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A truly industrial solution for the elimination of radioactive oils or solvents - 10404

Dr. A. Jacobs and W. Everett

DEWDROPS Company, France

ABSTRACT

Dewdrops has developed a comprehensive on site treatment service for toxic waste oils and solvents with a special capacity in the nuclear field. The process is based on the mineralization of a wide range of radioactive organic wastes using chemical and biological oxidation mechanisms. The oxidized organic materials form predominately carbon dioxide, water and inorganic salts. The major benefit of the process lies in its room temperature and atmospheric pressure working conditions. First the organic waste is oxidized using hydrogen peroxide with a catalyst in order to enhance biodegradability of the organic waste. Carefully selected microorganisms use the organic waste as an energy source for their metabolism. The aqueous phase is continuously separated from the biomass using cross flow filters. The output aqueous phase is treated with ozone to eliminate the remaining organic compounds. The final effluent obtained is in conformance with European water standards. It can also be adjusted to local requirements. The radioactive elements and heavy metals usually found in lubricating oils are trapped by biomass which is recovered by centrifugation and mineralized either by methanisation or by ozonation technology. The mineral residue obtained is suitable for long range storage. This paper details the procedure and the results obtained for a particular case at the Tricastin nuclear site of Areva NC (South France). The result of the tests was a radioactive waste reduction factor of 20. The mineral residue is a concentrate of the radioactive elements as well as heavy metals. The radioactive elements thus recovered can be consigned to an official repository or, in some cases, recycled.

INTRODUCTION

Managing radioactive organic waste has become an important issue for the nuclear industry. While several solutions exist such as incineration or supercritical water technology many of them are expensive or may not be compatible with all kind of organic wastes. For example organic materials containing chlorinated compounds or fluorine are not well suited for incineration as they will cause damage to the incinerator. Supercritical water technology may be very efficient in some cases but is still a costly solution using very high pressure (320Bar) and temperature (400°C) incurring safety issues. Alternative solutions are necessary for organic waste which cannot be treated by the technologies cited above. There is also room for considerable cost savings.

Dewdrops has developed and tested in a fully operational pilot plant a new way of eliminating a wide range of mixtures of radioactive oils and solvents. Together with a volume reduction factor of at least 20 times, the process combines reliability and versatility with a minimal environmental footprint.

The radioactive organic waste is completely mineralized by an original combination of soft chemical catalysis and biodegradation using carefully selected microorganisms to produce carbon dioxide and an aqueous phase which can be disposed of by normal means. The biomass is partially recycled in the

system and the excess is eliminated at the end of the process while the water and carbon dioxide can be released to the environment. The ultimate waste is a dry inert inorganic powder.

The originality of our process lies in the management of several specialized bacterial populations each with a different task. Cross-flow filters separate each stage maintaining bacterial population specificity and ensuring a micro-organism free outflow with a COD (chemical oxygen demand) < 150 mg/l in complete conformance with the usual European waste water standards. Separate tests have shown that our micro-organisms can handle radioactivity levels of at least 30 MBq/liter in the incoming oils / solvent mixtures but the theoretical limit is much higher.

The specific waste types that have specially been studied with the Dewdrops process are listed below: (other wastes are currently under investigation)

- Several non water soluble Lubricating oils
- Alcohols
- Trichloroethylene (TCE) and Tetrachlorethylene (PCE)
- Oils mixed with TCE and PCE

CASE STUDY: RADIOACTIVE OIL AND TRICHLOROETHYLENE MIX FROM THE TRICASTIN NUCLEAR SITE:

Our first tests were carried out with a radioactive waste originating from the AREVA NC Tricastin nuclear facility (South of France). Elimination of 3 types of organic wastes was demonstrated: lubricating oil, trichloroethylene and a mix of both with the ratio of 85/15 V/V. With the pilot plant used in this study, the organic waste could be eliminated at an approximate rate of 10ml per hour while the experience lasted for 3 months. The process can be divided into 3 main modules: (i) Catalysis, (ii) Biodegradation, (iii) Ozone Oxidation. A simplified flow sheet of the process is shown in figure 1:

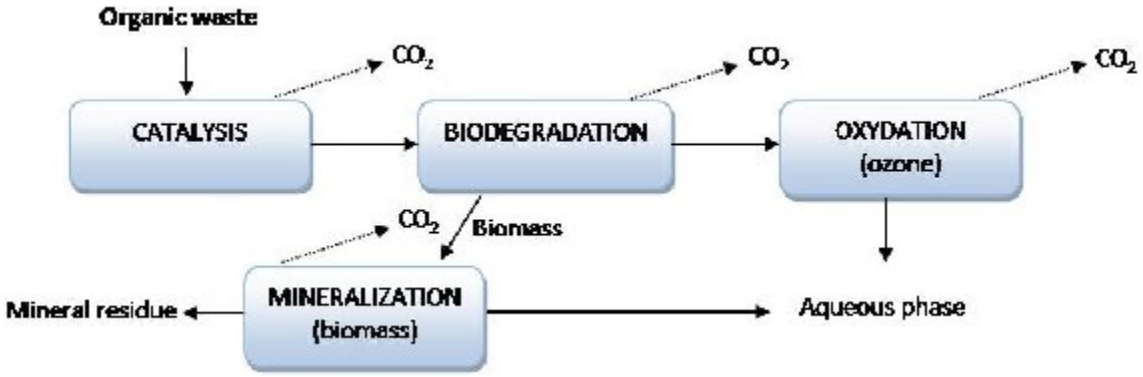

Figure 1: Simplified flow sheet of the process

Catalysis

The main role of the catalysis in this process is the elimination of solvents (like TCE), antioxidants and other none biodegradable elements which can be found in organic waste, enhancing the organic waste biodegradability. Chlorinated compounds like TCE are very difficult to eliminate biologically and antioxidants (which can usually be found in lubricating oils) inhibit microorganism metabolism. The chemical oxidation process used here is based on the Fenton reaction. In the presence of a metal catalyst (i.e. ferrous ions) and under acidic conditions hydrogen peroxide degrades to form a very power full oxidizing agent: the hydroxyl radical (OH• see equation 1).

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH\bullet$ (Eq. 1)

The hydroxyl radical has a higher reported electrochemical oxidizing power than any other species except fluorine. The hydroxyl radical reacts readily with organic compounds and other free radicals are formed as shown in equations 2.

$R\text{-}H + OH\bullet \rightarrow R\bullet + H_2O$ (hydrogen abstraction) (Eq. 2)

Each free radical (R•) will react further through mechanisms such as continued oxidation, rearrangement or radical-radical combination. Breakdown of the carbon structure will also take place as part of the oxidation and rearrangement reactions, with aromatic cleavage, fragmentation across unsaturated bond sites and decarboxylation being the most important mechanisms. Ultimately, oxidation and breakdown of the carbon bond structure continues until the final products of carbon dioxide and water are formed. In the case of small chlorinated organic compounds such as TCE the stoichiometric formula for the Fenton reaction is as follows:

$HC_2Cl_3 + 6OH\bullet \rightarrow 3HCl + 2CO_2 + 2H_2O$ (Eq. 3)

As the destruction of chlorine bonds dominate in the Fenton reaction, chlorinated compounds are oxidized before carbon chains. For this reason we were able to eliminate over 99% of the TCE in the lubricating oil/TCE mix. This was of significant importance in the process as bacteria used in this study cannot eliminate TCE and the presence of such compounds can even inhibit biodegradation when TCE concentrations are too high. The chemical oxidation is an important step to prepare the biodegradation process as it eliminates all the non biodegradable elements of the waste.

However the disadvantage of the Fenton reaction is the reactivity of the hydroxyl radical itself. Indeed, if the hydroxyl radical doesn't encounter organic material it may react wastefully either with hydrogen peroxide forming water or with ferrous ions. Organic destruction mechanisms dominate when the concentrations are high, but as their concentration diminishes futile reactions of the hydroxyl compound and thus hydrogen peroxide will increase. Wasteful usage of hydrogen peroxide will negatively affect the cost of the process and its economic reliability. This is the main reason why not all the lubricating oil is eliminated with the Fenton reaction rather than using biodegradation to complete its mineralization.

Biodegradation

Microorganisms have been used since the 70s for treating organic pollution particularly during oil-spills such as the Exxon Valdez catastrophe. Organic waste such as lubricating oil contains many compounds that are toxic for most life forms. However, microorganisms have established effective strategies involving specialized enzyme systems and metabolic pathways to access organic waste compounds as a carbon and energy source [1]. Such microorganisms are capable of degrading all kinds of organic material including oils and solvents, converting them to easily usable substrates. Scientists have observed that, during episodic or chronic pollution of an ecological system, the local bacterial communities adapt to the new situation and evolve to use the pollution. For the Dewdrops process a bacterial community was isolated from a polluted environment and was used to convert radioactive organic waste into water, carbone dioxide and biomass. The organic waste is used by the bacteria as their sole energy and carbon source while the sources of nitrogen and phosphorus (essential for bacterial growth) were added in a mineral form. The microorganisms used in this process are harmless for both health and the environment.

The total volume of the main digester was approximately 100L. Optimal biodegradation conditions were obtained by maintaining the temperature at 30°C and the pH around 7. Oxygen supply to the microorganisms is a main factor for optimal biodegradation and concentration must be superior to 3mg/l. Air was blown at a rate of 50L per minute through porous glass to obtain micro bubbles for maximum air/water contact surface and thus a higher oxygen uptake rate in the system. The medium was stirred at 400rpm for maximum homogeneity and an optimal oxygen transfer rate.

A picture of the biodegradation module can be seen below:

Figure 2: Picture of the digester and cross flow filters

To quantify the elimination of organic waste, the concentration of carbon dioxide in the off gas was measured continuously. Production of carbon dioxide in the off gas was 20 liters per hour during biodegradation of the lubricating oil.

During biodegradation, bacterial growth produced an excess of biomass in the digester which had to be recovered. The excess of biomass was separated from the media by centrifugation (2000rpm) and isolated

for further mineralization. The biomass separation operation has a double benefit: it avoids biomass accumulation in the digester and it traps the heavy metals as well as radioactive elements such as uranium. Bacterial cells are usually negatively charged by the presence of polysaccharides at the cell surface so trapping positively charged metals. The biomass can be mineralized either by ozone oxidation or by methanization technologies. After drying the final residue is an inorganic powder which is suitable for long term storage.

Ozone oxidation:

To separate the biomass from the aqueous phase in the digester cross flow filters were used. The ceramic cross flow filters had a pore diameter less then 0.5µm so all the bacteria were retained in the digester. The aqueous effluent had a COD (Chemical oxygen demand) of about 2 grams per liter which is significantly higher than European environmental standards. Ozone oxidation of the aqueous effluent was performed to obtain a COD less than 150mg per liter. It should be noted that 1 volume of radioactive waste generates about 20 volumes of clean water. The final aqueous output stream was in conformance with European standards and could be disposed of by normal means. Quality of the aqueous effluent was controlled on a daily basis with the usual water analysis tools (COD, Nitrogen, Phosphorus concentrations, etc.)

CONCLUSION

The three different types of organic waste treated were completely mineralized with the process. The volume of radioactive waste was reduced by over 20 times. The mineral residue, which is less than 5% of the original waste volume, is a concentrate of radioactive elements, heavy metals and salts. Such mineral waste can easily be consigned to an official repository and even recycled in some cases. Dewdrops is currently building a demonstration plant which should be fully operational by March 2010. The nominal capacity of the standard mobile plant is 100 liters per day with the actual production depending on the exact nature of the liquid to be treated. Treatments of other radioactive organic wastes are currently under investigation including PCB’s and organic solid sludge.