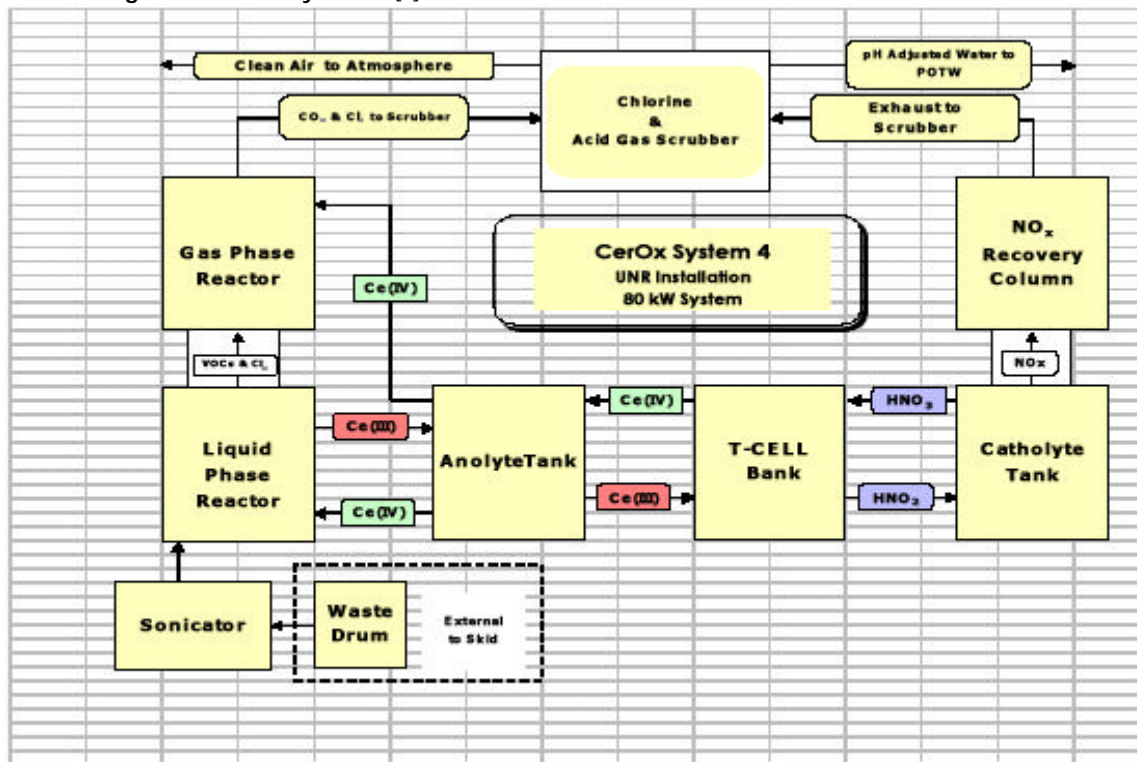


Name of Process: CerOx™ Process	Status: A pilot system has been successfully operating at pilotlabscale University of Nevada at Reno, US. Two (2) commercial systems have been sold.
Vendor: CerOx Corporation Web site: http://www.cerox.com	A System 4 has been installed at the University of California Irvine (UCI) and is expected to begin processing waste in 1 st Quarter of 2003. A System 2MW is being installed at Merck in New Jersey, with operation expected in 2 nd Quarter of 2003.
Applicable Pesticides and related POPs wastes: Toxic wastes, including chlorinated solvents, PCBs, pesticides, biological agents etc., chlordane, kelthane, permithrin, mixtures of 2,4-D and 2,4,5-T, phenols, alcohols, dioxins pharmaceuticals, cytotoxins, aliphatic amines, aromatic amines, chemical weapons, and mixed wastes (low level radioactive and organic hazardous).	In agreement, the regulators in 40 States of the US have Stated that the CerOx process does not require an EPA RCRA permit (Type B Permit).
Technology description: <p>The process belongs to the category of Mediated Electrochemical Oxidation or Catalysed Electrochemical Oxidation. The process involves electrochemical cells for the generation of the active cerium(IV) oxidant at the anode, a liquid phase reactor for primary organic destruction, a gas phase reactor to destroy any fugitive emissions from the liquid reactor and an acid gas scrubber for removal of acid gases prior to venting to the atmosphere.</p> <p>The catholyte loop indicated in the Process Diagram is designed to recover nitric acid from the nitric acid reduction products that are the result of the cathode reaction, a necessary part of any electrochemical process. The cathodic processes are separated from the anodic (waste destruction) processes by a fluorocarbon membrane, which confines the waste materials to the anolyte loops.</p> <p>In operation, the organic waste materials are injected into the oxidising electrolyte through an ultrasonic mixer, which emulsifies immiscible organics into the aqueous anolyte to maximise the contact area between the organic and the cerium (IV) oxidant. The organic/oxidant mixture is fed into the liquid reactor for completion of the oxidation reactions that convert the organic materials to, primarily, carbon dioxide and water while carbon bound chlorine is converted to molecular chlorine. An example destruction process is given in Equation 1 using chlorobenzene. Other carbon bound heteroatoms, such as</p> $\text{C}_6\text{H}_5\text{Cl} + 29 \text{ Ce(IV)} + 12 \text{ H}_2\text{O} \rightarrow 6 \text{ CO}_2 + 29 \text{ H}^+ + 1/2 \text{ Cl}_2 + 29 \text{ Ce(III)} \quad (1)$ <p>nitrogen, phosphorous and sulphur are oxidised to their respective oxyacids, i.e., nitric acid, phosphoric acid and sulphuric acid. As implied in Equation 1, the oxygen in the CO₂ product comes from water which makes the destruction reaction approximately thermoneutral. This, in turn, eliminates the potential for thermal runaway reactions in the liquid reactor.</p> <p>The active Ce(IV) oxidant is regenerated from the reduced Ce(III) by re-oxidation in the electrochemical cell according to Equation 2.</p> $\text{Ce(III)} \rightarrow \text{Ce(IV)} + \text{e}^- \quad E^\circ \quad 1.6\text{V} \quad (2)$ <p>The electro-chemical regeneration and recycling of the cerium oxidant makes the cerium a true catalyst in the process. The corresponding cathode reaction, the reduction of nitric acid to nitrous acid, is shown in Equation 3.</p> $\text{HNO}_3 + 2 \text{ H}^+ \rightarrow \text{HNO}_2 + \text{H}_2\text{O} \quad (3)$ <p>The cathode reaction is the major exothermic reaction in the process but, since it only occurs when dc power is applied, it also does not pose a thermal runaway potential. The electrochemical basis of the process makes the process absolutely controllable since it can be shutdown with the flip of the power switch as is done automatically should an upset occur.</p> <p>The nitrous acid product, HNO₂, from the cathode reaction, Equation 3, disproportionates in solution to produce nitric acid and nitric oxide, NO. The gaseous NO is oxidised with atmospheric oxygen to NO₂, which is then dissolved in water to make nitric acid. These oxidation/absorption processes recover much of the nitric acid consumed in the cathode reaction [1].</p> <p>The operation of the Ce(IV) based oxidation chemistry at atmospheric pressure and low temperature, < 100°C, precludes the formation of the more toxic dioxins and (benzo)furans during the destruction process.</p>	

Process diagram of CerOx System 4 [1]:



Performance:

Treatment efficiency:

The process has been applied at pilot lab scale, using a System 4, at the University of Nevada at Reno. The non-thermal process, using an electrochemically generated metal ion oxidant, was used to destroy chlordane, kelthane, permethrin and a mixture of 2,4-D and 2,4,5-T with their dioxin impurities (Tables 1 and 2). The process data showed destruction efficiencies >99.995% for the chlorinated materials and >99.9% for some remaining non-chlorinated (“inert”) components of the commercial product mixtures. CerOx Corporation has been operating for 2 years.

Table 1: Chlorocarbon Test Materials Used in the University of Nevada Reno Study [1]

Material	Formula	Manufacturer	% Active Ingredients	% Water in Feed
Kelthane	C ₁₄ H ₉ Cl ₅ O	Rohm & Haas	42%	50%
Permethrin (Ambush)	C ₂₁ H ₂₀ Cl ₂ O ₃	ICI	50%	50%
Weed-B-Gone		Chevron Chemical		50%
2,4-D	C ₈ H ₆ Cl ₂ O ₃		21.4%	
2,4,5-T	C ₉ H ₇ Cl ₃ O ₃		10.0%	
Chlordane	C ₁₀ H ₆ Cl ₈	Ortho	71%	50%

With these values for the upper limit concentrations in the exhaust stream, the destruction levels shown in Table 2 were calculated.

Table 2: Chlorinated Materials: Mass Flow And Destruction Efficiency [1]

Material	Gas Flow l/min	Gas Phase Concentration		Feed Rate G/min	Destruction %
		ppm	µg/min		
Chlordane	10	1	184	3.4	99.995
Ambush™	14	0.1	24	1.85	99.998
Kelthane™	6	1	99	4.8	99.998
2,4-D	10	0.1	10.0	0.6	99.998
2,4,5-T	10	0.1	12.1	0.3	99.996

Commercial formulations of the pesticide and herbicide materials listed in Tables 1 and 2 were fed as 50% emulsions in water. These mixtures also contained kerosene and suitable surfactants to maintain the emulsions. The presence of these inert ingredients was clearly evident particularly in Figure 5 (see [1]) with the many peaks in the $m/z = 50$ to 95 range. The peak shapes and their spacing at $m/z = 14$ is the classic signature for aliphatic hydrocarbons spaced every CH_2 grouping (Balzers Instruments, Partial Pressure Measurement in Vacuum Technology, BG 800 169 PE (9610)) [1].

In another successful application, Stone & Webster issued their conclusions in December 2001 on the destruction of chemical weapon simulants by the CerOx technology. After successfully destroying the simulated compounds, the U.S. Army is negotiating with the Company to treat additional weapons compounds followed by an on-site treatment study processing actual neutralized chemical weapon compounds such as mustard gas and sarin (used by Tokyo subway terrorists) [5].

For the objective of demonstrating stable operability at maximum continuous throughput, the following conclusions have been made [5]:

- The CerOx System 2 showed stable operation and processed 1.4 and 2.4 kg/hr of HD neutralent simulant and GB neutralent simulant respectively for up to 24 hours.
- The liquid effluent consistently fell below the 25 ppm TOC (Total Organic Carbon) test criteria and generally ranged from 2 to 6 ppm TOC.
- Estimates of overall destruction were based on the most reliable data, namely TOC concentrations on influents and effluents. The results of these calculations showed destruction efficiencies which ranged from 97 to 99%.
- During the validation testing, stack gases were estimated at 71-73 dscfm, scrubber effluent ranged between 0.6 and 1.5 gpm, and generated solids amounted to less than a couple of grams recovered from the anolyte solution.

CerOx has also completed an installation of the first California system at the University of California Irvine (UCI) in September 2002. This system is capable of processing 450 pounds of liquid laboratory wastes per day and will be used as our regulatory entry vehicle into the California marketplace. The system is expected to begin treating waste during 1st Quarter of 2003. Upon demonstration of successful treatment results at UCI, other universities throughout the State of California (Stanford, San Francisco, San Diego) will evaluate and implement the CerOx System where economically feasible.

Furthermore, CerOx will ship a system in December 2002 to Merck Pharmaceutical (New Jersey) for the treatment of mixed waste (low level radioactive and organic hazardous waste). The CerOx process is Conditionally Exempt for Mixed Waste Treatment (EPA Final Rule Published May 16, 2001; 66 FR 27218). The CerOx system allows mixed waste generators to convert the waste classification from mixed waste to low level radioactive waste; thereby significantly reducing the waste disposal costs.

Throughput:

The System 4 has a fixed cerium(IV) production capacity and the mass throughput is a function of the electron demand of the waste materials. While nominal capacity of the 80kW system shown in the Figure is approximately 1/2 drum of organic waste, containing 50% water, per day, the actual throughput is a function of the electron demand of the waste materials [1].

CerOx Corp.'s first designed and delivered commercial system was the CerOx System 4. This system has 4 electrochemical cellpacks (one full T-CELL) and is capable of destroying almost a drum (55 gal) per day of waste organic chemicals (in 24 hours). The other members of the CerOx Corp. product family are Model Sizes. Process requirements in excess of the 200 gal/day are met by multiples of the CerOx System 16 unit (basic large stream module). The product family scales with electrode area (number of cellpacks) typical for an electrochemical process which allows for modularization of the process technology.

Wastes/Residuals:

In agreement, the regulators in 40 States (of the US) have stated that the CerOx process does not require an EPA RCRA permit (Type B Permit). The conditions in the process are such that the reaction conditions, e.g., high temperature, needed for the synthesis of dioxins from chlorocarbon feed materials are never attained making the CerOx process a dioxin destroyer, not a dioxin maker [1].

Reliability:

As the system is in the first stages of commercialisation, no reliability data is currently available.

Limitations: The system will tolerate regulated quantities of heavy metals, alloys, halogens, sulfur and phosphorous. For these allowable but regulated components, please contact CerOx for a specialized assessment. The system is not recommended with waste streams containing arsenic, cyanide, selenium, tellurium, lead and fluorine (fluorocarbons).

Transportability:

The system is a self-contained, fully automated skid designed for permanent installation. Minimal site installation utility requirements include compressed air, cooling water, drain for water, and electricity (all depending on system size).

Detailed information:

(see attached Annex for typical System 4)

Conclusion: The absence of detectable peaks for the tested chlorinated pesticides and herbicides allows for the establishment of minimum destruction efficiencies on the order of 99.995% for these materials with the CerOx Process. The operation of the Ce(IV) based oxidation chemistry at atmospheric pressure and low temperature, < 100°C, precludes the formation of the more toxic dioxins and (benzo)furans during the destruction process [1].

The CerOx technology is a promising, dioxin free technology for the destruction of pesticides, however with the information available on the treatment of pesticides or other related hazardous wastes, still working at a small scale, which means that one has to reckon with a considerable period of upscaling until full scale application. More independent assessments (one assessment has been made available) are needed to evaluate this technology in the future. It must be mentioned that CerOx has indicated that 2 commercial systems have been sold.

Full Scale Treatment examples:**Vendor Contact details:**

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Patents:

CerOx Corp. has a worldwide, exclusive license for this proprietary ([US Patent 5,707,508](#)) technology which includes the cerium process chemistry and specialized equipment for its practice.

CerOx Process is licensed from the Pacific Northwest National Laboratory (PNNL).

(The CerOx Corps.' patent, covering the design and operation of this cellpack, has the number [US Patent 5,756,874](#).) This is the proprietary electrochemical T-CELL designed and patented ([US Patent 5,756,874](#)) by CerOx Corp.

**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 22. November 2002*

References:

1. Destruction of highly chlorinated pesticides and herbicides using the CerOx process, Norvell Nelson, Thomas Neustedter, G. Anthony Steward, Wendel Pells, Steve Oberg, Juan Varela, 6th International HCH & Pesticides Forum Book, 20-22 March 2001, Poznan, Poland, November 2001
2. Dioxin Test Run on August 29, Memorandum CerOx, September 18, 2000 (available at <http://www.cerox.com>)
3. PCB Destruction Test Run of August 30, CerOx, September 15, 2000 (available at <http://www.cerox.com>)
4. The CerOx Process: New Technology for Organic Hazardous Waste Destruction, Norvell Nelson, Thomas Neustedter, G. Anthony Steward & Wendell Pells, Steve Oberg and Juan Varela, Presented at the Spring 2000 American Chemical Society Meeting in San Francisco at the Symposium on Emerging Technologies: Waste Management in the 21st Century
5. Stone & Webster, Evaluation of the Limited Engineering Scale Testing of the CEROX™ Process To Treat NSCMP Neutralents, Prepared for: United States Army Non-Stockpile Chemical Materiel Program Manager Chemical Demilitarization Project, Report No. R37-V-04, Revision 2, December, 2001

CerOx System Four

Basic System Definition & Requirements

Capacity:	1-3 gallons per hour of organic content
Waste Type:	Liquid drummed waste (nominal container is 55 gallon drum)
Composition:	Neat organics - 100% organic content (see listing) Organics in water - maximum of 80-90% water Organics with inorganics - halogenated, inorganic/organic
Mixing:	All organic compounds (safe to mix) can be placed in same drum

Waste Limitations

Restricted Elements:	Lead, fluoride, arsenic, radioactive elements
Limited Quantities:	Phosphate, silicon, mercury, aluminum
Metered Quantities:	Alkaline earths/metals, transition metals, heavy metals
Solids and Sludges:	Requires and additional front end, available 1998

System Operation and Maintenance

Additional Operators:	None
Operator Training:	Training provided (8 hours)
Maintenance:	Virtually none by customer
Operator Interface:	Drum connect, Keypad input
Operation Monitoring:	Optional remote monitor, PC based with paging
Anolyte Regeneration:	Two drums of anolyte are exchanged bi-annually
Caustic Addition:	Disconnect existing drum and reconnect new drum
Nitric Acid Addition:	Disconnect existing drum and reconnect new drum

Facilities Requirements

Water (tap):	1/2 inch line (≥ 5 gpm)
Drain to Sewer:	Monitored for pH (on-board chart recorder)
Cooling Water:	Cooler will be added if not available (30 gpm at 30° C)
Vents:	To atmosphere
Compressed Air:	If available (45 CFM)
Electricity:	480/208 Volt 3 phase service with 100 kW available

Space Requirements

Floor Space:	Inside or outside, system has self contained sump(s) Main system: 7' by 10' by 9-12' high (Steel Chemical Bldg.) Waste input drum(s) containment area: 3'x5' Power Supply: 4'x3' (remote, inside or out)
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Permitting Requirements

Air Permit:	Varies by district/site, should not be needed
Sewer Permit:	Varies by district/site, may not be needed
RCRA Permit:	Exempt per 40 CFR 270.1 c.2.i.iv
On site Treatment Permit:	Not needed in 40 states*

* 1) All agencies reserve final judgment until a system can be examined
2) For generated waste only