

# Implications of the ACWA SILVER II programme for pesticide and herbicide destruction

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## Introduction

The SILVER II™ process has been developed by AEA Technology for a number of years from laboratory to plant scale for the mineralisation of a wide range of organic substrates, culminating in the Assembled Chemical Weapons Assessment program conducted on behalf of the US Army over the summer of 2000.

Initial work in the 1980s was directed towards the treatment of radioactive contaminated organic wastes - comprising solvents, extractants, ion-exchange resins, cellulosic tissues, and polymeric materials. The organic components were converted to CO<sub>2</sub> and water, which could be safely discharged into the environment, leaving a minimal volume of radioactive residues for immobilisation prior to storage and then disposal.

Chemical Weapons are a second category of hazardous materials requiring treatment as part of their management strategy. While the current reference route for disposal is incineration, a programme was initiated by the US Army, in response to public concerns in the USA, to investigate alternative treatment methods - including SILVER II. While initial work was conducted with small pilot-scale equipment, subsequent demonstrations were based on full-scale commercial electrochemical cells - as used in the chlor-alkali industry.

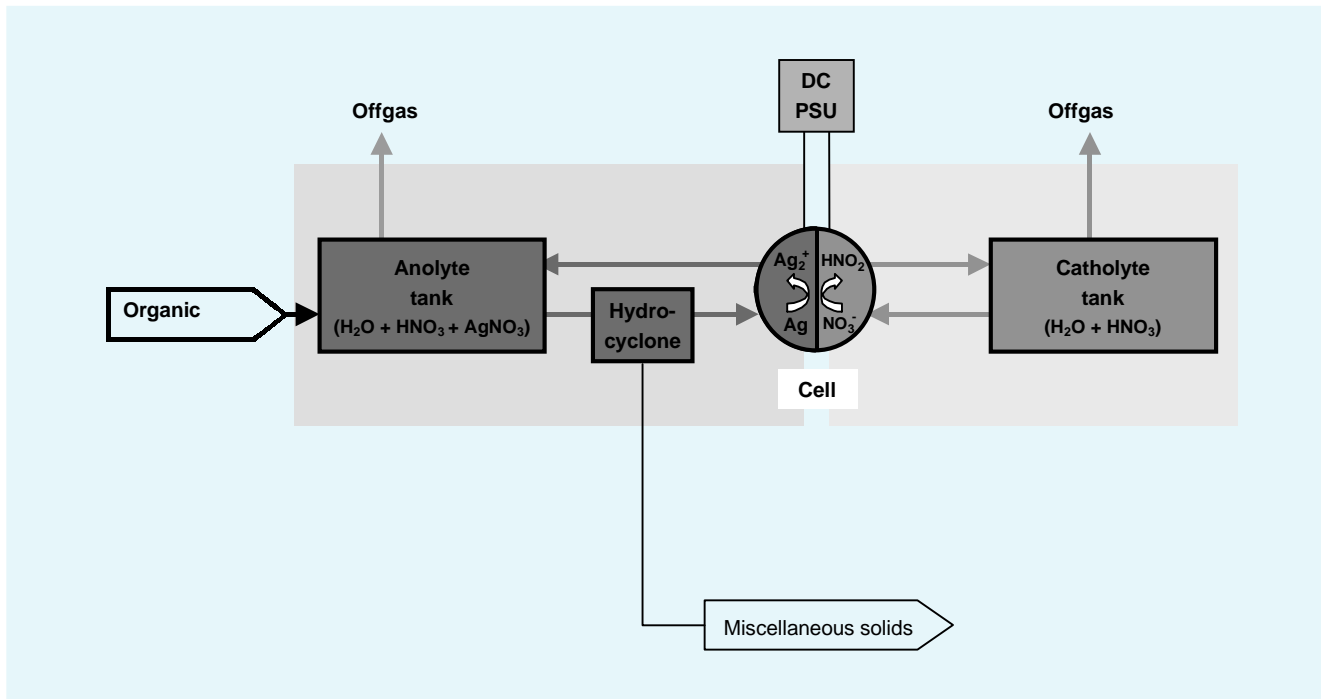
Toxic herbicides and pesticides may form a further category of wastes that could benefit from the environmentally friendly and safe mineralisation offered by SILVER II, as an alternative to incineration.

## Process description

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 (Figure 3). Radical species initiated by Ag[II] attack the organic substrate - progressively converting it in a series of steps irreversibly to CO<sub>2</sub>, 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.

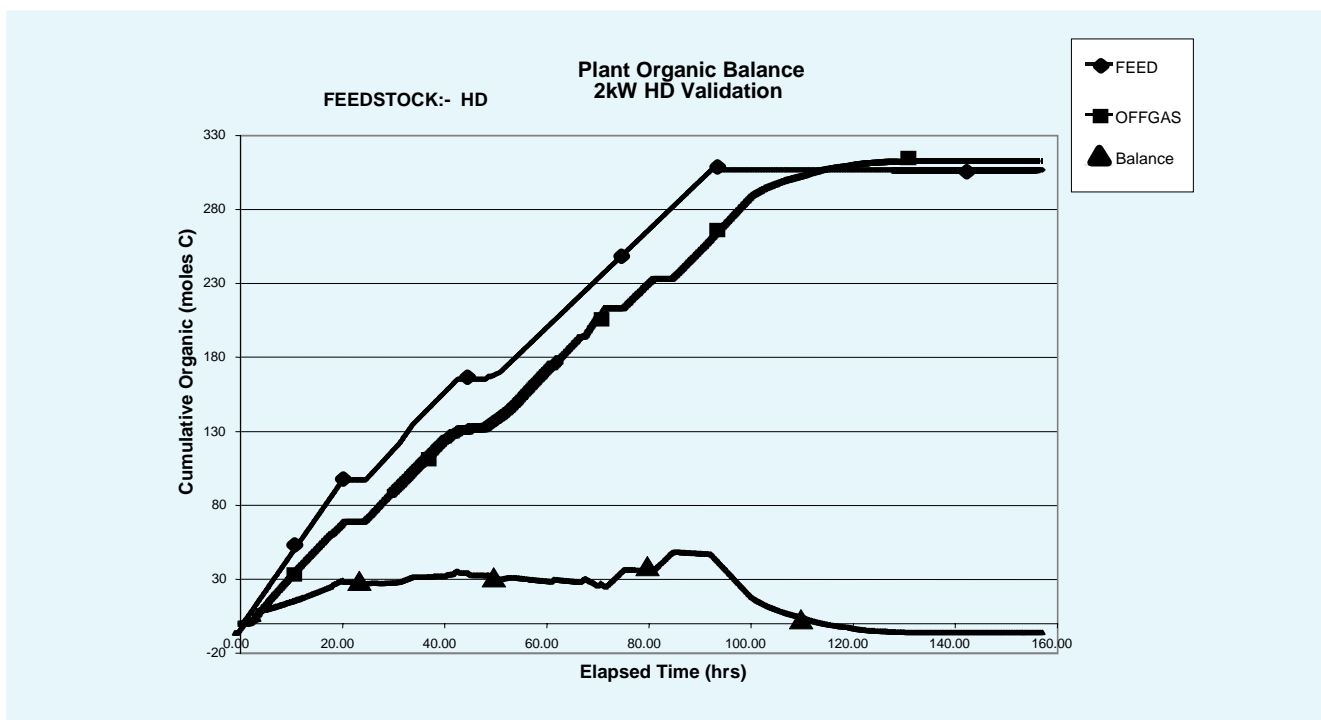
The organic species do not have to be water-soluble to be successfully treated by SILVER II, as has been shown by the successful treatment of solvents, oils, ion-exchange resins, tissues etc.

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<sub>2</sub> as a parasitic product. In order to minimise this loss route, the concentration of organics should be high (2-10 g/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 ~90°C and atmospheric pressure, where the reactions with the organic substrates are rapid. CO<sub>2</sub> is rejected from the acidic electrolyte into the gas stream, which is scrubbed prior to discharge to atmosphere.



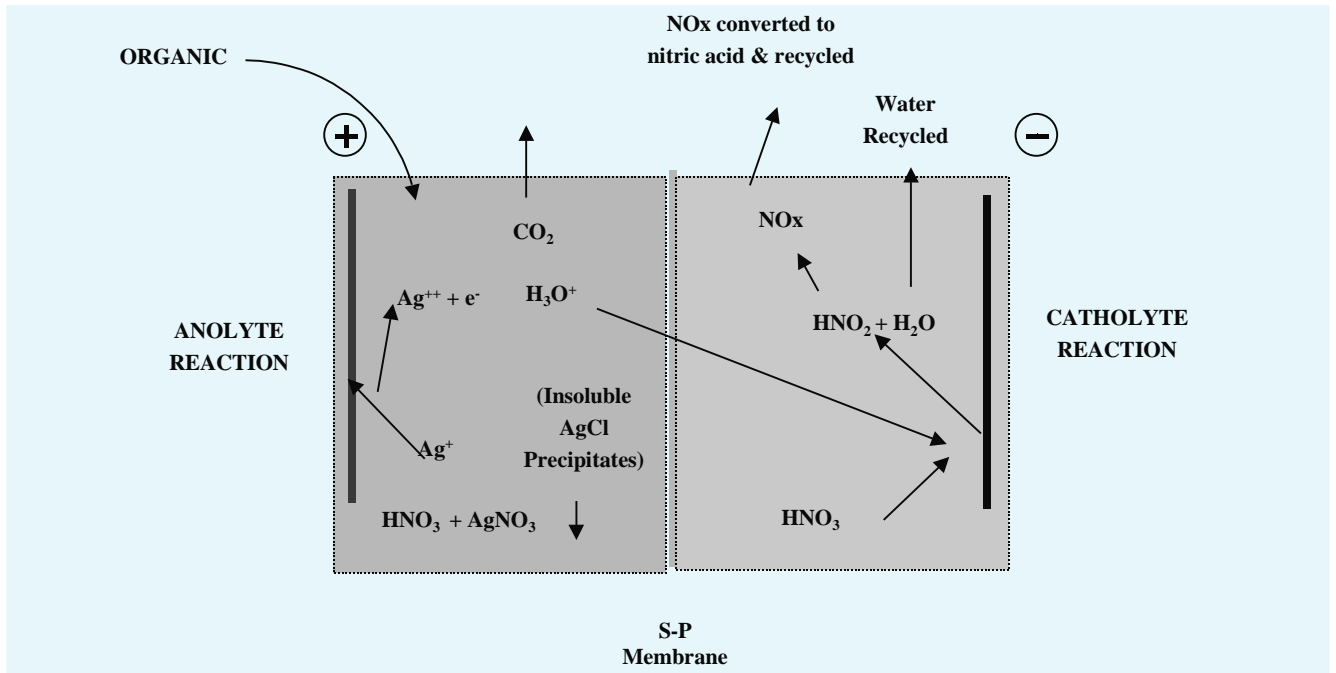
**Figure 1. Schematic layout of the core Silver II process**

The heart of the system is shown in Figure 1. The Ag[II] is generated in-situ electrolytically, at the anodes of commercially available electrolytic cells. It is the linkage between these two steps that provides the benefits of the process, in that the reaction rate can be controlled by the applied current. The rate of organic feed rate addition is matched to the rate of destruction defined by the electrolytic regeneration process.



**Figure 2. Organic balance during the treatment of HD in the 2kW ACWA plant**

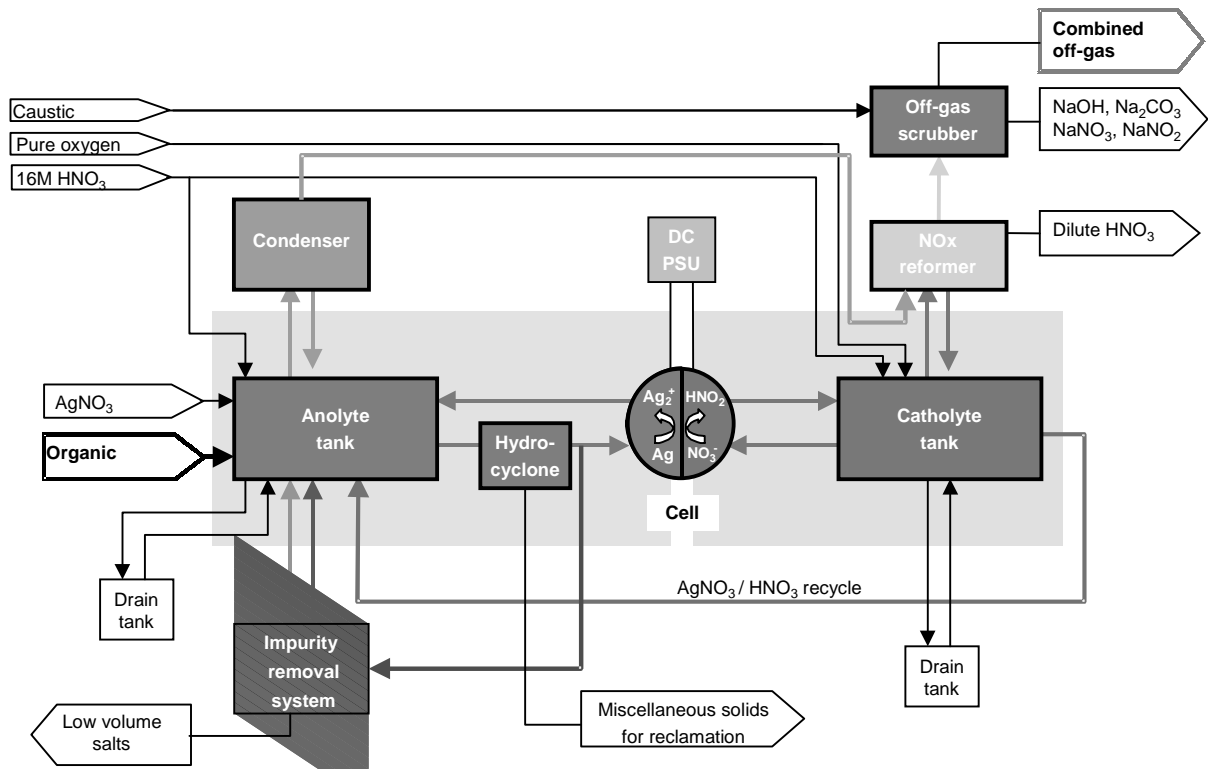
In the case of chlorine containing feeds, the chloride content will precipitate as silver chloride. This is prevented from entering the cell by solid/liquid separation in a hydrocyclone. The recovered material can be treated to recover the silver, which can be returned to the electrolyte for re-use.



**Figure 3. The SILVER II cell reaction**

The matching reaction at the cathode of the electrochemical cell is the reduction of nitric acid to nitrous acid - which results in the evolution of NO and NO<sub>2</sub> (Figure 3). Oxygen/air is drawn through the plant so that the NO<sub>x</sub> can be reformed back into nitric acid through simple chemical reaction. This stream can then be fractionally distilled to recover concentrated nitric acid for internal recycle within the process, and water (with minimal nitric contamination) for discharge of excess water resulting from the hydrogen content of the feed. After this stage, the off-gas is finally scrubbed prior to venting to remove any residual traces of NO<sub>x</sub>. The entire plant layout is shown in Figure 4.

As can be seen there, internal recycle of water, acid, silver are engineered to minimise environmental discharges. These are restricted to CO<sub>2</sub> (from the C content of the feed), excess H<sub>2</sub>O (from the H content of the feed) and acids (derived from the hetero atom content of the feed), which can be lime neutralised prior to discharge.



**Figure 4. Schematic of the integrated SILVER II plant**

## Track record

SILVER II pilot plants have been operated since 1988. Initial work on nuclear materials treated by SILVER II are summarised in Table 1.

**Table 1. Materials and scale of SILVER II operations in the nuclear industry**

Feed	Lab scale	Pilot scale	
		0.15 kW	4 kW
TBP/OK	√	√	√
IX resin	√	√	√
Cellulose	√	√	
Oil	√	√	

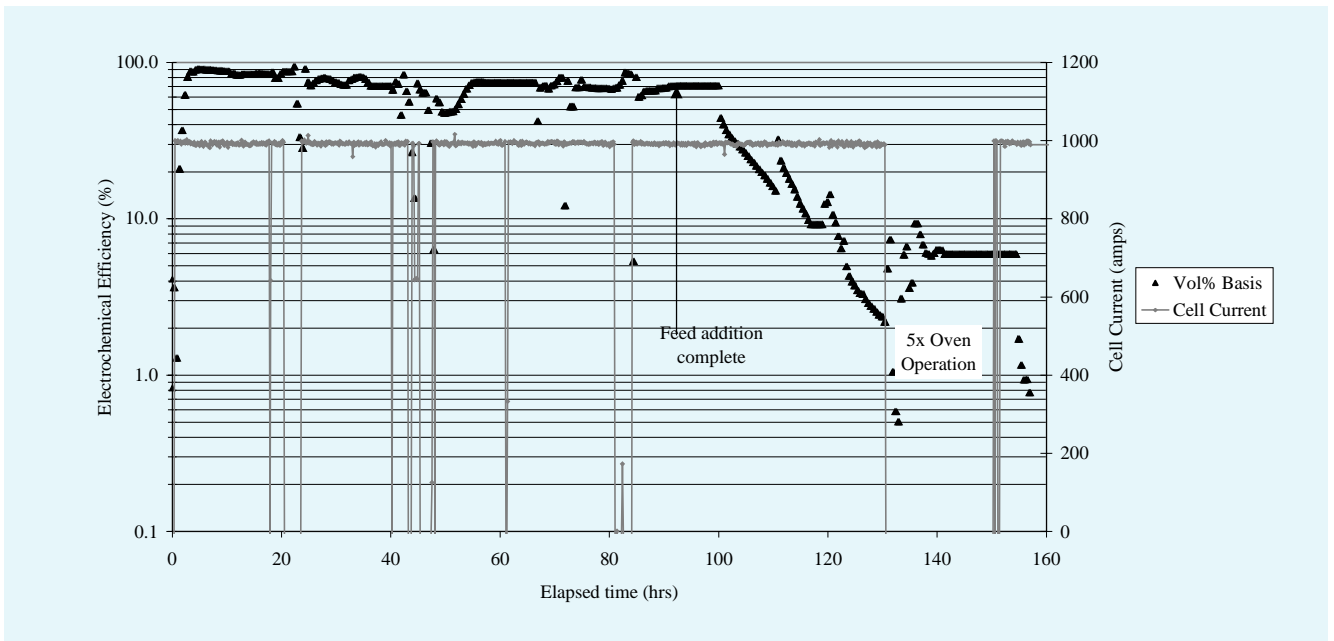
Complete mineralisations were achieved with current efficiencies in the range 70-95% at all these scales.

Table 2 gives the scales and materials treated for chemical warfare agents. The 4kW work was carried out at Porton Down in the UK, while the 2kW work formed part of the recent US Army ACWA Demonstration Program in the US.

**Table 2. Chemical warfare agents treated by SILVER II**

Feed	Plant size		
	0.15kW	2 kW	4 kW
VX		4 kg	14.5 kg
HT			18.6 kg
GB	0.1 kg	15.7 kg	
HD	0.1 kg	16 kg	
Lewisite	0.1 kg		
GA	0.1 kg		
Clark agents	0.1 kg		

In this programme, 99.9999 - 99.99999% destruction efficiencies were achieved, with current efficiencies in the range 50-90%. A validation run is shown in Figure 5 for Mustard Gas.



**Figure 5. Variation of current efficiency with time for HD treatment**

Recovery and recycle of silver was also demonstrated as part of this programme.

Energetic compounds have also been successfully treated, as shown in Table 3, using the 12kW plant shown in Figure 6.



*General View*



*View of Cell stack during assembly*

**Figure 6. 12kW SILVER II ACWA Plant**

In the ACWA 12 kW plant programme, M28 destruction was determined as 99.9999%, at a current efficiency of 80-100%. Due to a solids handling problem, Tetrytol was destroyed to 99.7% at a current efficiency of 20-30%, although at the smaller scale such problems had not been encountered. Design revisions have been put in place to rectify this - and increase current efficiency back to the 70% target, and destruction of 99.999%.

**Table 3. Energetic compounds treated by SILVER II**

Feed	Plant size		
	Lab scale	0.15kW	12kW
RDX	5 g	100 g	
TNT	5 g	200 g	
Triple base	5 g	100 g	
TETRYL		100 g	
Nitroglycerine	5 g		
DEMEX	5 g		
OTTO fuel	5 g		
M28			159 kg
TETRYTOL			73 kg

Overall, this plant destroyed 1 tonne of organic material. In addition, the recovery of concentrated nitric acid for recycle and also re-use in industrial applications was demonstrated.

Over 3,500 hours of plant operation were achieved without any lost time accidents.

Table 4 gives a list of industrial compounds successfully treated by SILVER II in lab and small pilot scale plants.

**Table 4. Industrial compounds treated by SILVER II**

Dodecane	Chlorofluorobenzoic acid	Octanoic acid
Tributyl phosphate	m-nitro p-toluidine	Butanol
Kerosene	Toluene	Petroleum spirits
Dioxan	Dinitrophenol	Isopropanol
Ther	Nitrosobenzene	Tetrahydrofuran
Cyclohexane	Urea-formaldehyde	Methylene Chloride
2-methoxyethanol	Triethanolamine	Aliphatic amines
Phenol	Methanol	Dimethyl formamide
Xylene	Chloroform	Trichlorobenzene
2 chloroethyl sulphide	Ethanol	p-toluenesulphonic acid
Chlorobenzene		

These, together with the nerve and blister agents discussed above contain the range of functional groups commonly encountered in herbicides and pesticides - thus giving confidence that SILVER II is worthy of further investigation as a sustainable alternative to incineration of redundant stockpiles.

## Environment and safety

The key aspects of the process contributing to the intrinsic safety of the process are that it operates at low temperature and pressure. As a result the creation of dioxins and furans is avoided. The control over reaction rate imposed by the electrical cell current makes the process controllable and fail-safe. On cessation of feed addition, the residual organics are progressively reduced, as the plant decontaminates itself (Figure 2). As part of the recent ACWA programme, destruction factors of as high as 99.99999% were determined - essentially on the limit of detection of agent compounds.

The streams discharged from the process are essentially a low volume of CO<sub>2</sub>/O<sub>2</sub> mixture from which NO<sub>x</sub> has been scrubbed to low levels. The water discharge (arising from the H content of the feed) is the condensate from a distillation column. This contains only low levels of residual nitric acid, which can be neutralised prior to discharge. The only other waste stream arises from hetero-atoms in the feed. Silver can be recovered from a bleed stream from the electrolyte and recycled to the anolyte, while the residual sulphate, phosphate etc can be neutralised by lime for disposal as a solid to landfill.

## Future developments

Plants have been demonstrated at bench-top, pilot scale and using full-scale industrial electrolytic cells - both singly and in multi-cell stacks. This has been based on the use of standard commercially available components. As in the chlor-alkali industry, process scale-up is simply by increasing the number of cells and the accompanying process stages.

AEA Technology has developed both mobile self-contained containerised plants, transportable modular containerised plants to 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, 300 te/y toxic organics can be mineralised/MW cell capacity installed. These applications include demilitarisation of CW agents and energetics, other military and nuclear wastes, toxic industrial and medical wastes.

## Conclusions

By analogy with organophosphorous, nerve agents, thio and halogenated compounds - all successfully treated by SILVER II - it is anticipated that the SILVER II process should be able to treat redundant stockpiles of herbicides and pesticides as a sustainable technology without resorting to incineration.

It is therefore proposed that as the result of the large scale ACWA demonstration using full-scale commercial electrochemical cells, specific herbicide/pesticide destruction be evaluated to establish the cost-effectiveness of this approach in comparison with incineration (including the extensive safety/off-gas treatment equipment required for the latter).