

## TREATMENT OF DIFFERENT WASTES BY SUPERCRITICAL WATER OXIDATION

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### ABSTRACT

If left to conventional treatment processes, the destruction of toxic organic wastewaters and associated sludge volume reduction clearly becomes an overwhelming problem. Two options, incineration and supercritical water oxidation (SCWO), exist for the complete destruction of toxic wastewaters and organic sludges. Incineration has associated problems such as very high cost and public resentment; on the other hand SCWO has proved to be a very promising method for the treatment of many different wastewaters and sludges.

In early 1998 Chematur Engineering inaugurated its 250 kg/h SCWO demonstration facility and since then several successful treatability tests have been performed. Among these are tests with different complex wastes, from a SCWO process point of view. They have been performed in two different ways: 1. Making the waste treatable in an "ordinary" SCWO unit, i.e. remove halogens and dissolved salts. 2. Making the SCWO unit able to handle the difficulties in the waste, e.g. halogens.

Another waste, de-inking sludge, has been treated several times. The appealing results from these tests are that, besides the complete destruction of the organic material, the remaining paper filler has shown to be good enough for reuse. This exemplifies the general possibility to destroy the organic material in the waste by SCWO and leave a "clean" valuable inorganic material in the effluent, which could easily be recovered. The extremely clean inorganic material recovered ought to increase the interest in SCWO treatment. This type of waste may very well be the breakthrough of SCWO.

### 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 rise 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.

Under normal conditions, water is seen in either of its three states: atmospheric steam, liquid water, or ice. If water is heated and compressed to sufficiently high temperature and pressure a new fluid state of water emerges. Water at high temperatures and pressures, above 374 °C and 221 bar, 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. Water gets a high solvating power, because of the low dielectric constant, obtained when becoming supercritical and most organic compounds and gases are completely miscible in all proportions in SCW.

In 1995 Chematur Engineering (CEAB) started its SCWO activities by a license agreement for SCWO signed with 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<sup>®</sup>. 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 waste have 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.

## THE PILOT PLANT

The feed tank is equipped with a stirrer designed for viscous sludge. The bottom outlet from the feed tank, Fig 1, is connected to a mono pump and a macerator in order to eliminate big particles entering the high-pressure pump. The plant is equipped with two different high pressure feed pumps, one for clear liquids and one for dispersions and sludges. The high pressure feed pumps raise the feed pressure to about 250 bar and pump the feed through the SCWO system. The feed enters the tube side of a double-pipe 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 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.

After passing through the reactor, the effluent flows through the economiser, outer tube, where it preheats the incoming feed. The effluent is cooled to its final exit temperature in the effluent cooler prior to passing through the pressure control valve or the pressure reduction coils. This proprietary pressure reduction system is used for pressure control when the effluent contains solid inorganic material. Adding choke water before the coils controls the pressure drop in the coils. The pressure is reduced from about 250 bar 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.

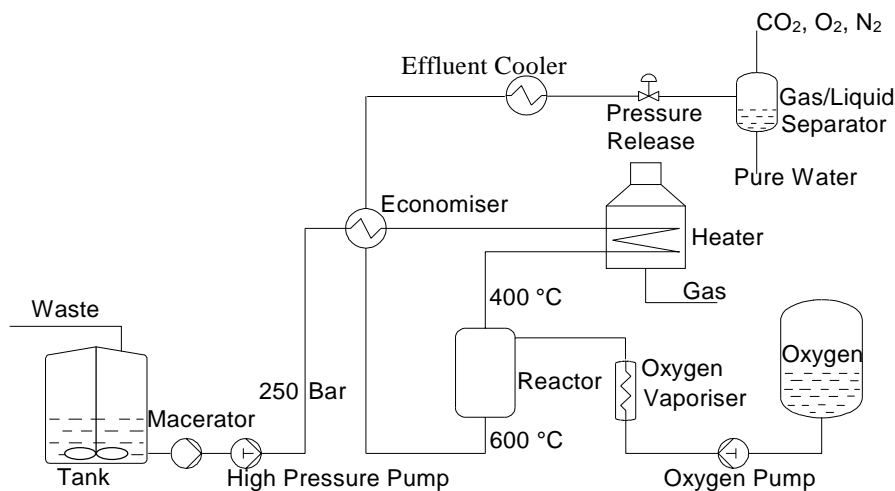


Fig. 1: Simplified flow sheet of the pilot plant.

## DE-INKING SLUDGE

When recycling paper, de-inking sludge is received as a by-product. This sludge contains about 3% organic material, mainly fibres, and 3% inorganic material, mainly paper filler. The ability of SCWO to destroy the organic material in this sludge completely has been proven elsewhere [2,3]. In addition to the destruction of organic matter, the industry has an interest in recycling the paper filler after the SCWO treatment.

Initial experiments showed fouling problems in the heat exchanger due to excessive amount of dissolved salts in the sludge. Hence, further experiments were performed with a partially dewatered sludge which was dispersed in fresh water to give a COD value of about 70 000 ppm before SCWO treatment.

Tests with this sludge were carried out without any problems and were performed at 540 and 580 °C. No significant difference in destruction efficiency was obtained between the two different reaction temperatures. After fine-tuning the reaction conditions very bright paper filler was recovered from the process, close to the value of virgin material, see Fig. 2.

Furthermore, later experiments showed that more concentrated sludge may be treated and that the fibres are the limiting material with regards to treatability. Test performed with sludge containing more than 6 % fibres showed the same excellent result as the earlier work. About 3 ton (dry substance) paper filler was produced during the last test period. The filler was used in a full-scale paper machine, producing paper for a major Swedish newspaper. The paper produced showed normal quality.

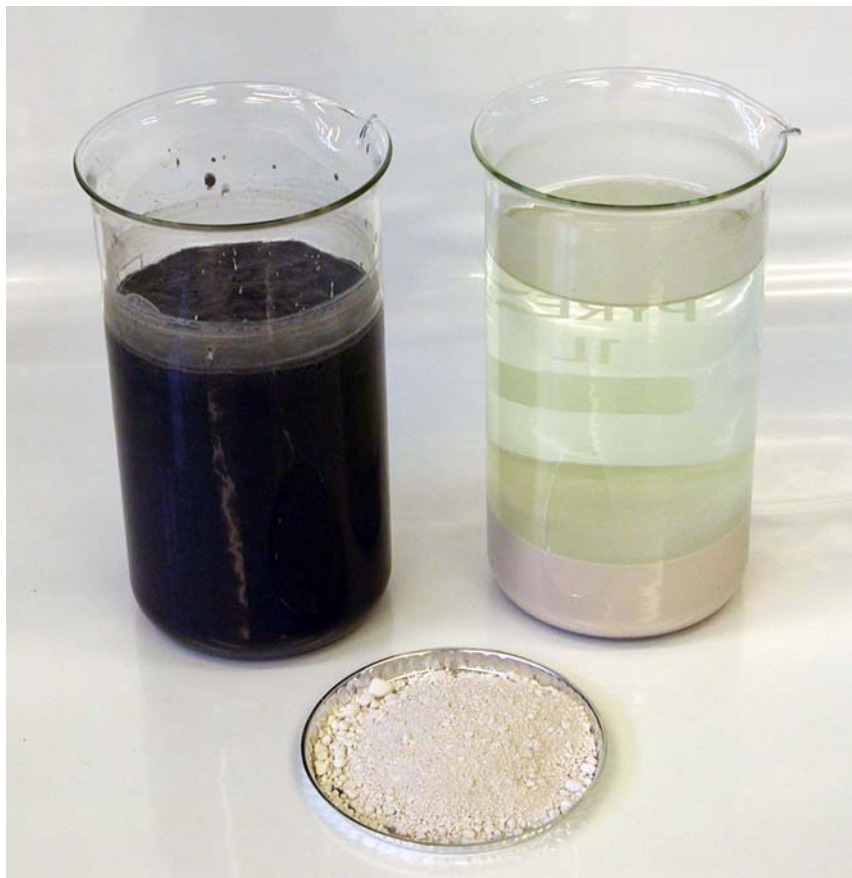


Fig. 2: The appearance of recovered paper filler, wet and dry, together with untreated de-inking sludge.

## WASTEWATER FROM FINE CHEMICAL PRODUCTION

A wastewater from a fine chemical producer has been treated with SCWO. The original wastewater was pre-treated in a forced circulation evaporator. The purpose of the evaporation was to remove the considerable amount of dissolved salt in the original wastewater in order to prevent scaling of the SCWO unit. The salt free condensate was then fed to the SCWO plant, Fig 3. The condensate contains the light organic compounds and water. The light organic compounds were mainly methanol, ethanol and acetone, see Table I, but also traces of toxic and persistent substances. The remaining solution, containing salt and heavy organic compounds, from the evaporation was filtered and the solids would be sent for destruction by incineration.

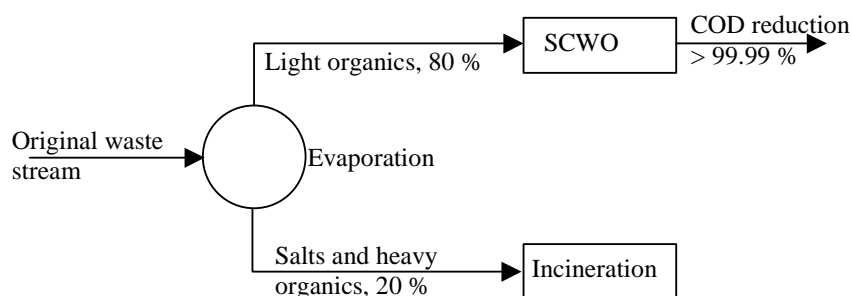


Fig. 3: Concept for treatment of a waste stream containing substantial amount of dissolved salt.

SCWO treatment of the produced condensate from the evaporator was completed in a satisfying way. The experiments were carried out at 570 °C and the conversion of the organic material to carbon dioxide and water was above 99.99%.

Table I. Evaporation results

	Feed	Condensate Sample 1	Condensate Sample 2	Condensate Sample 3
Methanol	1.45%	1.42%	1.3%	1.9%
Ethanol	1.53%	1.45%	1.3%	2.1%
Acetone	1.47%	1.00%	0.8%	1.2%
Total organic	4.49%	3.90%	3.4%	5.2%
Anions	6.28%	0.047%	-	-

By using evaporation and SCWO the amount of waste that needs to be incinerated is reduced to about 20% of the original waste stream. Even though this solution includes several steps, it is economic compared to direct incineration of the entire stream.

### A WAY OF HANDLING CORROSIVE MATERIAL IN A SCWO UNIT

The invention [4] uses the fact that no corrosion (almost/generally) appears in the supercritical region and that the corrosion is most severe between 270 - 390 °C [5-9]. Besides the nature of the corrosives, the lower limit depends of course on concentration and the higher on pressure. Consequently, the invention makes it possible to avoid this temperature range in the traditional SCWO system. The invention is described below as well as two different examples of its use.

#### Corrosive Feed

The pipe, feeding the cold corrosive waste, is led into a pre-heated stream, after the economiser and heater, see Fig. 4. A certain distance before this pipe ends and the two streams are mixed begins a pipe (mixing pipe) which is placed in the main pipe. This mixing pipe should have enough length for the mixing to be completed before it ends and the mixed stream temperature should be above 390 °C. The

mixing pipe, as well as the injection pipe, should be of a corrosion resistant material, e.g. titanium [10], and easy to change if corrosion does occur. The mixed stream is finally fed to the reactor or continuing its way through the reactor.

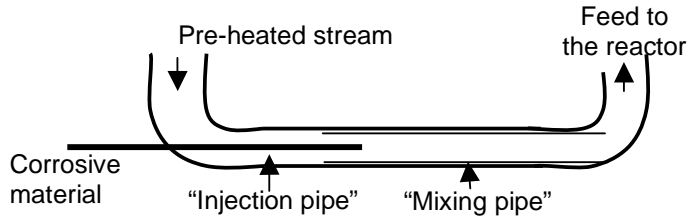


Fig. 4: Arrangement to avoid corrosion during heating.

### Cooling of Corrosive Effluent

In the same manner as above, the cooling of a corrosive effluent may be done by injection of cooling water. The effluent from the reactor is cooled to a temperature just above the critical point and enters into a bigger pipe, where the cooling water flows, Fig. 5. To ensure that no liquid elements are in contact with the main pipe before the mix is homogenous (considering temperature); a mixing pipe is installed. Just as for the feed system above, the mixing and injection pipe should be of a corrosion resistant material. The cooled effluent temperature is controlled by the amount of cooling water, e.g. to 270 °C, depending on the concentration and nature of the corrosive compound. Finally the cooled effluent is fed for further cooling.

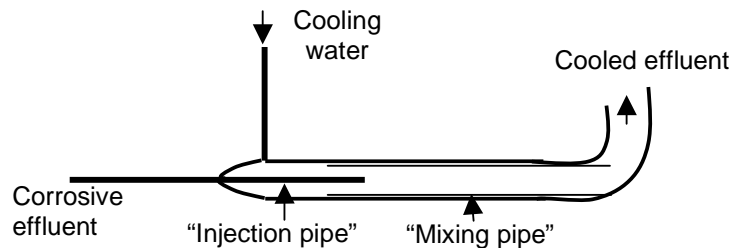


Fig. 5: Arrangement to avoid corrosion during cooling.

### Case 1: Wastewater from Amine Manufacturing

The invention has been used on a wastewater which was produced in a process for amine manufacturing. The waste contains ammonia and short chain amines and gives a nitrogen rich water containing almost as much total nitrogen (Tot-N) as total organic carbon (TOC), about 15 000 to 20 000 mg/l.

Although SCWO has been demonstrated to be effective for the destruction of most organic compounds, little success has been achieved in the complete destruction of ammonia or nitrogen in highly nitrogen containing wastes. However it is known that it is possible to destroy ammonia if the ratio of total organic carbon (TOC) and total nitrogen (Tot-N) in the wastewater is high [11,12]. If this ratio is low it is not possible to destroy all ammonia with oxygen but it is shown elsewhere [13,14,15] that it is feasible to destroy the ammonia using nitric acid for the oxidation.

The authors have described elsewhere [1], how the ammonia was destroyed using nitric acid. The experiment was carried out by injection of oxygen and after the oxidation by the oxygen was completed, nitric acid was injected into the reactor, as in Fig 4. The mixing pipe as well as the injection pipe was made of titanium, to withstand nitric acid with a concentration of 65%. At the end of the mixing pipe the mixed flow was well above supercritical temperature. Establishing the method for destroying of ammonia in a continuous process, the pilot unit was operating using the invention for about 100 hours. No damage could be seen on the titanium parts by visual inspection, at the end of the experiments. Even if titanium do not withstand concentrated nitric acid for an extended period, e.g. 5 years, it seems to cope with the conditions described above for several hundred hours and if needed the titanium parts could easily be replaced and the cost would be insignificant.

## Case 2: Different Wastes Containing Chlorine, Bromine and Iodine

Several tests have been accomplished with wastes containing, chlorine, bromine, iodine or a combination of those. Both wastes with the elements present as ions and in organic molecules have been treated. If the corrosive element is a part of an organic compound it is generally not a problem before the oxidation, unless hydrolysis occur.

However in one waste the halogen was present as methyl iodide and that molecule hydrolyses very easily. At the destruction of methyl iodide HI is formed. However, HI is reported to be oxidised to I<sub>2</sub> very rapidly [9]. The invention was used to insure that no HI, if any, could come in contact, at subcritical temperatures, with the material of construction (a high nickel alloy) used in the pilot plant. The methyl iodide containing waste was injected, cold, directly into the reactor, and mixed with a hot stream of water and oxygen, in the same way as for the nitric acid above. The concentration of methyl iodide based on the mixed stream varied between 1000 – 1500 ppm. Since almost all iodide was oxidised to I<sub>2</sub> the effluent was not corroding the nickel alloy downstream the reactor.

Another rather concentrated organic waste containing chloride and bromide was injected into the reactor using the invention as for the methyl iodide. The concentration of chloride and bromide based on the mixed stream was about 400 ppm each. In order to minimise the corrosion downstream the reactor, sodium hydroxide was added to adjust the pH to normal levels, pH=3,5-4, for SCWO effluent, without halogen ions. After the pH adjustment the Ni levels in the effluent decreased from about 5 ppm to about 0.3 ppm and the content of Cr was unchanged around 0.5 ppm. However, the Mo content in the effluent was significantly higher after pH adjustment in some of the samples, whereas in other samples it was basically unchanged.

Both experiments were carried out for about 100 hours. No damage could be seen on the titanium parts. However, for a continuous processing of the tested material containing the bromide and chloride, or a similar waste containing the same or higher amount of halogens it would probably be preferred to use the quench cooling in a titanium mixing pipe, Fig 5.

## CONCLUSION

The presented studies performed on a state of the art pilot plant, shows that the SCWO technology is ready for commercialisation. Furthermore for wastes like de-inking sludge, containing valuable inorganics, SCWO treatment offer, besides an extremely clean effluent, the possibility to recover these compounds. The extremely clean inorganic material recovered ought to increase the interest in SCWO treatment. This type of waste may very well be the breakthrough of SCWO.

SCWO has two major limitations with respect to substances present in the water, dissolved salts and acids formed of chlorine, sulphur etc. There are simply two ways of treating such wastes: 1. Making the waste treatable in an "ordinary" SCWO unit, i.e. remove halogens and dissolved salts. 2. Making the SCWO unit able to handle the difficulties in the waste, e.g. halogens. It is not probable that there will be a general SCWO system suitable for all such waste from both economical and technical point of view. It has to be reviewed from case to case which solution should be preferred.

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