THE FIRST INDUSTRIAL UNIT IN FRANCE FOR INDUSTRIAL LIQUID WASTE TREATMENT BY HYDROTHERMAL OXIDATION

Nathalie Bonnaudin*, Xavier Momboisse and Manuel Bottreau
Hydrothermale Oxydation Option - HOO
Parc Scientifique Unitec 1, 4 allée du Doyen Georges Brus - 33600 Pessac (France)
Email: n.bonnaudin@hoo-ingenierie.fr
Fax: +33 (0)5 56 15 24 09

The environmental regulation and the increasing waste water disposal cost, in France and more generally in industrial countries, lead to a new concept for complete destruction of both toxic substances and sludge. Thus, hydrothermal oxidation of wastes is developed as an alternative technique in order to limit the toxic end-products formation, the waste volume and the energy supply. Hydrothermal oxidation processes allow a total conversion of anything organic matter in CO_2 without energy supply due to the high exothermic reaction of oxidation and without toxic end-products [1].

This communication will describe a new concept of hydrothermal oxidation reactor [2] and the first industrial unit of hydrothermal oxidation in France with this new concept. The Syndicat Mixte Pôle Environnement Sud-Aquitain (SYMPESA) has identified an innovative technology that can be developed in the Lacq basin (France). This technology, hydrothermal oxidation, is interesting for the industrial chemicals companies that would gain access to a new solution to deal with some of their aqueous effluents. HOO is the commissioned agent of the SYMPESA for the design, construction and operational launch of this hydrothermal oxidation unit.
We will present also the first results of the treatment of aqueous wastes by hydrothermal oxidation on this new industrial unit.

INTRODUCTION

The treatment of effluent by hydrothermal oxidation has been developed on an industrial scale for the past fifteen years, notably in the USA and Japan.
In France over the last decade, *l'Institut de Chimie de la Matière Condensée de Bordeaux* (ICMCB - the Institute of Chemistry of Condensed Matter of Bordeaux), has developed the expertise necessary to master the chemical reactivity in an environment of supercritical fluids. Through multiple national and international collaborations, ICMCB has acquired sufficient know-how to design a reactor for the treatment of effluent, for which the CNRS (*Centre National de la Recherche Scientifique* – French National Center for Scientific Research) has patented the critical elements.
Shortly after its creation in May 2000, HOO acquired an exclusive license to these patents from the CNRS [2-3] and committed to two industrial pilots: one for the treatment of non-corrosive waste (Project OSTAU), the other for the treatment of corrosive waste (Project PIOS).

The PIOS project is scheduled to deliver a qualified prototype unit in September 2004. The following industrial partners participate in the pilot:
- SME (SNPE Matériaux Energétiques), final user with hazardous waste to be treated;
- HOO, process engineering;
- JEUMONT (AREVA Group), the manufacturer;
- ICMCB, the scientific consultant;
- PEA (Pôle Environnement Aquitain), a regional public agency.

The goal of the project is to design an industrial hydrothermal oxidation pilot with a capacity of 100 kg/hr for the treatment of corrosive waste water with high concentrations of chlorine and salts.

In this article, we only present in detail OSTAU project. The capacity of this pilot is 100kg/hr and it can treat non corrosive waste with low concentrations of chlorine and salts.

I - CONCEPT

HOO's process for waste water treatment by hydrothermal oxidation is based on reactor technology which offers destruction of the maximum organic load using a technique of multiple injections of an oxidizing agent (oxygen).
This process can be used to treat pumpable effluent containing less than 15% solids (total suspended solids).
Figure 1 shows the innovative process of waste treatment by hydrothermal oxidation that HOO industrializes.

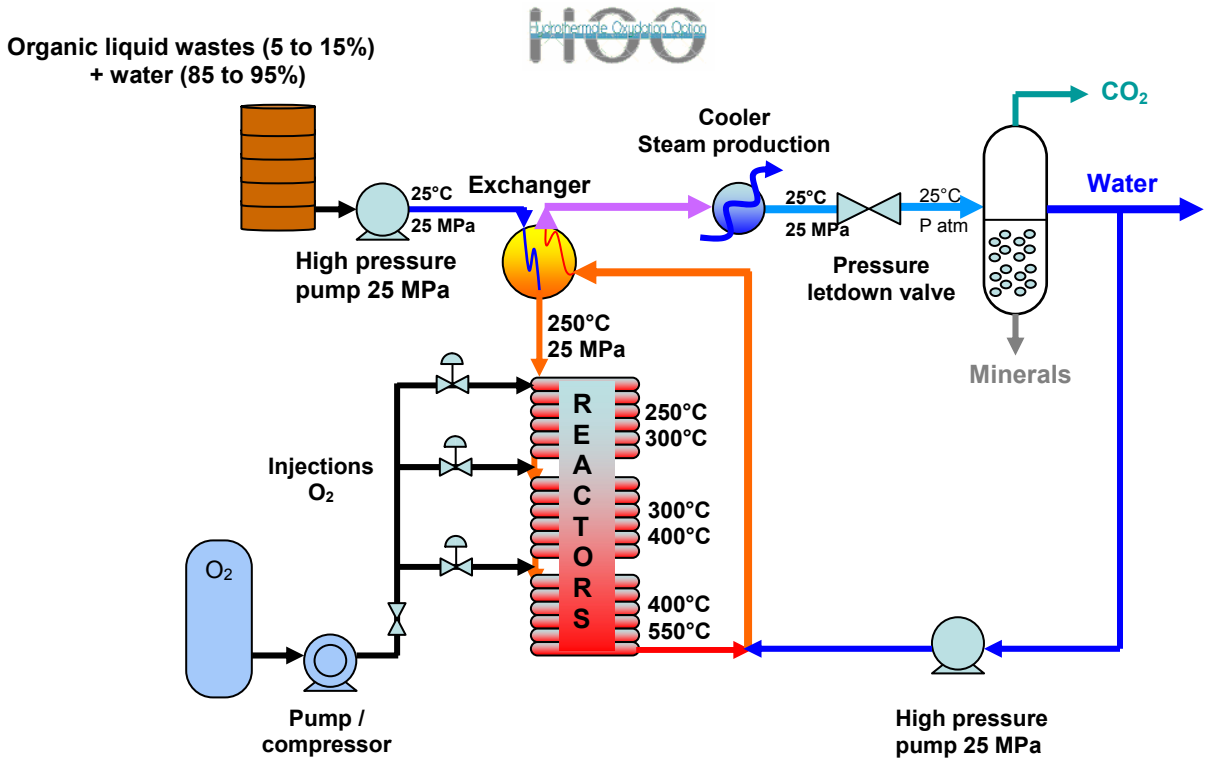

Figure 1: Schematic flow diagram of HOO process

The waste water is pressurized. The waste water is then preheated via a heat exchanger that recovers the energy given off by the oxidation reaction and thus heats up the effluent to 250°C.
The initial injection of oxygen is made at that temperature at the reactor inlet, where the molecules of waste water that are known to be easily oxidized, are degraded and enable the temperature to rise to 300°C.
A second injection of oxygen is made in the second section of the reactor. The energy given off by the reaction leads to a further increase in the temperature of the reactive environment to 400°C.
The third injection of oxygen is made in the supercritical fluid phase and enables decomposition of the molecules that are most resistant to hydrothermal oxidation (e.g. acetic acid, methanol, etc.); the fluid temperature at the outlet reaches 550°C.
After cooling and pressure reduction, the products are separated in a gas-liquid separator.
At the separator outlet, the outgoing effluents are made up mostly, for the gaseous phase, of carbon dioxide, oxygen and nitrogen. As for the liquid phase, it is free of all organic substances and it includes minerals initially present in the waste and/or hetero atoms in the form of solutes dissolved or precipitated in balance with the aqueous phase.
The concept industrialized by HOO enables improved energy control. Oxidation of the effluent is carried out progressively by multi-injection of the oxidizing agent, thus enabling efficient control of the temperature of the reaction (Figure 2). Contrary to competing designs, the preheating temperature of the effluent is between 150°C and 250°C on average. The resulting energy balance is favourable.

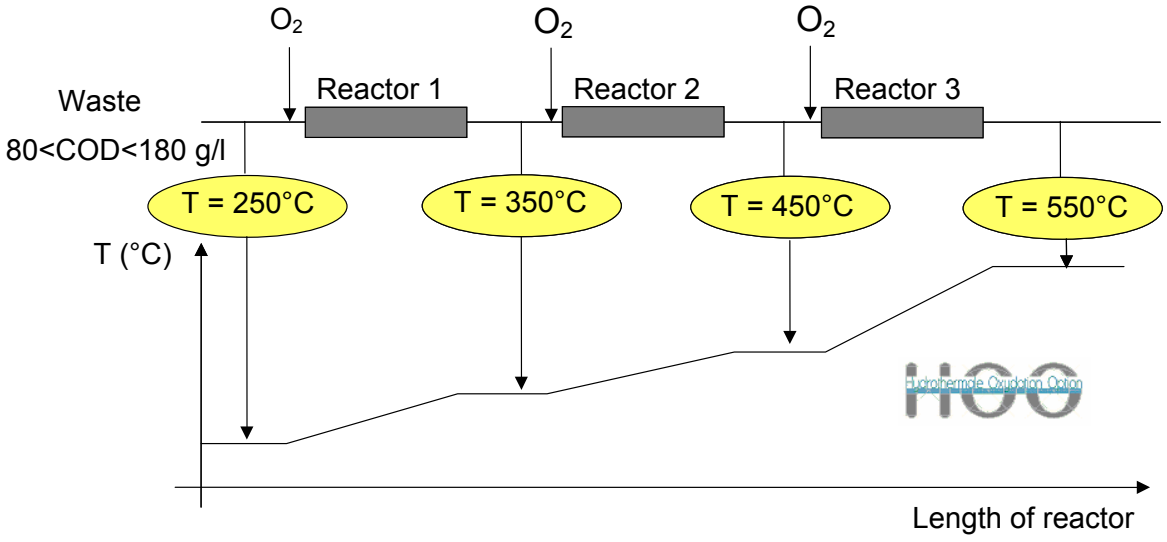

Figure 2: Schematic representation of new concept of reactor for hydrothermal oxidation

There are many advantages in this new concept:

- Improved control of the exothermicity of the reaction and hence improved process control;
- A more favourable energy balance linked to the lower preheating temperature, which provides a manageable heat surplus;

- Reduced treatment costs because the initial COD load of the effluent to be treated is higher, and hence the cost of treatment per tonne of COD treated is lower;
- Simplification of the equipment and hence reduction of the investment costs, especially concerning the heat exchanger.

II – THE INDUSTRIAL UNIT

The Syndicat Mixte Pôle Environnement Sud-Aquitain (SYMPESA) has identified an innovative technology that can be developed in the Lacq basin (France – 64). This technology, hydrothermal oxidation, is interesting the industrial chemicals companies that would gain access to a new solution to deal with some of their aqueous effluents.
SYMPESA has thus entrusted HOO with the task of building the OSTAU industrial pilot.
This pilot is located in CITBA company near Pau (64) in France. It is used to validate technically and economically the treatment of industrial waste.
The capacity of this pilot is 100kg/h.
HOO can operate on this pilot for feasibility studies on industrial waste.

The specifications of entry of the hydrothermal oxidation process are:
- Waste water: dry matter between 1% and 10%, size of particles < 500 µm;
- Chemical Oxygen Demand (COD) : between 50g/L and 150 g/L;
- Salts (others than chlorides): Inorganic matter concentration < 10 g/L;
- Chlorides: $[Cl^-] < 1$ g/L.

These specifications of entry are given as an indication. They could be discussed individually.

Below, examples of effluents which could be treated by OSTAU pilot:
- Waste water from chemical industries of organic synthesis;
- Process water of chemical industry;
- Residue of extraction liquid-liquid;
- Organic solvents;
- Sludge of water treatment plants.

Figure 3 : OSTAU pilot

CONCLUSION

HOO has acquired sufficient expertise to enable it to design, arrange for building and put into service these hydrothermal oxidation units for treatment of liquid effluents. As compared with the other solutions in direct competition, the patent licensed by HOO presents the following advantages:

- Optimization of process control;
- Treatment of high organic loads at the process inlet (reduction of the costs of treatment);
- Improved control of oxygen injection;
- Lower investment costs (simplification of the heat exchangers);
- Production of energy (steam).

HOO is involved in the construction of two prototypes (OSTAU and PIOS projects).
PIOS pilot can treat corrosive waste with high concentrations of chlorine and salts.
The other pilot, OSTAU can treat non corrosive waste with low concentrations of chlorine and salts.
On each pilot, HOO can operate for feasibility studies to validate technically and economically the treatment of industrial waste.

REFERENCES:

[1] BOTTREAU M., Hydrothermal oxidation: a new concept for treatment of industrial and urban liquid wastes. Supercritical Fluids & Materials, Ed. ISASF, 2003, p. 369

[2] CANSELL F., Patent WO 02 20 414

[3] CANSELL F., BOTTREAU M., Patent FRA 01 09 124