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Commercial Organic Chemical Waste Destruction using Supercritical Water Oxidation

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Supercritical water oxidation (SCWO) is an excellent process for the destruction of old or obsolete pesticides, obsolete paints, petroleum product manufacturing waste streams, pharmaceutical waste, energetic materials (explosives or propellants), flame retardants (containing BTBPE, TBECH, PEBE, TBBPA, and TCEP), contaminated waste waters and other organic waste streams.

As described in the abstract, GA uses SCWO as a destruction technology for organic compounds and toxic wastes that makes use of the unique properties of water exhibited at supercritical conditions, that is, temperatures above 374°C and pressures above 22 MPa. Under these conditions, oxidation reactions occur rapidly and to completion with by-products consisting of clean water or brine, clean gases, and inorganic ash with essentially no airborne particulates.

General Atomics introduced a commercialized SCWO process that is called iSCWO (Industrialized SuperCritical Water Oxidation) in 2014 based on extensive us of the SCWO process for destruction of energetics (explosives and propellant), military organic waste and nerve agents for the US Government. GA has been developing SCWO technologies and delivering SCWO/iSCWO systems to the US Government since 1991. The iSCWO systems that GA sells are simple, small and compact systems that are used for onsite organic waste destruction. The iSCWO process flow diagram is illustrated in Figure 1 and an operational system is shown in Figure 2.

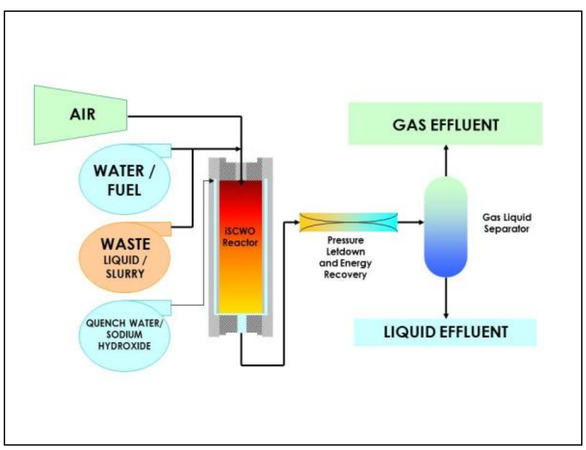

Figure 1 – iSCWO Process Flow Diagram **Figure 2 – iSCWO System Equipment Skid**

High pressure air is combined with water, fuel (if required by the specific application) and the waste liquid/slurry that is pumped into the iSCWO reactor where high temperature (650C) and pressure (23.5MPa) will destroy the organic compounds via oxidation reactions. The oxidant is high-pressure air to minimize process and safety issues associate with high-content oxygen supply systems (e.g., liquid oxygen). GA operates the iSCWO systems at a higher temperature and pressure regime to ensure excellent organic destruction (non-detect). Organics and oxidant are miscible with supercritical water, creating excellent conditions for oxidation with minimal mass transport limitations resulting in organic materials that are quickly destroyed. Heteroatoms such as chlorine, fluorine, phosphorus and sulfur are converted to inorganic acids or to alts if sufficient cations such as sodium or potassium are present. If present, metals such as iron and/or copper will produce metal oxides. The reaction by-products exit the reactor through a pressure letdown system and discharge into a gas-liquid separator. The gases (CO2, excess O2, and steam) are exhausted through a stack and the liquids (water, dissolved salts, oxidized inorganics) are discharged either into a holding tank or into a commercial sewer system (Public Owned Treatment Works).

These simplified iSCWO systems have been supplied to US Government entities as well as commercial users for the destruction of various chemical and hazardous wastes. The iSCWO system is available as a compact, transportable unit (see Figure 3) or available to be installed in a new or existing facility as a final installation (see Figure 4). The benefits of utilizing iSCWO far outweigh the use of

Figure 3 – Transportable iSCWO System **Figure 4 – Embedded iSCWO System**

alternative waste destruction approaches (e.g., incineration) especially if onsite treatment (or for transportable systems for multiple sites) use is desired. In addition, GA’s iSCWO systems do not require any afterburner or pollution abatement systems for gaseous effluent cleanup (no dioxin or furan production issues).

GA has demonstrated the destruction of hundreds of organic compounds and mixtures with SCWO technology including pesticides, organic contaminants and compounds containing flame retardants (Figures 5 and 6). Shown in Figure 7 is GA's test facility located in San Diego, California, which utilizes a 3gpm iSCWO system. GA's iSCWO systems are mature enough that R&D is not required; however, this test system is used to test customer wastes in order to demonstrate operability and waste destruction while generating data for customer permitting requirements. Effluent analyses (gas and liquid) are performed by independent laboratories to confirm high waste destruction efficiencies and look for customer specific compounds. The systems built for our customers are put through rigorous acceptance tests prior to shipment. Figure 8 shows a transportable system undergoing final acceptance testing for one of our commercial customers.

Organic Chemicals		
Acetic Acid	Dichlorobenzene	Nitrobenzene*
Acetone	4,4-Dichlorobiphenyl	2-nitrophenol
Acetylsalicylic acid(aspirin)	Dichloroethylene	4-nitrophenol
Adumbran	Dichlorophenol	Nitrotoluene
4[(2-Amino-3, 5-dibromophenyl)-	Diethanolamine*	Octachlorostyrene
methylamino]cyclohexanol	Dimethylformamide*	Octadecanoic acid magnesium salt
Ammonium acetate*	Dimethyl methyl phosphonate	Paracetamol
Ammonium formate*	(DMMP)*	Pentachlorobenzene
Ammonium oxalate*	Dimethyl sulfoxide*	Pentachlorobenzonitrile
Benzene	4,6-denitro-o-cresol	Pentachlorophenol*
Biphenyl	2,4-Dinitrophenol	Pentachloropyridine
Butanol*	Dinitrotoluene	Phenol
Calcium acetate*	Dipyridamole	Polychlorinated biphenyls (PCB*)
Carbon tetrachloride*	Diisopropyl ethanolamine	Polychlorotrifluoroethylene*
Carboxylic acids	Diisopropyl ethylamine	Sodium acetate
Carboxymethyl cellulose	Ethanol	Sodium formate
Cellulose	Ethyl acetate*	Sodium hexanoate
Cerium Acetate*	Ethylene chlorohydrin	Sodium isethionate*
Chlorinated dibenzo-p-dioxins	Ethylenediamine tetraacetic acid	Sodium propionate
6-chloro-2,3,4,5-tetrahydro-3-	Ethylene glycol	Sucrose
methyl-1H-3-benzazepine	Fluorescein*	Surfactant
hydrochloride	Freon 22	Tetrachlorobenzene
Chlorobenzene*	Glycerol	Tetrachloroethylene*
Chloroform*	Hexachlorobenzene	Tetrapropylene H
2-Chlororphenol*	Hexachlorocyclohexane	Thiodiglycol*
o-Chlorotoluene*	Hexachlorocyclopentadiene	Toluene
Cobalt acetate	Iron acetate*	Tributyl phosphate
m-Cresol*	Isooctane	Trlchlorobenzenes
Cyanide*	Isopropanol*	1,1,1-Trichloroethane*
Cyclohexane	Lead acetate*	1,1,2-Trichloroethane*
DDT	Mercaptans	Trichloroethylene
Decachlorobiphenyl	Mercaptoethanol	Trichlorophenol
Dextrose	Methanol*	Trifluoroacetic acid
Dibenzofurans	Methyl acetate*	1,3,7-Trymethylxanthine
3,5-dibromo-N0cyclohexyl-N-	Methyl cellosolve	Unsymmetrical dimethyl
methyltoluene-,2-diamine	Methylene chloride*	hydrazine
Dibutyl phosphate	Methyl ethyl ketone	Urea
Dichloroacetic acid	Methylphosphonic acid (MPA)	o-Xylene*
Dichloroanisole	Monoethanolamine*	Zinc acetate*

Figure 5 – Chemicals Successfully Treated by iSCWO

Complex Feeds

Activated carbon (spent)*	Explosives/energetics/propellants (hydrolyzed RDX, TNT, Tetryl, NG, NC)*	Paraffin oil
Adhesives*	Fermentation byproducts*	Pesticide manufacturing wastewater
Aqueous Cleaning Solution*	Fuel oil	Pharmaceutical waste*
AFFF	GB chemical agent (neat, hydrolyzed*)	Photographic developer paste
Antifreeze*	Gray water*	Photographic developer solutions*
Aroclor 1242	Greases (mixed)*	Polychlorotrifluoroethylene (PCTFE)*
Aroclor 1254	Human waste	Pig manure
Aroclor 1260*	Hydraulic fluid*	Propellants (hydrolyzed)*
Bacillus stearothermophilus (heat resistant spores)	Industrial biosludge	Protein
Brake fluid*	Ion exchange resins (styrene - divinyl benzene)	Pulp/paper mill sludge
Bran cereal	Kerosene*	Sewage sludge (black water)*
Caprolactam wastewater	Lube oil (molybdenum disulfide oil)*	Soil contaminated with organics
Casein	Malaria antigen	Soybean plants
Chlorinated plastics (shredded)*	Motor oil*	Sulfolobus acidocaldarius
Class 1.1 solid propellant*	Mustard chemical agent (neat, hydrolyzed*)	Transformer oil*
Class 1.3 AP-depleted solid propellant	Navy shore-based wastes*	Trimsol cutting oil*
Coal	Olive oil	VX chemical agent (neat, hydrolyzed*)
Coal waste	Organic salts (complex mixtures)'	Waste oils (chlorinated and non-chlorinated)*
Corn flakes*	Paint, paint sludges*	Wheat straw*
Corn oil	Paper	Wood fibers
Corn starch		Yeast
Diesel fuel		
E. coli		
Endotoxin (pyrogen)		

Inorganic Substances

Aluminum hydroxide*	Fluorides	Potassium chloride
Aluminum metal	Hydrochloric acid*	Potassium hydroxide
Aluminum oxide sodium	Hydrofluoric acid	Potassium sulfate
Ammonia*	Iron chloride	Silica
Ammonium chloride	Iron oxide*	Sodium bicarbonate*
Ammonium nitrate*	Lead chloride*	Sodium carbonate
Ammonium nitrite*	Lead sulfate*	Sodium chloride*
Ammonium perchlorate*	Lithium hydroxide	Sodium fluoride*
Ammonium sulfate	Lithium sulfate	Sodium hydroxide*
Ammonium sulfite*	Magnesium nitrate	Sodium nitrate
Boric acid	Magnesium oxide	Sodium nitrite
Bromides	Magnesium phosphate	Sodium phosphate*
Calcium carbonate	Magnesium sulfate	Sodium sulfate*
Calcium chloride	Mercuric chloride	Sodium sulfite·
Calcium oxide	Molybdenum disulfide lube oil*	Sulfur, elemental
Calcium phosphate	Nitric acid*	Sulfuric acid*
Calcium sulfate	Phosphoric acid	Titanium dioxide
Cerium chloride*	Potassium bicarbonate	Zinc chloride*
Copper chloride	Potassium carbonate	Zinc sulfate*

Figure 6 – Chemicals Successfully Treated by iSCWO

Figure 7 – iSCWO Waste Test System

Figure 8 – Final Acceptance Test

The iSCWO system has a limited number of components which makes maintenance and operation very easy. The control system uses off-the-shelf computer components such as programmable logic controllers (PLC), variable frequency drives (VFD), gas and liquid monitors, and workstation graphic displays for automated operation (calibrate, startup, operation, shutdown) complete with alarms and interlocks. The control system is highly intuitive and can be configured for English or Metric Units, and customized for specific languages.

The installed size of the iSCWO skid is 7.3 meters long by 4.5 meters high and 2.4 meters wide. For the transportable version, the iSCWO fits inside an ISO container that is 8.3 meters long by 2.9 meters high and 2.4 meters wide. Once the transportable unit is at the site, only a small number of equipment components need to be assembled before operation (e.g., heat exchanger).

To adequately treat powdered pesticides, flame retardants and other powdered or solid wastes, a front-end feed processing system is required. Preprocessing steps could include size reduction, slurrying, blending, filtering, and other waste preprocessing technologies to produce pumpable mixtures. Once in an acceptable form, the waste feed would be pumped into the iSCWO reactor as shown in Figure 1. The majority of iSCWO systems that GA supplies require some type of up-front pre-processing system (e.g., slurry feed systems) to create mixtures that can be delivered to the process in a reliable manner.

The first step in evaluating if iSCWO is applicable to specific waste processing operations is to determine from our customer the chemical compositions, concentrations, and form of the waste to be destroyed by iSCWO along with the customer desired destruction rate. Based on past customer requirements, generally multiple units are purchased to ensure optimum availability and redundancy to ensure that mission critical destruction operations are maintained. Computer models are run to predict the throughput rate, effluents to be discharged and the operational costs. This includes performing a mass and energy balance evaluation along with economic, safety and feasibility studies. Included in this first step is to identify from the customer if the iSCWO system will either be a transportable system or a fixed site system.

The next step would be to perform tests to demonstrate that the iSCWO system can process and destroy the waste, and to collect the test data to support design and permitting activities. Although this is not an R&D effort, these confirmatory tests are used to supply data to the customer's permitting group for site environmental permits. While SCWO destruction efficiencies typically exceed 99.999%, the actual requirement is driven by site specific needs especially if the liquid effluent is to be disposed of via the site sewer system or public treatment system. The collected test data will be used to characterize gas and liquid effluent compositions, determine operating conditions, and to quantify utility requirements (electrical power, water, fuel). Included in this analysis is the capital and operating costs of the iSCWO system for the specific waste(s) to be processed.

Once deemed acceptable, the final step would be the fabrication of the iSCWO system(s) based on the test results and specific customer requirements (e.g., safety and fabrication standards). Prior to shipment to the customer site, the system would be subjected to final acceptance tests to demonstrate operability and waste destruction efficiencies. Once at the customer's site, GA oversees installation, checkout and startup operations followed by training. Specific onsite plans can be selected by the customer during the iSCWO ordering process.

In summary, SCWO technology is an exceptionally clean waste destruction process suitable for destruction of all classes of hazardous and nonhazardous organic wastes. GA's iSCWO systems are perfect for onsite organic waste destruction, do not require any afterburner or complex secondary off-gas treatment system, are simple systems that are easily maintainable, are designed for little or no liquid post-treatment process, are easily permitted and are systems that can be fixed at one site or transportable all at an affordable cost. iSCWO provides a safe, cost effective and environmentally sound solution to replace alternative technologies that have high emission rates, post treatment issues and requirements, environmental and site permitting issues, and high installation and operation costs.