

DEVELOPMENT AND DEPLOYMENT OF THE MODULOX™ PROCESS FOR THE DESTRUCTION OF ORGANICALLY CONTAMINATED WASTES

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ABSTRACT

AEA Technology has been working for approximately 15 years on the development, demonstration and application of a low temperature, low-pressure technology for the destruction of organic waste. The process uses catalyzed hydrogen peroxide to oxidize organic material, with the main products being carbon dioxide, water and inorganic salts. AEA Technology's application of the technology is known as the ModulOx™ process.

The ModulOx™ process has been proven extensively at both commercial and laboratory scale as a treatment process which has the capability to treat certain types of organic materials such as organically contaminated tank waste (e.g., TK-48 Waste at SRS, PCB and VOC contaminated waste at INEEL), organically contaminated liquid effluents, chemical weapon agents, ion exchange resins and wastes containing organic chelating agents. The technology has proceeded from bench top units through to mobile demonstration plant and has been used to treat a wide range of organic waste streams including PWR type ion exchange resins, PWR circuit decontamination waste and active effluents and sludges.

The benefits of the ModulOx™ process are:

- Low temperature process;
- Low atmospheric pressure process;
- Simple single stage process design;
- Process output can be readily tailored to further conditioning, storage and disposal requirements;
- Potential for volume reduction of wastes and associated economic benefits;
- Removal of organic components to enable compliance with acceptance criteria for disposal;
- Treatment of a wide range of organic wastes.

The ModulOx™ system has been designed to be mobile. AEA has designed, built and is in the process of mobilizing the ModulOx™ system to treat V-Tank waste at the Idaho National Engineering and Environmental Laboratory (INEEL). The V-Tank waste is contaminated with a variety of chlorinated volatile organic compounds, heavy oils, and polychlorinated biphenyls (PCBs). The process consists of several mobile skids including a 2.27 m³ (600 gallon) reactor skid, a scrubber skid, an off gas skid that includes a HEPA and GAC filter, and a control trailer. There are also several auxiliary utility skids including a steam generator and a chilling system. The ModulOx™ system was built under AEA's International Agreement with DOE.

INTRODUCTION

AEA Technology has developed a low temperature, low pressure process for the destruction of both toxic organic and radioactive wastes, namely the ModulOx™ process. The process uses hydrogen peroxide with a catalyst at atmospheric pressure and a temperature of approximately 373 K (100°C) to oxidize organic materials, forming predominantly carbon dioxide, water and inorganic salts. The initial focus of process development has been the destruction of spent ion exchange resins, particularly where chemical chelating agents from decontamination, such as EDTA and citrate, are also present. Subsequently, a wide range of other hazardous organic materials has also been successfully treated.

The general categories of organic material which can be treated directly by the process are:

- any organics which are water soluble or partially water soluble
- organic compounds containing unsaturated carbon bonds
- organic compounds containing functional groups, e.g. carbonic acids, esters, sulphonate, phosphate, chloro and nitro substituted compounds etc.

The process is tolerant to the chemical nature of the waste stream, although pH adjustment to mildly acidic conditions is required for efficient operation.

The process will treat liquids, sludges and solids. The solids must be in a form capable of being dispersed and suspended in water.

The waste types that have specifically been studied and treated by the ModulOx™ process are listed below:

Radioactive Wastes

Organic ion exchange resins;
Organic ion exchange resins loaded with chelating agents;
Mixed organic/inorganic reactor sludge;
Organic decontamination liquors;
Organic scintillants;
Spent reprocessing solvent (destruction of tri-butyl phosphate);
Miscellaneous liquid effluents.

Toxic Wastes

Phenol, nitrophenols and chlorophenols	EDTA
carboxylic acids	PCB's (after pre-treatment)
Alcohols	Trichloroethylene
Thioacetic acid	Tetrachloroethane
Formaldehyde	Pharmaceutical wastes
Pyridine	Olive oil waste water
Thiophene	a range of pesticide effluents
Dimethyl Formamide	Organomercury compounds

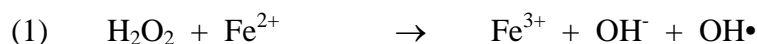
The presence of inorganic solids or intractable organic polymeric materials within the reaction mixture has no detrimental effect on the destruction of the treatable organic species. Sorting or separation of the wastes, other than by physical size, is therefore not required although for some wastes it may prove to be the most efficient strategy.

Process Chemistry

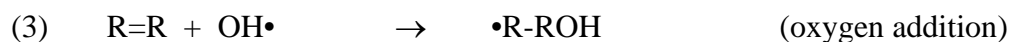
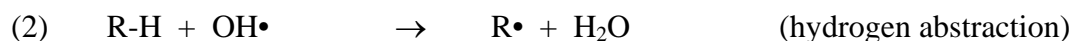
The ModulOx™ system utilizes aqueous phase oxidation process chemistry. Hydrogen peroxide in aqueous solution acts as a strong oxidizing agent, reacting with organic molecules under appropriate conditions. In fact, at ambient pressure and under acidic conditions, the hydroxyl radical has a higher reported electrochemical oxidizing power than any other species except fluorine [1]. The use of hydrogen peroxide, in the presence of the ferrous ion to destroy organic species, commonly known as Fenton's reaction [2], is the basis of the ModulOx™ system.

Hydrogen peroxide is a powerful oxidizing agent in its own right, more powerful than chlorine or permanganate. Despite this, oxidation reactions between organics and hydrogen peroxide alone are often slow or non-existent.

In the presence of a transition metal catalyst, such as iron, hydrogen peroxide degrades to form the even more powerful hydroxyl radical via the reaction:



Under acid conditions, the hydroxyl radical reacts readily with organics through two main pathways:



The addition reaction shown in equation 3 can be across either aromatic or aliphatic unsaturated bonds.

In each case, an organic free radical is formed which will react further through mechanisms such as continued oxidation, rearrangement (and possibly elimination) and radical-radical combination. Further oxidation will lead to production of alcohols, carbonyl compounds, carboxylic acids and organic peroxides, with many of the intermediates likely to contain multiple functional groups. Breakdown of the carbon bond structure will also take place as part of the oxidation and rearrangement reactions, with aromatic ring cleavage, fragmentation across unsaturated bond sites and decarboxylation being the most important mechanisms.

A number of these reactions lead to a reduction in the carbon chain length. Oxidation and breakdown of the bond structure continues until the final products of carbon dioxide and water are formed.

As well as reacting with organics, the hydroxyl radical may react wastefully, with Fe^{2+} or hydrogen peroxide for example, generating products such as hydroxide and oxygen.

Where significant concentrations of organics are present and in acid conditions, the organic destruction mechanism dominates. As organics are destroyed and their concentration reduces, wasteful reactions become increasingly important and have a significant effect on the efficiency of peroxide usage.

The transition metal in the system acts as a true catalyst, with the redox couple providing a means of electron transfer. Iron(II) can be regenerated from the iron(III) formed in equation (2) by reactions such as:



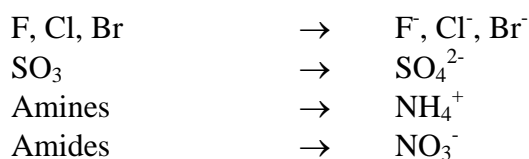
Hydroxyl radical production is the precursor to both organics destruction and wasteful degradation of hydrogen peroxide. Despite being a fast reaction, hydroxyl radical production is slow in comparison to the subsequent radical interaction reactions and is usually the rate determining step for the overall reaction (phase transfer may be the rate determining step for partially soluble species). The overall reaction rate for the ModulOx™ system is regulated by controlling the hydroxyl radical production rate through control of hydrogen peroxide addition rate, temperature, catalyst concentration and pH.

A summary of the overall oxidation reaction for a wide variety of molecules may be written as:



where (X) is a functional group.

Different functional groups will behave in different ways during the reaction. Some common functional groups behave as follows:



The extent of reaction is generally dependent on the specific compound involved and the reaction residence time.

The organics destruction reaction is highly exothermic, generating more heat than the equivalent incineration reaction. It is important that the factors that influence the rate of heat production are properly understood and controlled within the reaction scheme if safe and efficient operating conditions are to be maintained.

This discussion of the process chemistry is a simplification of what is, in reality, a highly complex scheme often involving hundreds of reaction pathways. The experience that AEA has gained over many years provides us with the understanding needed to be able to identify and focus on the factors that are of most importance in any particular waste processing operation.

The ModulOx™ Process

A general ModulOx™ process flowsheet is shown in Figure 1.

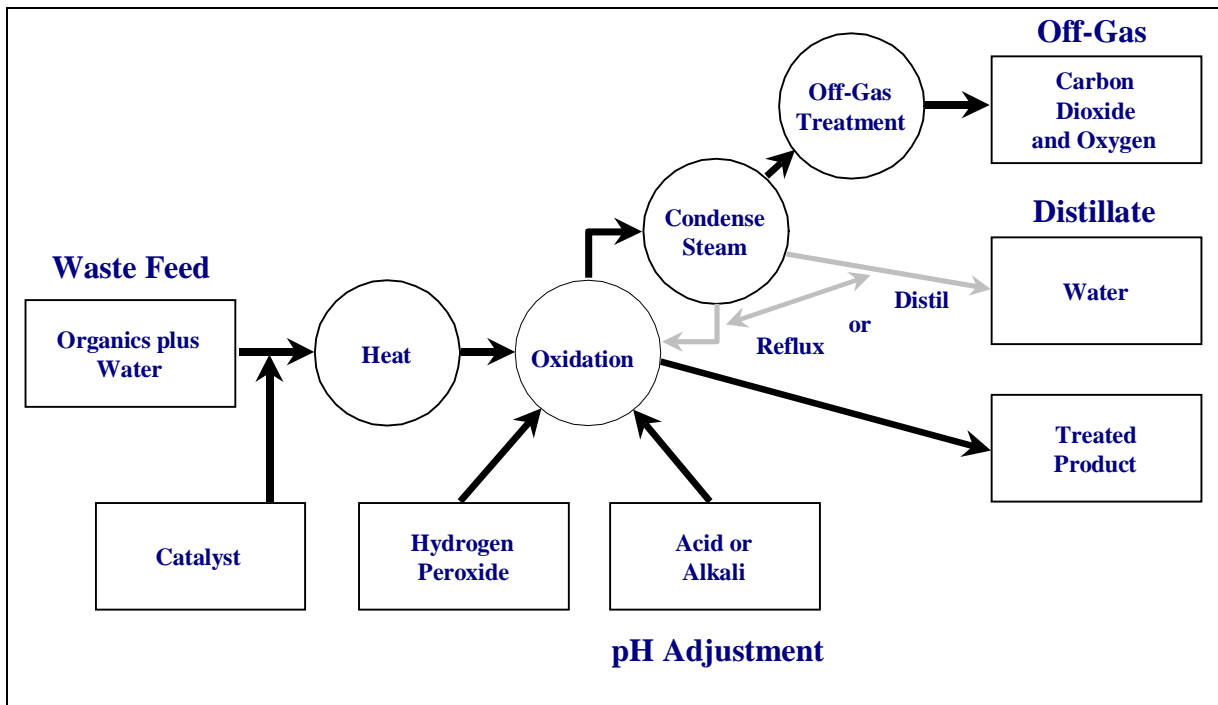


Fig. 1. General ModulOx™ process flowsheet

The process can be operated in batch or semi-batch mode (where an initial waste charge is fed to the reactor, followed by further batches prior to product emptying). Catalyst is added to the waste as needed, with hydrogen peroxide then added continuously throughout the reaction until the target destruction efficiency is achieved. A typical process sequence is to add the waste to the reactor, heat to a temperature that will sustain the reaction, add catalyst and then begin the addition of hydrogen peroxide. Also, the system has both acid and base feed available for pH control. The reaction takes place at temperatures close to boiling point and at atmospheric pressure.

During the reaction, steam and other gases produced by the oxidation reaction pass through a heat exchanger where the distillate may be collected or refluxed to the reactor. Non-condensed gases pass through a scrubber and High Efficiency Particulate Air filter (HEPA) before discharge to the atmosphere.

After treatment, the product may be disposed of as liquid waste at an appropriate disposal facility or stabilized/solidified and disposed of as a solid waste.

AEA, under its International Agreement with DOE, has built a modular and transportable ModulOx process for destruction of organic waste and delivered it to the Idaho National Engineering and Environmental Laboratory (INEEL). The process was initially built to destroy ion exchange resin waste at the Oak Ridge National Laboratory (ORNL), however, an avenue for disposal of the waste was identified that did not require treatment. Consequently, the equipment was shipped to INEEL for destruction of organic constituents in waste from the V-Tanks.

The skid-mounted Modulox™ Process currently located at INEEL consists of three primary modules with several support systems. The primary modules are the reactor module, the off-gas scrubber module and the off-gas module. The support systems include a chemical feed

module, a steam generator module, a peroxide feed module, and a chiller and associated valving.

Organically contaminated waste is received in the reactor (shown in Figure 2), where nitric acid and the metal catalyst are added. The solution is heated to boiling, at which point anti-foaming agent and 50% hydrogen peroxide are added. Sodium hydroxide is also added to maintain an optimum pH condition; toward the end of the reaction, nitric acid may be added for the same purpose. The process operates under reflux, with condensed liquors returned to the reactor. The internal reactor volume is nominally 2.27 m³. Mounted atop the reactor is a plate condenser that allows reflux of the reactions media.



Fig. 2. The reactor module (photograph taken in Oak Ridge).

The off-gas system directs non-condensable gases from the reactor to the scrubber module shown in Figure 3. The scrubber is designed to handle a gas flow rate of approximately 7-40 cfm and can utilize a variety of scrubbing media depending on specific process needs. The scrubber is a standard, off-the-shelf, industrial scrubber unit.



Fig. 3. Scrubber module (photograph taken in Oak Ridge).

The third primary module is the off-gas module shown in Figure 4. This module has two stages of HEPA filtration to provide primary and secondary protection with each stage having a maximum penetration on the order of 0.05%. The HEPA filters are a bag-out design. A direct-drive centrifugal fan, sufficient to overcome pressure drops due to the ductwork, equipment and filters, aids in the airflow through the system.



Fig. 4. Off-gas module (photograph taken at Oak Ridge)

The ModulOxTM system was delivered to INEEL with the intention of commencing operations in the latter part of 2004. A re-evaluation of priorities at INEEL has resulted in the treatment element of the V-Tank program being put on hold. The system remains at INEEL, pending re-scheduling of treatment operations, despite interest in the plant from other USDOE sites.

REFERENCES

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2. Fenton H J H. "Oxidation of Tartaric Acid in Presence of Iron". J Chem Soc, 65:899 (1894).