts, the other preferably includes oxidizable material. The heat produced by the reaction of the oxidizable materials within the reactor preferably allows the mixture to remain at supercritical conditions for a time sufficient to oxidize substantially all of the oxidizable material. |
| 6264844 | Jul., 2001 | Modell et al. | Supercritical water oxidation process and apparatus of organics with inorganics | Modell Environmental Corporation (Cambridge, MA) | A method and apparatus is disclosed for oxidation of aqueous mixtures of organic material, including toxic material in the presence of inorganic materials, by reaction of said material with water and oxygen at supercritical conditions. Oxygen and the aqueous mixture are separately pressurized to greater than about 218 atmospheres, combined to form a reaction mixture and then directed through a tubular reactor having a substantially constant internal diameter. The velocity of the reaction mixture is sufficient to prevent settling of a substantial portion of solids initially present in the reaction mixture and of solids which form during passage through the reactor. The mixture is heated to temperature above about 374.degree. C. in the tubular reactor. A substantial portion of the organic material in the reaction mixture is oxidized in the tubular reactor to thereby form an effluent mixture. Inorganic salts in *the effluenet mixture,* which are insoluble at conditions of supercritical temperature and pressure for water, are dissolved in a liquid water phase during cooldown of the effluent mixture at an outlet end of |

# Appendix B

| Question | Responses |
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| What do you believe are the major engineering hurdles still facing SCWO? | corrosion (6), salt plugging (3), reactor chemistry, pumping of high solids concentrations (2), saftey concerns, stable operation (2), scaling (4), feed prep and concentration, solutions have been found to all major engineering hurdles |
| What do you believe are the major non-engineering hurdles still facing SCWO? | public skeptism (3), industry skeptism, SCWO being a new technology (5), economics (7), perception of safety problems with high pressure / high temperature (3) |
| In what primary applications do you see SCWO playing a large role during the next 5 to 10 years? | demilitarization of chemical weapons (4); non-corrosive feeds; low salt content feeds; biological wastewater; high end highly isolated applications; municipal sludge (3); hazardous waste; radiological waste; paper mill destruction and recovery; special industrial waste; 10-20% organics concentration feeds that are low in chlorine, sulfur, and phosphorous |
| In what primary applications do you see SCWO playing a large role farther in to the future, in possibly the next 20 to 50 years? | more corrosive feeds, higher salt content feeds, cruise ships, aircraft carriers, space stations (2), large government facilities, concentrated animal feeding operations, undiscovered chemistry, non-waste treatment applications (i.e. power generation), industrial sludge (2), municipal sludge (3), water recycling process, difficult to say (4), broad spectrum of hazardous waste disposal, biological waste |
| What are the major competing technologies for these potential applications? Compared to SCWO, what are the competing technologies' major advantages/drawbacks | incineration (5), biotreatment (2), plasma assisted oxidation (2), glass aggregate vitrification, wet air oxidaiton (3), catalytic wet air oxidation, SCWO is too underdeveloped for application analysis, electrochemical oxidation, pyrolosis, chemical dechlorination |
| What type of SCWO reactor designs do you believe will be developed to meet the needs of these applications? | each company has unique designs to handle solids handling and corrosion issues, need government support until industry trust is gained, tubular reactor is cost effective, vessel reactor is ideal where space is a premium, SCWO is too immature to say, Batch, DSTR, PFR, TWR, simple tubular and special designs |