SUPERCRITICAL WATER OXIDATION OF SEWAGE SLUDGE – STATE OF THE ART

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ABSTRACT

Supercritical water oxidation (SCWO) is an innovative and effective destruction method for organic wastewater and sludge. Several tests of the destruction of sewage sludge by SCWO have been done at two state of the art pilot plants. These units have capacities of 250 kg/h and 1100 kg/h, respectively. The test results show that the technology easily destroys the organic material in the sludge and the inorganic material left in the effluent is virtually not leachable and is very easily settled. The very encouraging results indicate that the technology is ready to be commercialised for treatment of sewage sludge. Furthermore, the advantages and possibilities of the method has attracted possible end users and extensive tests containing long continuous operation to finally prove the long term reliability of the technology will be performed during the second quarter 2001.

INTRODUCTION

Oxidation of organic wastes to carbon dioxide, water, and other small molecules can effectively minimise waste volume and detoxify many hazardous compounds. Incineration in air at atmospheric pressure is the most common oxidation technique currently practised. However, incineration meets an increasing opposition from the public and furthermore the cost for incineration of waste has a tendency to raise constantly because of the increasing demand on the flue gas cleaning. A supercritical water oxidation (SCWO) system can handle aqueous streams containing organic material in relatively low concentrations and offers inherent control over emissions and coupling to energy recovery systems.

In 1995 Chematur Engineering (CEAB) started its SCWO activities by a licensing the SCWO process from Eco Waste Technologies (EWT) and early 1999 Chematur acquired the exclusive world-wide rights to EWT's SCWO technology. The Chematur SCWO process is marketed under the trade name Aqua Critox®. In early 1998 CEAB inaugurated its 250 kg/h SCWO demonstration facility based on the EWT process and since then several successful and extensive treatability tests with real wastes has been done (1)

CEAB has a Japanese licensee, Shinko Pantec, they have built a pilot/small full-scale SCWO unit, with a capacity of about 1100 kg/h. The unit was commissioned and started up about half a year ago. Shinko Pantec foresees the treatment of sewage sludge to be the main market for SCWO within Japan. The size of their unit corresponds to the production of sewage sludge from a sewage works for more than 50 000 inhabitants. When they have proven the technology they intend to move the unit to the City of Kobe's sewage works.

SUPERCRITICAL WATER

Under normal conditions, water is seen in either of its three states: steam, liquid water, or ice. If water is heated and compressed to sufficiently high temperature and pressure an additional fluid state of water emerges. Water at high temperatures and pressures, above 374 °C and 221 bar, figure 1, is a fluid that is neither a gas nor a liquid, it is in its supercritical state. The reason for the efficiency of SCWO in destroying organic compounds is the unique properties of water above its critical point.

The change in magnitude of different properties is very rapid at entrance into the supercritical region. Any substance above its critical point has properties that are in between those of a gas and a liquid. The density of supercritical water (SCW) is comparable with liquid water densities, and high enough for reasonable throughputs in a process. On the other hand the viscosity and diffusivity in the supercritical region are more like that of a gas.

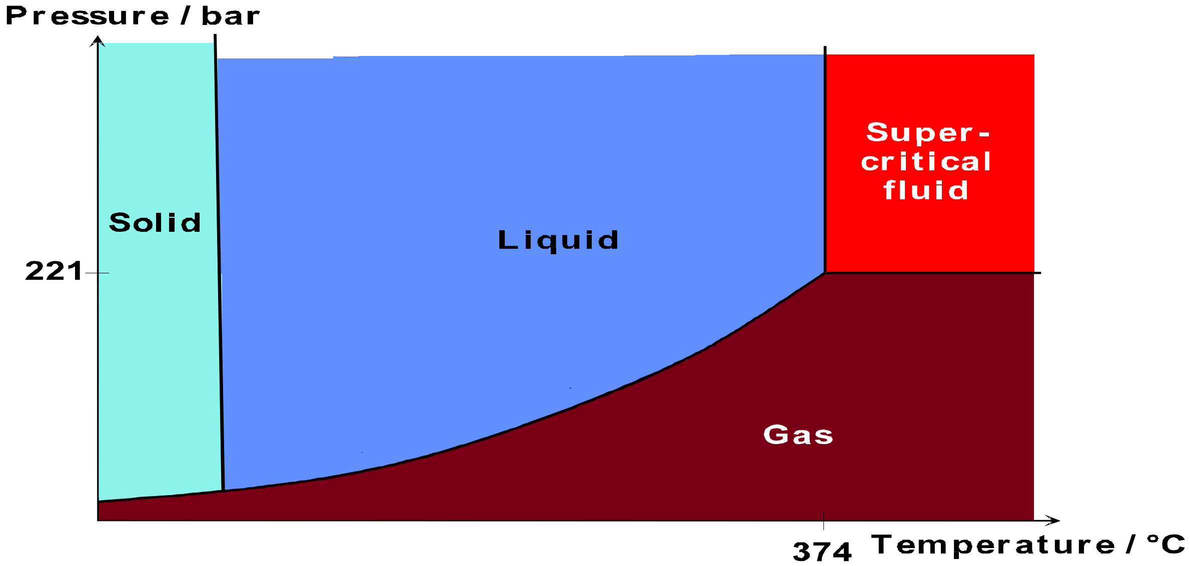

Figure 1: A simplified phase diagram of water

Because of the low dielectric constant water gets a high solvating power, when becoming supercritical and most organic compounds and gases are completely miscible in all proportions in SCW.

The high solubility of gases and organic material together with the high diffusivity gives an insignificant mass transfer resistance in SCW. This is very important to achieve rapid reactions.

DESTRUCTION OF ORGANIC MOLECULES IN SCWO

SCWO destroys essentially all organic wastes containing any combination of elements. While the higher molecular weight organic compound are destroyed or transformed almost immediately, smaller molecules such as acetic acid typifies the rate controlling intermediate for pure organic compounds.

Nitrogen gas is the predominant SCWO end product, when nitrogen is present in the waste. Ammonia and acetic acid would represent the rate-controlling compounds for nitrogen containing substances such as amines.

PROCESS CHARACTERISTICS

Perhaps the greatest appeal of SCWO systems is their capability to destroy any organic compound completely. Low biodegradability or high toxicity has no influence on the treatability by SCWO. No NO_x or dioxins will be formed; in fact it has been shown that SCWO will destroy Dioxins and PCB.

Some typical characteristics for SCWO are:

- The reaction time for complete destruction is between 30 - 90 seconds. This time strongly depends on the reaction temperature
- The reactions takes place at about 250 bar and 400 - 600 °C, this relatively low operating temperature means the process is not likely to produce nitrogen oxides (NO_x).
- Complete conversion of the organic waste is achieved, however traces of acetic acid and nitrous oxide (laughing gas, N_2O) may be found.

THE PROCESS

The feed tank is equipped with a stirrer designed for viscous sludge. The bottom outlet from the feed tank, figure 2, is connected to a mono pump and a macerator in order to eliminate big particles entering the high-pressure pump. The high-pressure feed pump raises the feed pressure to about 250 bar and pumps the feed through the SCWO system. The feed enters an economiser where it is preheated by the reactor effluent. After leaving the economiser, the feed enters the heater. At start up or if the organic concentration is lower than about 3% the feed has to be heated further, before reaching the reactor, e.g. in a gas fired heater.

From the heater outlet, the hot feed enters the reactor. In the reactor, oxygen is injected to start the oxidation reaction. The oxidation reaction generates heat and, as a result, the reactor temperature increases. The inlet feed concentration may be too high for complete oxidation of the organic material to occur in one step without exceeding the reactor's design temperature, 600 °C. As a result, the waste may be oxidised in two stages. At the beginning of the second stage quench water is added with the oxygen.

The water cools the effluent from the previous stage enough to allow the additional oxygen to continue the oxidation reaction without exceeding the temperature limit.

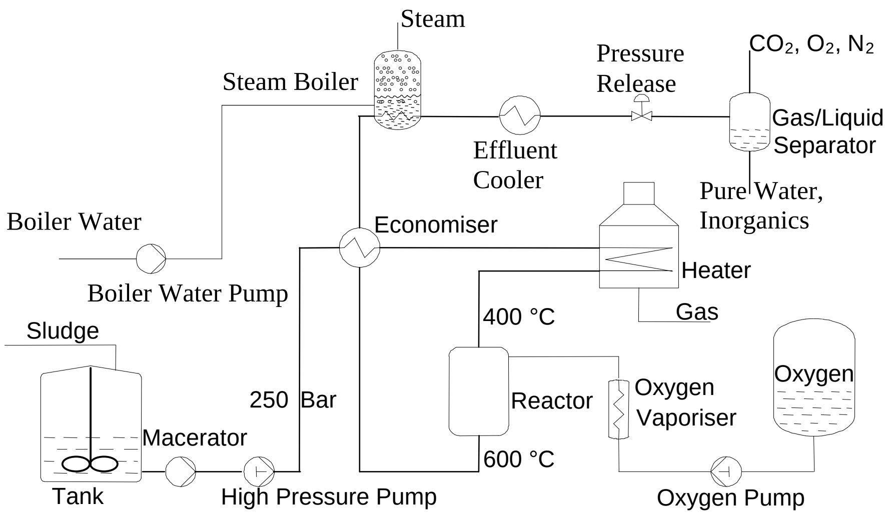

Figure 2: Principal flow sheet of the Aqua Critox® process.

After passing through the reactor, the effluent flows through the economiser, where it preheats the incoming feed. The heat of reaction may easily be recovered in a steam generator, e.g. producing a specified quality of steam. The effluent is cooled to its final exit temperature in the effluent cooler prior to passing through the pressure reduction coils. Adding choke water before the coils controls the pressure drop over the coils in a proprietary way. In the coils the pressure is reduced from about 250 bar a to slightly above atmospheric pressure. The effluent then enters a gas/liquid separator where the carbon dioxide generated in the process is separated from the effluent.

ENGINEERING DESIGN CONSIDERATIONS

In the engineering the properties of sewage sludge has to be considered in order to achieve an efficient, reliable and economic process. To achieve a process with good economics the dry substance of the sludge should be optimised, i.e. maximised. The Chematur Engineering SCWO plant is able to handle at least 15 % dry solids.

First of all it is important to secure a constant supply of sludge without big particles to the high pressure pump. A small enough particle size will be secured by using a macerator and by feeding it by a positive displacement pump (e.g. a mono pump) a stable suction pressure, for the high pressure pump, is achieved.

The use of a high pressure pump designed for handling of sludge is important. The pump used is a hose diaphragm piston pump, illustrated in figure 3. The pump type has a straight pass through the pump and the only pump parts in contact with the sludge are the hose and the check valves, which minimise the risk of clogging. The check valves are typically of ball type and may be doubled to secure sealing.

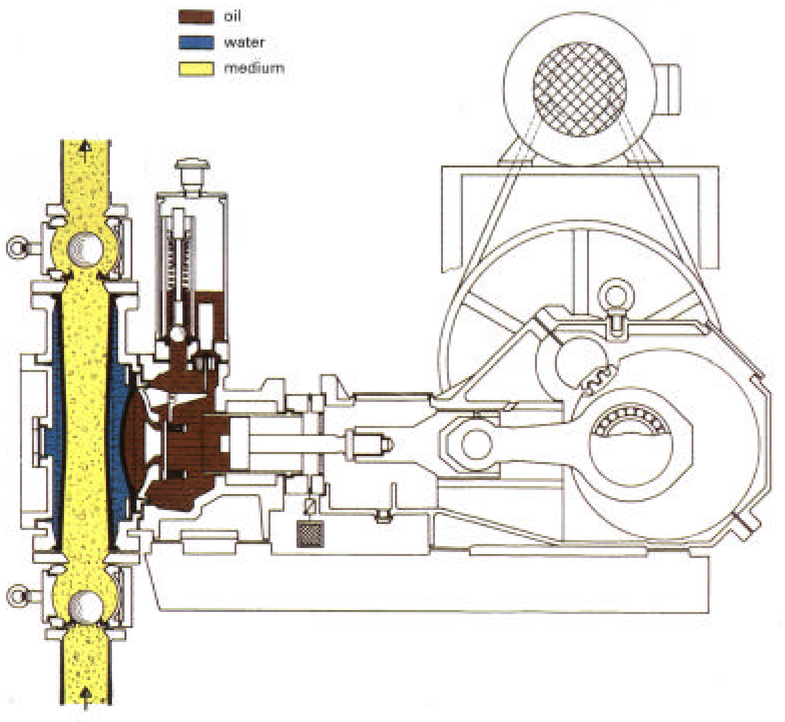

Figure 3: The principle of the hose diaphragm piston pump.

To avoid fouling in the heat exchangers before the destruction of the organic material, It is very important to keep high velocities. This is also true in the reactor and in the heat exchangers after the reactor, to ensure good transportation of the inert inorganic material through the process. However, it is important to control the velocity so that erosion is avoided. To minimise the possibility of plugging caused by the inert inorganic material the reactor is of tubular design and the heat exchangers are of double pipe type. If material starts to settle in a single tube, the velocity in this part increases and the chance for the material to be flushed away increases. Making a tubular reactor also minimises the reactor volume since this is the most efficient type of reactor.

Another important detail is the pressure reduction system. If a pressure regulation valve controls the system pressure, the total pressure drop is taken at one single point. This results in an extremely high velocity and severe erosion because of the inert inorganic material. In the CEAB design the pressure drop is distributed over a number of long capillaries and for the exact adjustment of the pressure, a controlled amount of water is injected in the effluent pipe before the capillaries. This proprietary method minimises the erosion and the capillaries are cheap to replace when needed.

TREATABILITY STUDY

A number of tests have been performed with an undigested mix of primary and secondary sludge. The test has been accomplished at the Chematur pilot plant, which is designed as described above, besides it has no steam boiler. Both dewatered sludge and sludge "as received" has been used. The influence of temperature and concentration was studied.

The main reason for varying the reaction temperature is to find the minimum temperature needed to destroy all nitrogen in the liquid phase, since a minimum temperature is needed for a certain ratio between carbon (total organic carbon, TOC) and nitrogen (total nitrogen, Tot-N) (1-3). The higher the ratio is, the easier the nitrogen is destroyed and this temperature is normally higher than the temperature needed to destroy the organic compounds.

In the tests with pre-concentrated sludge, two oxygen injections with intermediate quench cooling where needed to completely destroy all organic material without exceeding the thermal limit of the construction material. In recent tests, highly concentrated sludge has been treated and these tests will continue in the near future to find out the long-term stability and reliability, using sludge with approximately 15% dry solids.

RESULTS AND DISCUSSION

The tests show that all organic material is very easily destroyed, table 1, However, a minimum temperature of about 540 °C is needed to completely destroy the nitrogen too. The reduction of COD (chemical oxygen demand) is >99,99 for sample 3-5. No significant difference in final COD is received, with varied influent concentration. The realised tests indicate that a solid content of 15 % in the sludge is a realistic operation concentration.

Table 1: Summary of the test results.

Sample	Residence time (s)	Reactor temperature (°C)	COD, feed (mg/l)	COD, effluent (mg/l)	Tot-N, feed (mg/l)	Tot-N, effluent (mg/l)
1	60	510	40000	4.8*	1400	200
2	60	560	40000	3.9*	1400	38
3	60	520	110 000	<5	4400	51
4	60	540	110 000	<5	4400	12.5
5	60	580	110 000	<5	4400	12

Note: * Total organic carbon (TOC)

The destruction efficiency of organic material with SCWO is much higher compared to what is achieved with wet air oxidation and similar processes, operating below the critical point. A number of such plants are used for treatment of sewage sludge and they typically destroy about 70% of the organic carbon (e.g. 4), needing very long residence time.

The inorganic solid residue in the effluent is virtually not leachable (i.e. very low solubility at the pH of the effluent) and the analyses done show a non-hazardous material. This depends of course on the amount of heavy metals in the sewage sludge. Furthermore, the solids settle very easily. The solid residue should be possible to use as building material etc.

The off gas contains almost no VOC and no NO_x, but some of the nitrogen in the starting material is converted to nitrous oxide, N_2O, (not accounted as NO_x). Although N_2O is today not a compound that environmental authorities generally have discharge limits for, it is a green house gas and there may be regulations in the future. However, the nitrous oxide (laughing gas) may also be destroyed be feeding the gas through a bio bed. Furthermore, if needed N_2O can be converted to N_2 and O_2, either thermally, just below 1000 °C (1), or catalytically, between 500 and 600 °C.

ECONOMICS AND CONCLUSION

The results presented, above, show that SCWO is a viable alternative for the treatment of sewage sludge. Also economic calculations, our own as well as others (5,6), indicate that SCWO has the potential to be the cheapest alternative for this treatment.

Table 2 shows the operating cost including personnel, maintenance and consumption of various utilities. The example is a unit treating 7 m^3 sludge (15% DS)/hour, this corresponds to slightly more than one dry ton/hour. The total operating cost would be about 70 GBP per dry ton. The by far biggest variable cost is the consumption of oxygen. However for smaller units the operator cost starts to get important. The value of steam corresponds to 7 GBP/MWh. The system could of course as well produce hot water for internal use or district heating. The variable cost for concentration of the sludge to 15% DS, is not included, since it is assumed to be done for all alternative treatment methods, to at least the same concentration.

Table 2: The operation costs for a SCWO unit treating 7 m^3 sewage sludge, at 15% DS/hour. Corresponding to treatment of slightly more than 1 ton DS/hour.

Operating costs	Consump-tion/hour	Unit price	Unit	Cost (£/h)	Cost (£/m^3)	Cost (£/ton DS)
Operator + overhead 50%	0.5	20	h	15	2.1	14
Oxygen	1100	0.05	kg	55	7.9	52
Electricity	240	0.018	kWh	4.3	0.6	4.1
Process water	1.8	0.07	m^3	0.1	0	0.1
Natural gas	23	0.07	Nm^3	1.6	0.2	1.5
Cooling water	105	0.05	m^3	5.3	0.7	5
Maintenance (2% of cap. cost)				12.5	1.8	12
Steam (income)	4.4	4.5	ton	20	2.8	19
Total operating cost				**74**	**10.5**	**70**

The capital cost would be about 5 million GBP and this includes, the SCWO process, oxygen system, building and auxiliary equipment such as tanks. The cost for a sludge concentration unit is not included, since it is assumed to already exist at the sewage works. The capital cost per treated dry ton of sludge will be 79 GBP, if an interest rate of 8% and a depreciation time of 12 years are used. This gives a total treatment cost of 149 GBP/dry ton of sewage sludge. The treatment cost would decrease to 132 GBP/dry ton of sludge, if the concentration of treated sludge could be increased to 18% DS in a full-scale unit.

Furthermore, the advantages and possibilities of the method has attracted possible end users and extensive tests containing long continuous operation to finally prove the long term reliability of the technology will be performed during the second quarter 2001.

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CEAB and SCWO

- CEAB has been working with EWT and SCWO since 1995
- Demo plant (250 kg/h) in operation since 1998
- Acquired the EWT SCWO technology 1999

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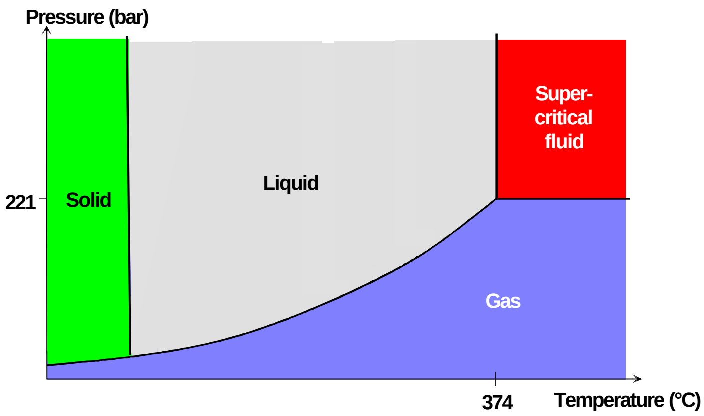
Phase Diagram of Water



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Physical Properties

	Liquid	SCF	Gas
Density (kg/m^3)	10^3	$3x10^2$	1
Viscosity (Pa s)	10^{-3}	10^{-5}	10^{-5}
Diffusivity (m^2/s)	10^{-10}	10^{-7}	10^{-5}

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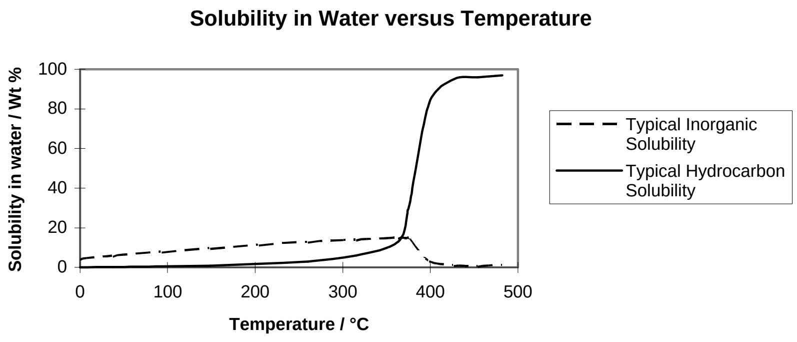
Solubility



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Performance

- Up to 99.9999 % conversion of contaminants
  - Organic carbon to CO2
  - Org. and inorg. nitrogen to N2 (no NOx)
  - Org. and inorg. halogens to H-X
  - Org. and inorg. sulphur to H2SO4 (no SOx)
- Volatile solids destroyed
- Heavy metals oxidised to highest ox. State
- Inerts separate as fine, non-leachable ash

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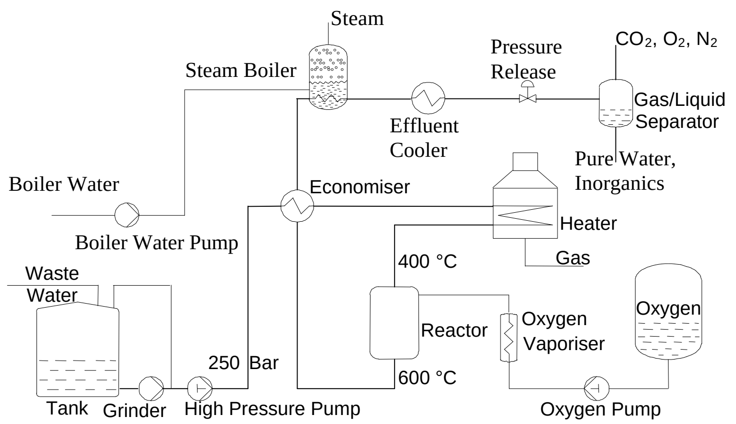
The Process



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Characteristics

- Immediate reactions - 30-90 seconds
- Reactions at about 275 bar and 400-600 ^{o}C
- Complete conversions - 99% - 99.99% - 99.9999%
  - CO_2
  - N_2
  - H_2O
  - HCl
  - H_2SO_4
  - H_3PO_4

  Traces of HOAc and N_2O can be found

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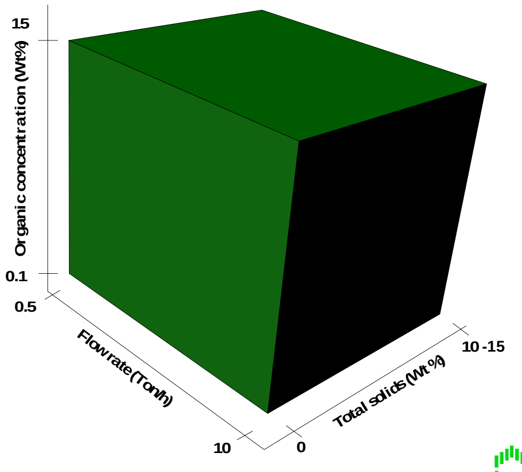
Operating Envelope



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The Demonstration Plant

Reactor and Heat Exchangers

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Test Results

Sample	Residence time (s)	Reactor temperature (°C)	COD, feed (mg/l)	COD, effluent (mg/l)	Tot-N, feed (mg/l)	Tot-N, effluent (mg/l)
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SCWO Economics

(£/ton)

Application	Capacity (ton/h)	Variable cost (£/ton)	Income (£/ton)	Capital cost (£/ton)	Treatment cost (£/ton)
Sewage sludge	6	12	4	12	**20**
Amines	3	18	4	17	41
Fine chemicals	2.5	12	2	15	25
Fine chemicals	3.6	15	6	13	22
De-inking sludge	6	10	2+14	12	8
Industrial sludge	1	23	3	33	53
Water based paint	2	15	4	19	30

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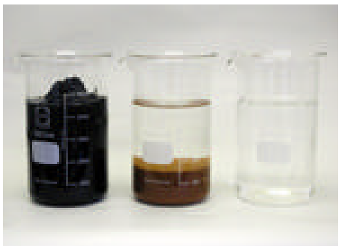
Treatment of Sewage Sludge by SCWO



- COD reduction > 99.99%
- Inerts are easily separated as non leachable ash
- Competitive economics

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