Supercritical water oxidation presented as alternative to incineration – An update.

September 23, 2008, -- Environmentally benign waste disposal is becoming a more and more acute problem. A process now being commercialised, supercritical water oxidation is demonstrating extremely efficient organic waste destruction (99.99%) plus excellent environmental characteristics (none of the emissions associated with incineration). The process is especially suitable for the treatment of wastewater and sludges from domestic sewage and the paper and pharmaceutical and biopharmaceutical industries.

Supercritical Water

Water enters a special condition, or 'fourth phase', in addition to the familiar solid, liquid and gaseous phases, when its temperature and pressure are above 374°C and 221 bar. In this region, its properties change, density being less than that of the liquid, viscosity the same as the gas and diffusivity about mid-way between the liquid and the gas. Most importantly, the solubility of gases and organic compounds are increased to almost 100 per cent while inorganic compounds become almost insoluble.

These special properties have been known theoretically for a long time and in the 1970s and 1980s work began on exploiting them for practical applications. An oxygen supply was introduced and the process is now know as Supercritical Water Oxidation (SCWO). With organic molecules and the added oxygen fully dissolved, a uniform homogeneous mixture is created and reactions can proceed at the intrinsic rate, i.e., the theoretically maximum rate for chemical reactions. Consequently, residence time in the reactor is only about one minute. Despite this brief residence, the method achieves a 99.99 percent destruction of the organic contaminants.

Complete oxidation.

Incineration is also an oxidation process but suffers from several disadvantages, one of which is incomplete combustion and the consequent need to scrub the stack gases to rid them of environmentally dangerous compounds such as dioxins. SCWO results in complete destruction irrespective of the feed entering the process, even PCBs. Due to the lower reaction temperatures, the harmful oxides of nitrogen are not formed; these are toxic and acidic and can cause eutrophication (algal blooms) in fresh water. Traces of nitrous oxide (laughing gas, N_2O) may be formed if the feed contains a nitrogen source. However N_2O is easily separated into nitrogen and oxygen if required.

Benign output.

Unlike incineration, SCWO is a totally enclosed process and the reaction products are discharged at very close to atmospheric pressures and temperatures. Furthermore, they are benign, consisting mainly of CO_2, water and nitrogen. These substances do not need expensive scrubbing to make them suitable for discharge to the environment. Organic and inorganic halogens are converted to the corresponding acids and organic and inorganic sulphur are converted to sulphuric acid. These are far easier to deal with in liquid form than as gases like sulphur dioxide which causes acid rain. Heavy metals are oxidised to their highest oxidation state and are separated together with any inert materials as a fine, non-leachable ash which can be used much like power station ash for landscaping, aggregates and similar applications.

Heat economy

Both SCWO and incineration are auto-thermal, or self-sustaining, once the process is up to operating temperature. However, they both need sufficient organic material in the feed stock or external heating must be applied; incineration needs well in excess of 25 percent before becoming auto thermal whereas SCWO can be auto thermal with only 3-4 percent of organic material in the feed. The SCWO process can therefore show considerable primary fuel savings when compared with incineration.

Modern plants of any kind, which have excess process heat, try and utilise this heat or sell it to defray operating costs and reduce dependence on fossil fuels. Most liquids have higher specific heats than gases so the heat transfer equipment on the SCWO plant is less bulky and expensive than that on incineration plant which gives up its excess heat from the stack gases.

Commercial beginnings.
The Swedish-based company, Chematur Engineering AB, began developing the SCWO process under licence from Eco Waste Technologies in 1995. Chematur acquired the world-wide rights to the technology in1999. The company built a large-scale, pilot plant close to its head office in Karlskoga in central Sweden. The company used this plant to trial the process for the treatment of different wastes for eight years. Encouraging results were obtained for wastes such as sewage sludge, paper and de-inking sludge, msw, food waste, black and grey water, catalyst recovery, pharmaceutical residues, cutting oils and many more.

In 2007, SCFI Group, Cork, Ireland acquired the super critical fluids division of Chematur Engineering and now hold the world wide rights to the patented Aqua Critox® SCWO technology. Recently a large demonstration plant has been built by SCFI Group at Cork, in southern Ireland.

'Wet Air' Comparison.
The SCWO process has similarities to wet air oxidation which is in use in a number of plants already. However, the wet air process operates at temperatures of up to 300 degrees C and 200 bar (depending on the process). This is below the critical point of water and typically achieves only 70 percent destruction of organic carbon, even with residence times in the reactor of up to six hours. Such long residence times require much larger reactors, typically 100 times larger than those required for supercritical processing.

Safety Issues
Chematur's Development Director, Lars Stenmark suggested that, "the wet air process may have paved the way for SCWO: people in industries which normally use unstressed equipment have a psychological barrier which makes them wary of high temperatures and pressures. In fact, compared with many modern pressure vessels, the SCWO process uses very modest pressures and temperatures - the pressures are no higher than those in common gas bottles found in workshops world wide and the reactors are not much larger."

Inline with all modern pressure equipment AquaCritox® plants are designed and tested in full compliance with the European Pressure Equipment Directive (PED). The plants are heavily automated and there is little requirement for operator interaction in what is a very safe and efficient process.

The Salt Limitation
Other problems that are sometimes associated with SCWO are salt deposits and corrosion. SCFI state that "these issues are also more manageable than may be commonly thought. SCFI suggest that obviously, wherever possible it is advisable to avoid dealing with flows which contain high salt saturations which may inhibit heat exchange capacity necessitating increased heat exchange capacity to be installed. When salt concentrations are high we will always consider the possibility of pre-treating flows to remove salts where possible. as well as adapting the process so that higher salt concentrations are not a problem. In fact, scaling is minimal for slurries which contain inert materials because suspended particles act as nuclei for salt precipitation before the fluid reaches the walls of the heat exchanger. Additionally, these inert materials can also scour the walls and pipe work, acting as an abrasive cleaner to remove salt deposits. One of the most important applications, domestic sewage, normally contains considerably less than one percent salt and so does not cause a problem".

SCFI points out that, "difficulties with salt clogging have been exaggerated because of the small diameters of tubes used in the first laboratory-scale experimental plants. Small diameters obviously block easier; in SCFI's large demonstration plant, which has a capacity of 250 kg per hour, the smallest pipe diameter is about 1/2 inch. Because of the size increase, scaling is not a significant problem,"

Corrosion
Halogens and hydrochloric acid for example can be highly corrosive, especially at high temperatures. "The Forschungszentrum in Karlsruhe did studies on corrosion in super critical water during the 1990s and discovered that no corrosion takes place at temperatures above 380 degrees C because there is no dissociation above that temperature." The problem is therefore in the transitional stage from 300 degrees to about 370 degrees and therefore the vulnerable part of the process is the heat exchanger where the flow is raised to this temperature. There is no corrosion in the reactor itself. Chematur developed a proprietary method to overcome any corrosion problem in the heat exchanger. This patented method has been proven over both short and long duration operation of the Aqua Critox® demonstration plant.

Sewage Sludge Treatment
Sewage sludge was brought from two communities near Karlskoga, where Chematur's plant was situated. These tests are being carried out in co-operation with IVL [the Swedish Environmental Research Institute in Stockholm]. The test results confirmed 99.99% destruction of the organic material and the generation of an inert residue. SCFI Group have subsequently performed extensive testing on its demonstration Aqua Critox® plant located in Cork, Ireland using sewage sludge and is sufficiently confident with the test results to approach large municipalities with proposals for treating their sludge. SCFI Group are offering the Aqua Critox® SCWO technology on a design, finance, build, own, operate and maintain basis.

In many countries, sewage sludge is spread on the land. This practice has in more recent times come under cost pressure due to the need for compliance with regulations. Aqua Critox® is a competitive sludge destruction process. The Aqua Critox® process offers complete destruction of the organic fraction of sludge, converting it into carbon dioxide, nitrogen and sterile water. Aqua Critox® does not produce any hazardous byproducts. The residual inorganic fraction from the Aqua Critox® process can be subjected to a process to recover phosphorous and other materials for resale. The inorganic solid residue from the Aqua Critox® process is inert and can be used in the construction industry for roads and other projects without fear of leaching.

Costs
A considerable body of work has been carried out on the costs associated with SCWO and comparisons have been made with incineration. As regards the treatment of sewage sludge, indications are that the process will emerge as more economic than incineration with total treatment costs in the region of £50 per wet tonne as at the beginning of 2008. This £50 figure for SCWO is based on a throughput of six tonnes per hour and is made up of a variable cost, plus a depreciation figure for the plant, minus income from the energy produced. SCFI Group points out that the variable cost very much depends on how the labor cost is calculated and there are bound to be wide variations in accountancy practices throughout the world. Another component of the variable cost is the oxygen which is needed for the oxidation; the cost of this too varies in different locations. Compressed air may be used instead, but the investment then increases by up to 20 per cent. The depreciation is based on 10 per cent over 10 years. This too may change according to accounting practices used by different authorities.

John O'Regan of SCFI comments that, "those responsible for sewage sludge disposal often see incineration as the main option but planning can be a serious obstacle in the face of NIMBY (not in my back yard) protests. SCWO plant's, on the other hand, have none of the emissions problems of incinerators and, provided suitable precautions are taken with the import of the sludge, it operates entirely without odour. They're also smaller and obviously have no chimney stack, so there's no reason why their presence should disturb surrounding communities."

De-inking Sludge
Extensive trial work was performed on de-inking sludge. It was proven that de-inking sludge can be easily processed using Aqua Critox® scwo technology to give significant energy recovery and a reusable filler material. This could result in significant cost savings for paper mills with a corresponding carbon foot print reduction.

Filler Recycling?
SCWO has a number of advantages over this routine; dewatering is much reduced or even eliminated completely. The inks, which mainly consist of carbon and fibers, are completely oxidised to CO_2 and water. Many papers contain inert fillers, mainly china clay, which end up in the sludge and these could be recycled after separation from the Aqua Critox super critical process. Paper mills could satisfy a large part of their paper filler requirements from this source since the filler brightness is close to that of virgin material. No land filling is required which always involves the danger of contaminants leaching into the soil and environment. The filler is inert but it can discolour water courses. The heat value from the process may also be available at the site as a form of energy.

Pharmaceuticals
John O'Regan believes that the pharmaceutical industry could benefit widely from SCWO since it would provide a highly attractive environmental solution in the near future. He points out that, "Because the process can destroy any organic compound without leaving undesirable by-products, it could eliminate the risk of escape into the environment of potent active ingredients. These have been known to kill fish and cause other environmental damage; waste products know as mother liquors for example, could be treated and broken down into harmless CO_2 water and nitrogen."

SCFI is planning to treat biological sludge from the pharmaceutical industry; if successful, the process could largely replace incineration which, with landfill is the preferred method of disposal at the moment. As regards heavy metals, John O'Regan points out that, "they would be oxidised to their highest oxidation state at which ooint the metal oxides are inert. This removes the environmental threat; the same would be true for all other substances."

Cutting oils
Cutting oils containing amines are used universally in manufacturing industries with metal cutting equipment. Chematur performed a number of tests on spent cutting fluids, varying the temperatures and varying the ratio of total organic carbon to total nitrogen by adding methanol. In all experiments the organics were destroyed resulting in a COD < 30 ppm. A small quantity of nitrous oxide was formed, in the order of a few thousand ppm. This corresponds to about 5 per cent of the nitrogen in the influent.

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Sludge before and after treatment