DEMONSTRATION OF THE MODAR SUPERCRITICAL WATER OXIDATION PROCESS

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ABSTRACT

Stone & Webster Engineering Corporation was Program Manager for the development and demonstration of a supercritical water oxidation (SCWO) process. The program, sponsored by the Assistant Secretary of Conservation and Renewable Energy through the Office of Industrial Energy Efficiency and the Industrial Energy Efficiency Division, was initiated through a cooperative agreement in 1988. Stone & Webster, working with MODAR, Inc., of Natick, Massachusetts recently completed the fabrication and testing of a 500 gallon-per-day pilot plant of the MODAR SCWO process. Over an eight-month demonstration program, the MODAR process, has proven itself to be an effective treatment for aqueous wastes including hazardous and toxic materials. In addition, the process, with its patented vessel reactor system, has the potential for the treatment of mixed waste materials to destroy any organic constituents and concentrate most radionuclides.

INTRODUCTION - SUPERCRITICAL WATER OXIDATION

Supercritical Water Oxidation (SCWO) is an aqueous oxidation process. It is similar to wet oxidation processes in that oxidation of organic substances occurs in the presence of water at moderate temperatures. The major difference is that while subcritical systems are operated to maintain water in the liquid state and are called 'wet,' supercritical systems are operated above the critical point of water. Within the reaction zone, the water is not present as a conventional vapor (steam) or liquid. It exists as a supercritical fluid phase that is a hybrid with properties of both liquid and vapor. The supercritical fluid has unique solubility properties in that organic materials and gases are completely miscible, while inorganic materials are only slightly soluble. These properties remove the mass transfer limitations, and subsequent lower destruction efficiencies, of subcritical (wet) systems. This enhanced mass transfer combined with a moderate temperature of operation (575 - 625°C) results in a system capable of complete destruction (99.999+%) of organic materials, while providing a means of separating and concentrating inorganic compounds.

Supercritical water oxidation systems have a solid history of bench scale testing, and have been shown to be capable of complete destruction of a variety of organic compounds. To date nearly 200 materials have been oxidized with continuous bench scale units. However, previous pilot scale demonstrations of this technology have experienced limited success.

In the reaction zone, the organic material is oxidized at approximately 600°C. Metals tend to precipitate as their oxides, while anions such as Cl^- and S^{--} form their respective acids. In the event these inorganic anions are present in quantities sufficient to affect corrosion, they are neutralized by the addition of NaOH or $Ca(OH)_2$. Experience has shown that neutralization of acids formed is required to maintain the reactor effluent pH above 2 to limit corrosion and potential failure of high pressure components. During neutralization, the salts formed are insoluble in the supercritical fluid.

A significant advantage of SCWO is that there are minimal air pollution problems compared with thermal incineration. Since the oxidation occurs in water, all acid forming anions (S, P, Cl) are soluble as acids or their neutralized salts, and exit the process as solutions, or in the case of nitrogen, as inert gases. NOx is routinely less than 1 mg/m^3 in the gaseous effluent of any existing test unit. In addition, the main effluent streams are liquid and can be contained and can be tested prior to discharge.

The major stumbling block for the technology is handling certain inorganic solids that are present or generated during processing. In the mid-1980's, MODAR engineers observed that when processing a chlorinated waste which required neutralization, the resulting salts plugged the reactor. To date the most effective neutralization technique has been in-situ through the addition of a base. However, while the neutralization is effective in limiting corrosion, the resulting salts formed (NaCl, Na_2SO_4, $CaCl_2$) are virtually insoluble in the supercritical fluid, and are "sticky", depositing on the walls of the reactor or piping and will eventually plug the system. It has been observed that even when these sticky salts are introduced into the reactor in their pure form (not generated in-situ), they are still sticky.

RECENT DEPARTMENT OF ENERGY PROGRAM

In 1988, the Department of Energy initiated a program to evaluate and demonstrate a water oxidation system to recover energy by processing an industrial waste. In the reaction heat liberated during oxidation, maintains the process temperature. In current embodiments of both sub and supercritical systems, the process is adiabatic - that is the heat of reaction is removed from the process as hot effluent flow. During processing of organic materials, the heat of reaction may be recovered through heat exchange with the reactor effluent. This concept of energy recovery was the motivation for the Department of Energy in initiating this program.

As originally envisioned, the program consisted of four distinct phases:

- Phase I Feasibility Evaluation
- Phase II Proof of Concept
- Phase III Industrial System Development
- Phase IV Testing Under Industrial Conditions

To date, Stone & Webster has completed Phases I and II. The result of Phase I was a report issued in September 1989. Phase II is the subject of this report. During the Phase I evaluations, Stone & Webster concluded that energy could be recovered from wet oxidation systems. In addition, while subcritical processes were commercially mature, supercritical water oxidation was still under development. Furthermore, it was concluded, through an industrial review panel, that commercial users wanted the complete destruction of hazardous or nuisance wastewaters that SCWO provided. A further conclusion was that the MODAR SCWO process was the most commercially mature, and therefore it became the focus of the development and demonstration program.

In 1990, Stone & Webster began Phase IIA, which was an extensive review of the MODAR SCWO process to determine its readiness for commercial application, and develop a plan for future testing to prove the concept, or, if appropriate, proceed directly to Phase III for commercial demonstration. Key conclusions of Phase IIA were that the MODAR process, while supported by a solid background of laboratory and pilot scale testing, was not ready for commercial application, and several critical aspects needed to be demonstrated at a larger scale.

During Phase IIA, Stone & Webster worked with MODAR to develop a cost effective plan to prove the critical concepts and equipment associated with the process through the refurbishment of MODAR's existing pilot plant. This program plan included extensive modifications to the existing reactor vessel, as well as upgrading the balance of plant to support the new process configuration. Since the goal of the program was demonstration of maximum energy recovery, the reactor and process were configured to produce a solid-free hot effluent from the reactor for heat recovery.

It is critical to the commercialization of the MODAR SCWO process to demonstrate the capability to treat materials that contain/generate sticky solids. MODAR's approach to controlling these materials is two-fold. First, the solids generated are directed into the liquid brine within the vessel reactor. Secondly, any entrained material is removed through mechanical filtration. The filter was designed to remove virtually all entrained particulate matter in the reactor effluent and could be cleaned without shutting the unit down. This is a significant advantage over other systems that shutdown, cooldown and redissolve the solids. The test program evaluated the process' ability to maintain continuous operations without plugging the downstream lines or the filter.

In Phase IIB, Stone & Webster and MODAR executed the demonstration program by refurbishing the existing MODAR pilot plant. The refurbishment was extensive and included reconfiguring most equipment and updating the control system. The program was designed to effectively "prove the concept" of supercritical water oxidation, and provide data necessary for scaleup to commercial units. Stone & Webster, as Program Manager, developed the performance specifications for the pilot plant, and provided design oversight and assistance as required. Key to this demonstration was a pilot-scale design that effectively simulated full scale operations using commercially available equipment.

Key objectives of the pilot demonstration program included:

- Continuous processing of a sticky solids feed;
- Characterization of the process effluent;
- Materials testing;
- Equipment evaluation and testing; and
- Measurement of heat/energy available for export.

The pilot plant was fabricated, and testing initiated in December 1992. Stone & Webster was responsible for setting experimental objectives and had one process engineer assisting as a Shift Supervisor during operations. MODAR provided the other staff to allow around the clock experimental operation. Plant staffing included a Mechanical Operator, Computer Operator, and Supervisor on each shift.

The test program included a series of tests of increasing duration and processing difficulty. Once the system's operation was verified, testing focused on solids deposition and removal from the reactor. These short-duration tests were primarily to optimize nozzle performance.

For all testing, a simulated hazardous waste feed material was used because of permitting limitations. During each test, data was gathered regarding organic destruction, inorganic solids distribution, available energy for recovery, and general system operation. Each test was evaluated and equipment or procedures adjusted prior to proceeding. The test program concluded in August 1993 with a 7-day (168 hour) continuous system test processing the simulated hazardous waste containing 2% (by weight of the total feed) sticky solids.

PILOT PLANT DESCRIPTION

The pilot plant process flow diagram is included as Fig. 1. This design is based on processing a feed that contains or generates sticky solids and controls their deposition to produce a hot solid-free effluent suitable for energy recovery. The pilot plant consists of the following major subsystems:

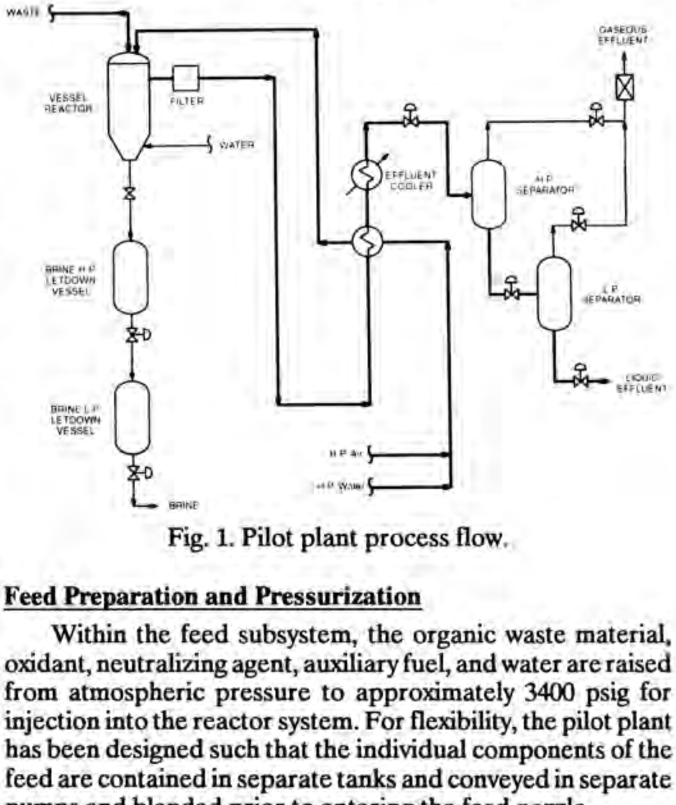

Fig. 1. Pilot plant process flow.

Feed Preparation and Pressurization

Within the feed subsystem, the organic waste material, oxidant, neutralizing agent, auxiliary fuel, and water are raised from atmospheric pressure to approximately 3400 psig for injection into the reactor system. For flexibility, the pilot plant has been designed such that the individual components of the feed are contained in separate tanks and conveyed in separate pumps and blended prior to entering the feed nozzle.

The liquid feeds are pressurized in their respective pumps and enter the reactor through the core of a concentric nozzle at near room temperature. This cold feed arrangement allows the system to process higher concentrations of organic materials, and hence destroy more material. In addition, the operational problems of feed/effluent heat exchange (control and fouling) are avoided. The oxidant, in this case air, is compressed, and heated to reaction temperature (600°C) and combined with supercritical water. This hot stream enters the reactor through the annulus of the feed nozzle and aids in reaction initiation.

Reaction

The feeds enter the reactor through a nozzle and are instantaneously brought to supercritical conditions and the reactions proceeds. At the nozzle tip several things are occurring: the entire mixture is becoming miscible in a single phase; the oxygen is combining with organic carbon and hydrogen to form CO_2 and H_2O; inorganic materials are being oxidized to form insoluble salts; and the acid-forming anions (Cl^-, S^{--}) are being neutralized.

The reactor vessel operates as a continually stirred tank reactor with the nozzle providing the mixing force. Within the reactor three distinct fluids exist as well as transition zones. In the upper portion of the vessel the temperature is maintained at near 600°C by the heat liberated during reaction. This supercritical zone is maintained in the reactor and through the filters into the second stage reactor (a small pipe with the provision for injecting fuel to raise the mix temperature 30 - 50°C to ensure complete destruction of organics). Following the second stage reactor is a one-liter material test chamber (MTC-1). When the second stage reactor is on-line, MTC-1 represents the hottest temperature in the system.

Just below the nozzle tip, the inorganic materials (metal oxides and salts) are precipitated from the supercritical mixture. These materials fall into the bottom of the reactor or are entrained in the flow and captured in the filters. In the case where organic compounds containing chloride or sulfur are processed, the Cl^- and S^{--} that are liberated in reaction are neutralized by the addition of NaOH and form their respective sodium salts. These salts present the challenges in operating the system because they are very sticky. Sodium carbonate (which is also sticky) is formed by caustic reacting with the excess CO_2. Ideally, these sticky salts are projected straight down into the brine at the bottom of the reactor where they dissolve.

The bottom portion of the reactor vessel is cooled by the injection of cold water to maintain a pool of liquid water at approximately 200°C. The liquid level is maintained in the bottom of the reactor due to the extreme density difference between the hot supercritical fluid above and the cooler liquid water phase. The sticky solids that fall into the brine are immediately dissolved in the cool water and can be removed.

At the reactor exit, filters have been installed to effect complete removal of the sticky solids. This prevents plugging of downstream components due to the presence of sticky solids. Parallel filters are used to facilitate cleaning without system shutdown. The specific design and material of construction are proprietary to MODAR.

Effluent and Brine Cooling and Letdown

Upon exiting MTC-1, the main effluent is cooled through regenerative heat exchange with the process air and supercritical water. A second material test chamber (MTC-2) is installed to represent subcritical water at high pressure. The effluent is further cooled and enters the first of two pressure letdown stages. The gases (N_2, CO_2, and excess O_2) exit through a carbon trap, while the liquid is saved for subsequent analyses and discharge. The gas effluent is continuously monitored for CO, CO_2, NO_X, O_2, and N_2.

The liquid brine exiting the reactor is reduced to atmospheric pressure in the same manner and collected for treatment (precipitation of heavy metals if required) and disposal. The gas is combined with the main effluent gas and discharged.

Filter Backwash

The filters are designed to be periodically cleaned by dissolving the accumulated solids in liquid water. The backwash water is heated to prevent thermal shock to the system, and injected onto the off-line filter. The backwash fluid is collected using a process identical to the brine letdown system.

Computer Control

The pilot plant is capable of complete computer control. The control hardware is a Leeds and Northrup, MicroMax II unit. The single CPU supports both the bench and pilot unit. The pilot unit is configured to monitor 150 analog inputs (temperatures, pressures, levels, etc.), read 29 digital inputs (level switches, pressure switches, etc.), manipulate 24 analog outputs (control valves, pump stroke adjusts, proportional heaters, etc.), and activate 106 digital outputs (on/off valves, on/off heaters, pump power, etc.). The bench unit is configured with 68 analog inputs, 15 digital inputs, 8 analog outputs and 30 digital outputs.

CONCLUSIONS

Our testing has shown that scaleup of a SCWO process designed to process a sticky solid feed, was not a trivial task. Our work to date has been valuable in evaluating the mechanical integrity, operation, and limitations of the process. Much of the plant exceeded performance goals. In fact, we have processed more sticky solids during this program than all other programs to date combined (1180 pounds). However, the primary objective of demonstrating effective control of sticky solids was not achieved. This was due in large part to the limitations imposed on the process to meet the Department of Energy's programmatic goal of producing a hot effluent for energy recovery.

Overall, the major conclusions of this development and demonstration program were:

Organic Destruction

Three streams make up the effluent of the MODAR SCWO process: 1) the main effluent which is the water contained in the feed and any generated by oxidation, 2) the gas which consists of CO_2, excess oxygen and any nitrogen, and 3) the brine which is removed from the reactor and contains the inorganic salts and any ash formed. All three streams were monitored to determine the organic destruction efficiency of the process.

During the test program, the organic material exiting the process was monitored in several ways. Total organic carbon (TOC) was used to monitor gross carbon destruction. Using the available equipment, this technique could validate destruction efficiencies of up to 99.996% of total carbon. The limitation was due to the detection limit of the liquid TOC analyses. With the exception of one run, greater than 99.99 percent destruction was achieved during each of the runs.

Destruction of the specific organic constituent (perchloroethylene) was determined by GC/MS analyses of the three effluent streams. In all tests perchloroethylene destruction was in excess of 99.999%, assuming the minimum detection limit as present in all effluents. The detection limit for perchloroethylene was greater than 99.9999 %.

Use of Standard Equipment

The test program verified that commercially available equipment can be used in the MODAR SCWO process. The pilot plant was fabricated using catalog items for all items but the reactor vessel. During operations all of the ancillary equipment met or surpassed expectations. Specifically the liquid effluent pressure control valves, feed pumping modules, and brine pressure reduction system operated without incident throughout the program. In addition, a commercial distributed computer control system was used that controlled the plant effectively and efficiently.

Materials of Construction

The SCWO process presents unique material challenges. Within the process there are high and low temperatures, basic and acidic pH, free oxygen, and various inorganic materials. In addition, since the process operates at high pressures, the same materials are subjected to high sustained stresses, and fabrication techniques may introduce tensile residual stresses which exacerbate the corrosion problem.

The program represents one of the most comprehensive materials test efforts in this field to date. The size of the pilot unit afforded the opportunity to test not only coupon samples but evaluate materials, components and fabrication techniques in actual service equipment. The results were highly enlightening. Broadly speaking, the MODAR SCWO process is made up of four zones/chemical environments: the area where the subcritical fluid mixture is cooled to liquid water, the hot supercritical fluid reaction zone, the liquid effluent zone where final cooldown and gas/liquid separation occurs, and the liquid brine zone. Each of these areas is a unique chemical and thermal environment. Temperatures range from 40 to 600°C, pH from 2 to 8, oxygen concentration from ppm to percent levels, and salt (NaCl, Na_2SO_4) concentrations from ppm levels to nearly saturated.

This test program has verified that controlling corrosion to acceptable levels is one of the greatest challenges to commercial application of the process. The critical control parameter to limit corrosion is maintaining the effluent pH. In this program it was observed that corrosion increased significantly at effluent pH levels below 2.

Most metals and alloys were susceptible to corrosion of varying degrees. Many of the high-nickel alloys also experienced stress corrosion cracking in some environments. At this time we have not identified a single metal/alloy that can be used in all zones of the process, however several ceramics show promise. Stone & Webster and MODAR have identified materials (metals/alloys and ceramics) that are appropriate for each of the zones, and are confident that they can be used in commercial applications with acceptable corrosion rates. Materials of choice include high-nickel alloys, as well as specialized grades of other materials. In addition, several ceramic materials have been identified that show excellent corrosion resistance. However, their use may be limited due to mechanical limitations in strength and fabrication techniques. Table I is a summary of recommended materials.

TABLE I
Recommended Materials for SCWO Process Applications

Zone	Conditions	Material
1	Subcritical (acidic) 350°C ≥ T ≥ 250°C	Ti (Grades 2 and 12)
2	Supercritical (acid/base) 650°C ≥ T ≥ 350°C	Proprietary (alloy and ceramic)
3	Liquid Effluent (acidic) T ≤ 250°C	Ti (Grades 2 and 12)
4	Liquid Brine (basic) T ≤ 350°C	Ti (Various Grades)

Handling of Sticky Solids/Nozzle Performance

This configuration of the MODAR process was developed to produce a hot solid-free effluent that could be used for energy recovery. In order to achieve this end, the process design incorporated a feed nozzle that would both provide sufficient mixing to ensure complete chemical reaction (oxidation and neutralization) as well as effectively direct the solids generated during neutralization into the brine. In addition, filters were installed on the vessel effluent lines to capture any solid material that might plug the effluent lines.

The filters performed well. During all tests, there were no indications that any solids passed into the downstream lines. On-line cleaning of the filters was accomplished using liquid water and a backwashing procedure. Physical examinations of the filters were conducted several times during the program, and showed no deterioration even after repeated backwashing.

As testing progressed it became apparent that the nozzle design was critical to efficient operation of this configuration. The nozzle was required to perform two functions - provide sufficient mixing to achieve organic destruction and neutralization, and direct any solids formed into the liquid brine at the bottom of the reactor. These objectives tended to be in opposition, to minimize solids deposition on the vessel walls, a quiescent reactor is needed, while the chemical reactions (oxidation and neutralization) require a turbulent environment. Complicating matters we found that while obtaining and maintaining organic destruction was simply accomplished using a variety of nozzles, neutralization of the acid-forming anions was very difficult, and required the use of high energy nozzles and acceptance of their increased salt deposition within the reactor.

An alternative of operating without neutralization and its associated sticky solids, was not considered since corrosion is highly dependent on the pH in the system. This was confirmed by increased concentrations of metal cations (Cr and Ni) in the effluent at pH levels below 2.

MODAR has developed and patented an alternative process reactor configuration in which the effluent is quenched. This configuration will produce a cooled reactor effluent and removes a degree of constraint from the nozzle by allowing some neutralization and associated salt formation to occur in the quench area of the reactor effluent. This affords the nozzle a larger window of success in its objectives of mixing and solids control. Although this design is better suited for processing sticky solids feedstocks, energy recovery from the effluent will be limited.

RECOMMENDATIONS

At this time the future of SCWO can proceed along two paths. The direction is most dependent on whether one perceives the process as a waste destruction technique, or an alternate combustion technique. Interestingly enough there is enough evidence to support either conclusion.

The embodiment of the MODAR SCWO process tested in this program focused on demonstrating the ultimate SCWO process. It attempted not only to demonstrate the destruction of industrial and hazardous wastes containing sticky solids - it also had to demonstrate such effective control of the sticky solids that the effluent could be used for energy recovery. In retrospect it appears that this program goal was beyond the current technology, and that development in the near term should focus on more specific process applications/markets.

- Recommendation 1 - A commercial demonstration of SCWO to destroy sewage sludge while recovering energy through heat exchange with the process effluent should be conducted.

  When considered as an alternative combustion technique with the ultimate goal of producing energy while processing a fuel or waste material, the focus of further development should be directed towards the design and demonstration of processes and reactor systems to process feedstocks that do not generate sticky solids. Based on the system performance demonstrated in this program, the SCWO process is ready for commercial demonstration of this application. At the present time the most promising feedstocks appear to be sewage sludge and coal waste. Heat recovery techniques include the generation of steam or high temperature water through heat exchange, or expansion of the hot high-pressure effluent through an expansion turbine.

- Recommendation 2 - A program to demonstrate the MODAR quench reactor system should be initiated.

  Considering SCWO as a technique to destroy industrial wastes is also appropriate. SCWO is unique in that it is a process that has demonstrated the ability to effectively destroy organic material contained in an aqueous matrix. When compared with alternative techniques such as incineration, solvent recovery, and landfilling, SCWO has distinct advantages. These include SCWO's complete indiscriminate, non selective destruction of material, as well as a perceived safeguard against process upsets and accidental releases since the major process effluents are liquid and easily contained to verify destruction prior to discharge.

  Any survey of industrial wastes that are amenable to treatment by SCWO would reveal that the majority contain appreciable amounts of chlorine or sulfur. Processing these materials in a SCWO process results in the generation of hydrochloric and sulfuric acids. As discussed previously, operating a SCWO process under extremely acidic conditions (pH less than 2) results in an aggressive environment that degrades most materials. At the current time only certain ceramics and alloys have shown appreciable resistance. The MODAR SCWO process relies on in-situ neutralization of acids formed. However, this generates the sticky solids that can potentially plug the system.

  MODAR has developed an alternative configuration in the quench reactor that should be more effective in its ability to control the problems associated with acid-forming anions in the feed. This patented reactor is designed to quench the reactor effluent. This concept has several advantages over the filter reactor and provides more latitude in the nozzle performance by allowing a portion of the neutralization to occur in the quench system thereby reducing the demands on the nozzle. This test program clearly indicated a direct relationship between neutralization efficiency and solids deposition on the vessel wall (at high neutralization efficiencies there was increased solids deposition). While some degree of neutralization will be required in the reaction zone, the new design allows the quenching of the effluent with a dilute caustic to neutralize acids in the process effluent.