Name of Process:
SILVER II™ process

Vendor:
Accentus plc (subsidiary of AEA Technology)
Web site: http://www.accentus.co.uk;
www.silver-2.co.uk

Applicable Pesticides and related POPs wastes:
The chemical warfare agents and Organophosphate extractant solvents that have already been successfully treated are closely related to pesticides in their chemical composition - containing chlorinated hydrocarbons, phosphorous and sulphur groups. The process has also been used to manage organic radioactive wastes

Status:
4kW plants have been operated at both Dounreay (Scotland) for nuclear waste destruction and also at Porton Down (England) for Chemical Warfare Agent destruction. Destruction of Chemical Warfare Agents in the US has also been carried out in a 2kW plant as part of the US Army ACWA Demonstration Program. A 12 kW plant has also been successfully used in the US to process energetic material as part of the ACWA program.
A small commercial plant has also been supplied for the treatment of ^{14}C labelled organics in the UK. More than 1.2 ton toxic organic waste has been successfully treated so far.

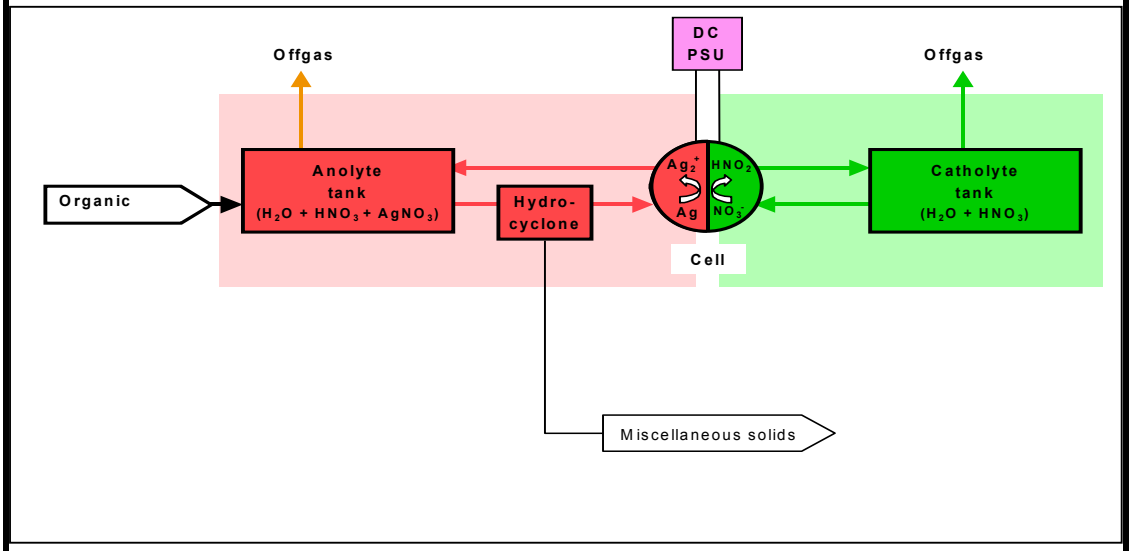
Technology description:
The process belongs to the category of Mediated Electrochemical Oxidation or catalyzed Electrochemical Oxidation.

At the heart of the process is the chemical oxidation of organic molecules by the Ag[II] ion. This is one of the most oxidising species that can be generated at an anode in an electrochemical cell in aqueous solution (Process diagram 1). Radical species initiated by Ag[II] attack the organic substrate – progressively converting it in a series of steps irreversibly to CO_2, water and residual salts from hetero-atoms (including halides, sulphur, nitrogen and phosphorus). During the oxidation step, Ag[II] is reduced back to Ag[I]. This is then regenerated to Ag[II] again at the electrochemical anode. This "catalytic" use of silver makes this a Mediated Electrochemical Oxidation Process.

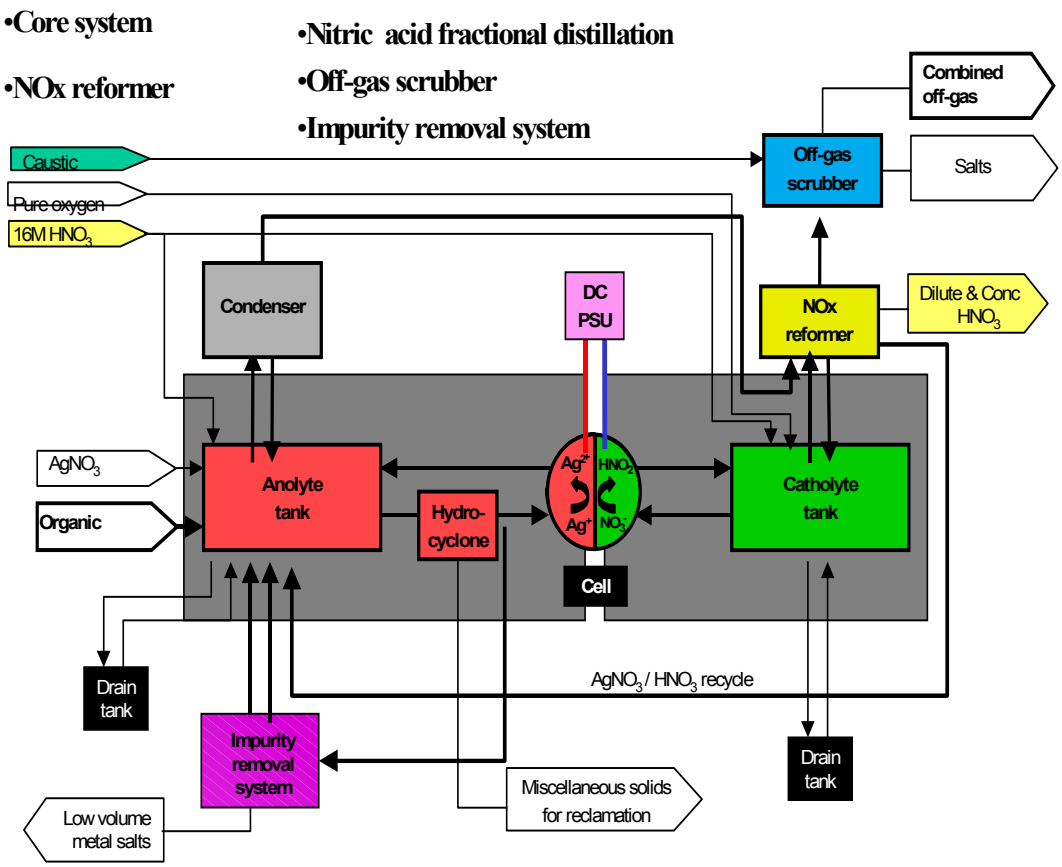
The organic species do not have to be water-soluble to be successfully treated by SILVER II, as has been shown by the successful treatment of solvents, oils, ion-exchange resins, tissues etc.

The series of reaction steps between Ag[II] and the organic intermediates is like a pipeline in the steady-state, where the relative concentrations of each intermediate is inversely proportional to the reaction rate with Ag[II]. Ag[II] can also react slowly with water – giving O_2 as a parasitic product. In order to minimise this loss route, the concentration of organics should be high (2-10g/l C), with high mass transfer rates to optimise the coupling of the generation and reaction steps by maximising interfacial area between immiscible phases. The optimal temperature for efficient usage of electrical energy is 60-90°C and at atmospheric pressure.

Process diagram 1:



Process diagram 2:



Performance:

Treatment efficiency:
Since 1988, the SILVER II Process has treated a wide range of chlorinated compounds (trichlorobenzene, chlorobenzene, chlorofluorobenzoic acid, methylene chloride, chloroform, chloro-ethylethyl sulphide) and tributyl phosphate at Dounreay, as part of an assessment programme. In addition, Chemical Agents have been treated at laboratory (60W) and pilot scale (4kW) at the Porton Down in the UK, and subsequently in the 2 kW plant within the ACWA programme. Dimethylmethylphosphonate has also been treated in a 12kW plant as part of the same program. From an initial ten technologies/vendors, after a series of pilot-scale demonstrations conducted in collaboration with CH2MHill, SILVER II has been judged as one of the three remaining technologies suitable for potential implementation at the Blue Grass site.

In the ACWA programme, 99.9999 – 99.99999% destruction efficiencies were achieved, with current efficiencies in the range 50-90%.

In the ACWA a 12 kW plant programme, M28 destruction was determined as 99.9999%, at a current efficiency of 80-100%.

Throughput:
Typical plant throughputs are of the order of 0.1kg/kWh cell capacity. A 4kW plant is able to process ~ 10kg organic content/day, while a 12kW plant can process 29 kg organic/day. A 400kW plant will process 1 te organic material/day.

Wastes/Residuals:
The process mineralises the organic material to CO_2 (which is rejected to the atmosphere), water which can be discharged as either vapour or liquid, and neutralised salts from the hetero-atoms present in the original feed (as either sodium salts of sulphate, phosphate, or chloride) which can be discharged to a water treatment plant - or else as solid calcium phosphate/sulphate to land-fill.

Reliability:
In the most recent phase of the ACWA programme, 97% plant availability was achieved. Over the complete program, some 2,700 hours of electrochemical operation of the plant by US Army staff were achieved without any lost time accidents.

John Vijgen, International HCH and Pesticides Association, Fellowship report: "New and emerging techniques for the destruction and treatment of pesticides wastes and contaminated soils." NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)"

Limitations:
Organo-silicone compounds mineralise to silica suspensions in the acidic electrolyte, which can foul the cell membranes. Heavily chlorinated feeds produce silver chloride precipitate. However, the effective recovery and recycle of the silver back into the process has been demonstrated by a number of routes, which could be operated either alongside the SILVER II plant, or else by a silver recovery contractor.

Transportability:
Accentus has developed a number of plant concepts - mobile self-contained containerised, transportable modular containerised and large static plants - to address a number of potential applications within industries where waste disposal or conditioning costs are high, or the alternative technologies do not provide the required level of safety or environmental protection. Typically, as 300-750 ton/year toxic organics can be mineralised/MW cell capacity installed, the size of an installation can be defined from the required treatment rate. These applications include demilitarisation of CW agents and energetics, other military and nuclear wastes, toxic industrial and medical wastes.

Detailed information:
See data in Annexes.

Conclusion:
The vendor offers a range of modular systems that may be suitable for a range of remedial situations. Of course, the actual performance in use will depend on a range of factors including regulatory criteria.
At present Accentus has no commercial plant(s) with sufficient capabilities available, although as part of the ACWA program has a costed design for a 1MW fixed installation.

On the basis of the experiences gained in the ACWA project, it is estimated, however that for the development of a commercial plant with treatment capacities of say 400-500 tons/year, still a period of at least 2 years will be needed. As many of the Warfare Agent Components were originally developed from pesticides, the suitability for the technology towards the treatment of these materials seems favourable.

Full Scale Treatment examples:

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References:

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3. The application of SILVER II to Chemical Weapon Demilitarisation - recent progress on ACWA - AD Turner, T Graham B Bixler. CWD2002 - The Hague, May 2002.
4. SILVER II as a broad spectrum waste destruction process AD Turner, Accentus ; 15th International Forum on Electrolysis in the Chemical industry (Florida, November 2001)
5. Optimization Studies for the treatment of combustible residues by mediated Electrochemical Oxidation (MEO) processes. Wayne H Smith, Michael E Cournoyer Los Alamos National Laboratory. 13th International Forum on Electrolysis in the Chemical industry (Florida, November 1999)
6. SILVER II mediated electrochemical oxidation for fissile residue recovery and organic waste treatment in the nuclear industry DF Steele, 4th European Conference on Electrochemical Processing, Barcelona, April 1997.
7. The low temperature destruction of organic waste by electrochemical oxidation DF Steele, D Richardson, JD Campbell, DR Craig, JD Quinn Trans IChemE, Vol 68, Part B, May 1990

**Note: This NATO/CCMS fellowship report does not certify any particular technology, but tries to summarise the state of the art of the concerned technology on the basis of data deliver by the company or other sources been made available to the author and refers the reader to original documents for further evaluation.*
*** Note:The text for this report is verified by the Technology supplier on 28. October 2002*