COMMERCIALIZATION OF COMMODORE'S SOLVATED ELECTRON TECHNOLOGY

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ABSTRACT

Commodore Advanced Sciences, Inc., Inc. has developed and commercialized an innovative non-thermal process for environmental remediation, which utilizes a patented (1) chemistry called Solvated Electron Technology (SET). During the past year, Commodore has successfully built and deployed their Commercial S-10 and SL/2 mobile units. This equipment is capable of treating drum quantities to 10 tons of hazardous material per day.

A nationwide EPA operating permit has been issued for the non-thermal destruction of PCBs in soils, oils, surfaces and solid materials using this process. The permit further allows for the recycle of treated PCB containing oils. The process is a total solution that incorporates pre- and post- treatments, where necessary, for environmental clean up. It is applicable to a broad range of substrates including liquids, solids, soils, personnel protective equipment and job materials. Contaminates destroyed include dioxins, PCBs, PAHs, halocarbons, explosives, chemical agents and pesticides. The treated waste meets TCLP and LDR for both TSCA and RCRA regulated organics. The paper describes the process, details the commercial equipment and discusses several commercial projects including PCB contaminated soils at a Harrisburg, Pennsylvania site, low level radioactive waste from a commercial facility and government agencies.

OVERVIEW OF SET

Commodore has commercialized its patented [1] solvated electron technology, better known as SET, which has become a proven system in the remediation of many of the world's most pressing and dangerous environmental problems. SET is a treatment process that destroys the hazardous components in waste, including mixed waste, leaving the resultant material free for reuse or disposal. SET is highly effective in the destruction or neutralization of hazardous materials that rank among the world's most persistent toxic pollutants. The process is totally effective in destroying polychlorinated biphenyls (PCBs), dioxins, polyaromatic hydrocarbons (PAHs), pesticides, fungicides, herbicides, chlorinated fluorocarbons (CFCs), explosives and chemical warfare agents, and has been successfully tested on many of the wastes listed in 40 CFR 261.

SET is based on a scientific phenomenon first observed by Sir Humphrey Davy early in the 19th century – alkali metals dissolved in ammonia create a solvated electron solution. As solvated (free) electrons are formed in the solution, they produce one of the strongest chemical reducing agents known. As such, they react with most organic molecules including hazardous materials. SET utilizes this chemistry in a simple, safe, non-thermal process that has proven effective on commercial projects in both hazardous and radioactive environments.

The beneficial features of SET are numerous. SET is not only effective but also safe. SET operates as a non-thermal destruction process under low pressure. The process is a closed system producing no hazardous off-gases and no regulated by-products such as dioxins or furans or their precursors. Benefits of SET include:

- **Organic contaminants are destroyed**, not just removed or concentrated – there can be no recombination.
- Operates as a **closed system** – produces no off-gases.
- **EPA TSCA permit** for PCB destruction.
- Operates at **ambient temperatures** (70°F).
- **Transports** and sets up quickly in less than 4000 sq. ft of space.
- **Can be scaled** to accommodate the size of the project.
- Requires **minimal** amounts of **power**, **water** and other outside **resources**.
- Handles **heterogeneous waste streams** in all phases.

Through an extensive research, development and commercialization effort, SET has been developed using the properties of solvated electron solutions. SET is unsurpassed in destroying hazardous and highly regulated halogenated toxic materials such as PCBs. Halogenated compounds are organic and contain chlorine, fluorine or iodine and comprise most waste regulated by environmental laws. Whether found in soils, oils, sludge, sediments, metals, concrete, liquids or other media, SET can safely turn halogenated contaminants into non-toxic substances. In application, contaminated materials are placed into a treatment cell and mixed with the solvated electron solution (sodium dissolved in anhydrous ammonia). In the case of PCBs or other halogenated contaminants, chemical reactions strip the halogen ions from the aromatic ring producing sodium chloride and high molecular weight hydrocarbons. At the end of the reaction, ammonia is removed and recycled. The reaction products (such as salt) produced in the process remain with the matrix.

The U.S. Environmental Protection Agency (EPA) has issued a nationwide TSCA (toxic substances control act) treatment permit for SET for mobile PCB chemical destruction in soils, metals, oils, organics and debris. Recognized by EPA as a non-thermal process equivalent to incineration, SET is believed to be the only multi-matrix PCB chemical destruction process approved for nationwide operation.

The destructive abilities of SET have been demonstrated to EPA, DOE (Department of Energy), DOD (Department of Defense) and private sector clients in commercial operations as well as numerous pilot and treatability projects. These projects have been performed in both radioactive and non-radioactive environments. In addition, SET has been tested on explosives and chemical warfare agents. Recent projects on radioactive materials have been performed at the DOE Weldon Spring Site Remedial Action Project, for a Fortune 500 company's wastes at a New Mexico site, and for a treatability study at the Envirocare site in Clive, Utah. Removal of the RCRA (Resource Conservation Recovery Act) and TSCA contaminants allowed all these wastes to be disposed as low-level radioactive wastes (met land ban requirements for burial). In a non-radioactive environment, SET was used to perform on-site PCB treatment to <1 ppm demonstrating destruction efficiencies of over 99% for the U.S. Navy Pacific Division and on a commercial project at a Pennsylvania Air National Guard site. The process has met stringent design and operational safety requirements, proven its versatility on heterogeneous waste streams and done so in a simple, safe, non-thermal treatment process. The SET process is commercial, currently performing commercial work, and it can be mobilized to a commercial site in a matter of months.

BACKGROUND OF THE CHEMISTRY

Solvated electron solutions are one of the more powerful reducing agents known. Solvated electron solutions, also referred to as dissolving metal solutions, are formed by dissolving alkali or alkaline-earth metals, including sodium, calcium, lithium, and potassium, in anhydrous liquid ammonia. Formation of the solvated electron is believed to occur as illustrated in the following equation:

$$\mathbf{Na^{o}} \xrightarrow{NH_3} \mathbf{Na^{+}} + \mathbf{e^{-}} \qquad \text{(Eq. 1)}$$

The solutions, which form rapidly when the metal enters the ammonia, are characterized by a deep blue coloration and an electrical conductivity approaching that of liquid metals. For convenience, the solvated electron systems are frequently regarded as solutions of the metallic cation and electrons, a concept supported by the results of a number of physical measurements (2)

Halogens can be split from organic halides by solvated electron solutions, yielding quantitative amounts of the halogen anion. By properly controlling reaction parameters, it is possible, in the case of the alkyl and aryl halides, to direct the reaction pathway so that the fully substituted parent hydrocarbon and the metal-halide are the sole reaction products. For the case of aromatic material, the parent hydrocarbon can react further to produce high molecular weight oligomers (3). The chemistry of reaction of aromatic halides with solvated electrons has been extensively described in a thesis (4).

In addition to halogens, many other organic molecules are reactive towards solvated electrons. Several review articles have appeared that addresses the broad application of the chemistry (5-7). Organic phosphorous and sulfur compounds such as pesticides and chemical warfare agents are known to be reactive to solvated electrons (8). It is also well understood that aromatic materials such as benzene and poly aromatic hydrocarbons are chemically reduced by the Birch reaction using solvated electrons (5).

PROCESS DESCRIPTION

The process consists of a solvated solution unit, treatment cell, and ammonia recovery system. The process is modular in nature. Several process variations have been developed depending on the nature of the material being remediated. Various modules are designed to be tailored to each particular remediation site in a manner such that the most cost-effective sequence is utilized. A flow diagram of a typical process cell is shown in Figure 1.

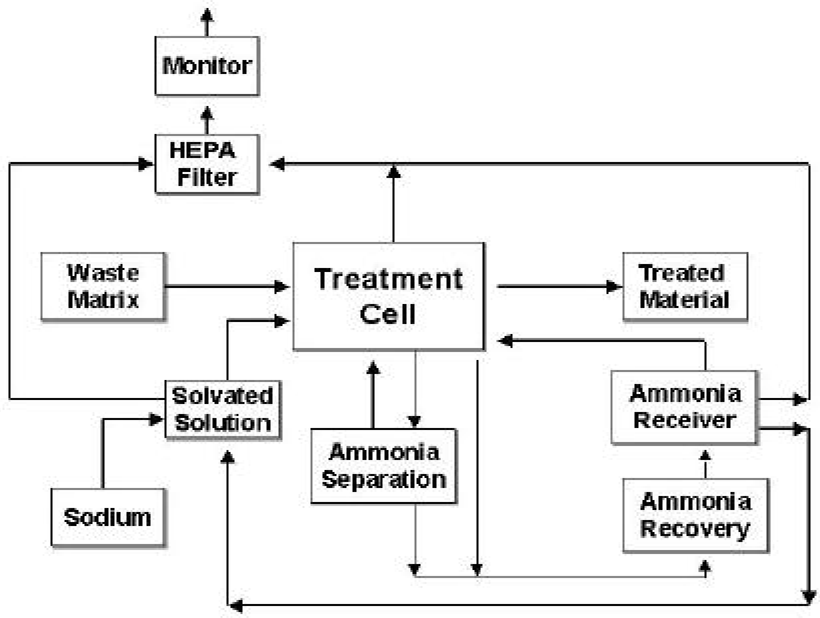

Fig. 1. SET Process

Unit Operations

- **Load Waste**

Waste may be pre-treated (discussed in a later section) by any of several processes such as shredding. Waste is then placed in the treatment cell.

- **Create Ammonia Slurry**

Once the waste is in the treatment cell, the cell is closed to the atmosphere and ammonia is pumped from the ammonia receiver into the treatment cell. Stirring of the waste ammonia slurry at approximately 70°C proceeds for at least 15 minutes. The purpose of this step is to extract the organic contaminant such as PCBs into the ammonia.

- **Prepare Solvated Electron Solution**

Ammonia is added to the solvated solution tank and the tank agitator is turned on Molten sodium (98 ^{o}C) is pumped into the tan from the sodium reservoir. The solvated solution tank is stirred for approximately 15 minutes to ensure complete dissolution of the sodium. At this point, sodium metal no longer exists. Rather, the solution is now a negatively charged solvated electron (free) and a positively charged sodium cation identical to the cation in sodium chloride.

- **Destroy Organic Contaminant**

The solvated electrons can now be pumped into the treatment cell. The chemical reaction between the solvated electron and the contaminant such as the PCB molecule takes place almost instantly. Once the solvated electron and the PCB molecule come in contact, the reaction is complete.

- **Recover Ammonia**

Hot water or steam is circulated through the jacket of the treatment cell. The ammonia is subsequently evaporated through the ammonia compressor and heat exchanger back to the ammonia receiver.

- **pH Adjust Waste**

At the end of the SET reaction, the matrix may have a high pH, which requires adjustment prior to disposal. A dilute acid solution is made in a separate tank using water and acid. Once all the ammonia is removed, the treatment cell is opened to the atmosphere through the HEPA Filter. The dilute acid is pumped from the tank to the treatment cell and the matrix is stirred for approximately 5 minutes.

- **Remove Waste From Treatment Cell**

The treated material is removed from the treatment cell by opening the bottom valve and dropping the treated material into a container such as a drum for final disposal.

- **Ship Waste for Final Disposal**

SET treated waste is suitable for shipment using 55-gallon drums or larger containers. The consistency of the waste can vary depending on the original waste. The consistency is discussed in more detail below under final waste form. It is no longer considered hazardous in regards to organic contaminant or pH. If the waste was mixed waste, it must be shipped according to DOT (Department of Transportation) regulations for radioactive materials.

ROBUSTNESS AND FLEXIBILITY OF SET TO DIVERSE WASTE STREAMS

SET has successfully remediated a wide variety of materials contaminated by toxic substances. Almost any matrix can be treated using the non-thermal SET process, including heterogeneous waste streams. The process is capable of destroying a wide range of hazardous organics in a mixture of matrices at the same time. For example, soil, rock, cement, PPE (personal protective equipment) and absorbents can be treated together at the same time. Numerous remediation projects using solvated electrons have been completed including in-house and on-site projects. Table I is a list of waste types treated to date:

Table I: Materials Treated by SET

- Soils - sand, clay, sediment
- Filter media
- Oils and solvents
- Glass
- Organics and organic debris
- Organic liquids
- Aqueous liquids
- Plastics
- Absorbents
- Metals, metal parts, tools, metal debris
- Sludges
- Wood and sawdust
- Carbon or graphite
- Rags
- Paper and cardboard
- Sandblast residue
- PPE
- Pipe
- Paint chips/sludge
- Electric cable
- Rubber
- Fiberglass
- Rubber
- Concrete and brick
- Rocks and gravel

COMMERCIAL SYSTEMS

Several commercial units have been developed including the S-10. The S-10 is capable of treating upwards of 10 tons of material a day. The S-10 has successfully treated over 250 tons of contaminated soil containing PCBs at a DOD facility in Pennsylvania. Soil was pretreated by sieving out stones and rocks and drying the soil. Following this pre-treatment, the soil was consistently treated to below 1 ppm of PCB. Figure II is a photograph of the S-10. Typically, 3 batches were run per day with each batch comprising approximately 5000 pounds of soil. The equipment shown in Figure 2 is configured for soils. However, the equipment can easily be configured to treat other materials such as liquids.

Fig. 2: S-10 Commercial System

In addition to the S-10, a mobile drum size commercial treatment unit (SL/2) has been deployed. The SL/2 has been commercially deployed to treat radioactive waste containing RCRA contaminants. Figure 3 is a photograph of the SL/2

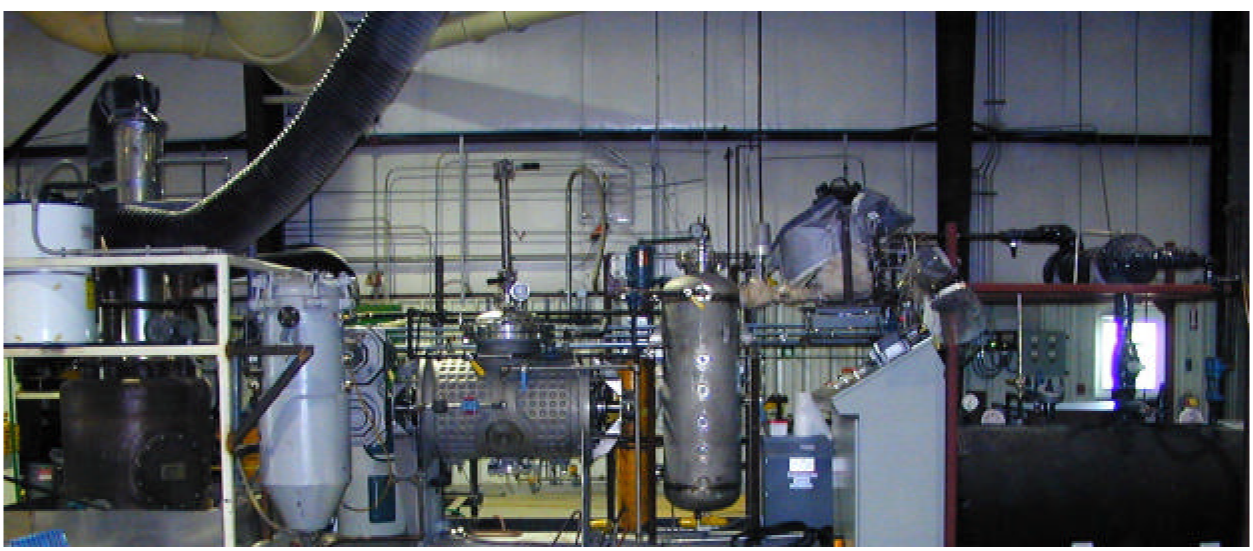
Fig. 3: SL/2 Drum Size Commercial System

Contaminated Solids

Table II includes field data for treatment of diverse waste streams. Metal surfaces are the easiest materials to remediate. Absorbing matrices such as soils and corncobs are more complex and require appropriate amounts of sodium for processing. Adjustments in the sodium to matrix ratio allow any of these matrices to be treated. The organic contaminant must be extracted into the liquid ammonia for destruction to take place. Fortunately, most halogenated and hazardous organics have a reasonable solubility in liquid ammonia.

Table II: Destruction of Organics in Various Solid Materials

Source of Material	Analyte	Material Type	Pre Treatment (mg/kg)	Post-Treatment (mg/kg)
Harrisburg, PA	PCB	Sand, clay	777	<1.0
Los Alamos, NM	PCB	Sand, silt, clay	77	<2.0
New York	PCB	Sand, silt	1250	<2.0
Monroe, LA	PCB	Sand, silt, clay	8.8	<1.0
Hawaii	PCB	Volcanic Soil	102	0.2
North Island Naval Shipyard	PCB	Activated Carbon	512	0.93
ConTech	PCB	Solid Resin	1212	0.5
New Bedford, MA	PCB	Sludge	32,800	1.3
New Bedford, MA	Dioxin	Sludge	.04	ND
Dahlgren, VA	DDD	Clay	15	<. 02
Weldon Spring, MO	TCE	Corn cob	6,400	<0.5
Weldon Spring, MO	PCB	Metal Capacitors	5.6	<0.2
Los Alamos	RDX	Soil	3850	<1.0
Eastern Utility	TCE	Soil	48,000	0.5

Liquids

The SET process has been also applied to many different liquid waste streams including: oils, aqueous sludges and neat liquid waste. Liquid wastes with contaminated concentrations varying from 100% to low ppm levels have been treated. Table III contains representative data for the treatment of various liquid waste streams.

Table III: Destruction of Halogenated Materials in Liquids

Material	Analyte	Pre-Treatment (mg/L)	Post-treatment (mg/L)
Used Motor oil	PCB	23,339	<1.0
Transformer oil	PCB	509,000	20*
Mineral Oil	PCB	5000	<0.5
Hexane	PCB	100,000	0.5
Aqueous sludge	Freon 113	276	ND
Aqueous sludge	TCE	262	ND
Oil	CCl	200,000	<0.5
Refrigerant	R 23	999,999	ND
Oil	Dioxin	0.4	.000002
Oil	Malathion	900,000	ND

Liquids are some of the more easily handled materials. Post treatment levels below 1 ppm are achieved. Typically, the solvated electron solution is formed first and the liquid is pumped into the solvated electron solution until the solvated electron solution is depleted. Thus, the appropriate kinetics can easily be controlled.

Mixed Wastes

One particularly vexing problem for waste management professionals is mixed wastes (radioactive plus RCRA and/or TSCA waste). Mixed waste streams and matrices contaminated with two or more types of contaminant represent a greater level of difficulty and expense to remediate. Illustrative of this problem are soils contaminated with PCBs and with radioactive metals such as thorium, or uranium.

Another example, frequently found at nuclear facilities, is soil contaminated with RCRA listed organic compounds and low-level radioactivity. Because the SET decontamination process employs solvated solutions in closed systems at or below room temperature, it has application to mixed waste streams that could not be treated appropriately with thermal processes. Commercial quantities of absorbent contaminated with organics including PCBs and radioactive material have been successfully treated at a DOE site in Weldon Spring, Missouri. Multiple waste streams, including grease, sludge, paint residues, and soils from three public utility sites have also been treated.

In the case of soils containing low-level radioactive components, in conjunction with halogenated organic compounds, the SET process can successfully destroy the halogenated organic component without oxidizing or volatilizing the metallic component. The radioactive species remains in the matrix for subsequent disposal.

Table IV: Destruction of Halocarbons in Various Radioactive Materials

Analyte	Site	Material	Pre-Treatment (mg/kg)	Destruction Efficiency (%)
PCB	Weldon Spring, MO	Shredded Corn Cobs	1270	99.8
PCB	Weldon Spring, MO	Un–shredded Corn cobs	944	97.4
PCB	Weldon Spring, MO	Transformer Capacitor parts	6	99.8
TCE	NE Utility	Soil	48,000	99.99
Chlorobenzene	NE Utility	Soil	360	99.99
Methylene chloride	Mid West Utility	Paint sludge	10,000	99.99
Freon 113	MD Nuclear	Grease	32,070	99.99
Freon 113	DOE Site	Aqueous (70 % H_2O)	652	<0.1

PRE- AND POST-TREATMENT

Several process variations for SET are available depending on the nature of the material being remediated. The various modules of SET™ are designed to be tailored to each particular remediation site in a manner such that the most cost-effective sequence is utilized. The SET treatment module is the centerpiece of the process and is a critical component of each process.

Pre-Treatment

Pre-treatment is sometimes necessary to allow the material to fit in the treatment cell. For example, large rocks may be separated from soils, soils may be dried of excess water, and PPE may be shredded. Post-treatment is only necessary to adjust the resulting pH of the material depending upon the amount of sodium used to treat the material to allow easy disposal of the material. The following paragraphs describe these processes by matrix.

- **Soils**

Pre-processing of soils usually involves sieving the soil matrix to remove rocks, large stones and debris. Soils may also require drying prior to treatment with solvated electrons. This is usually accomplished in the treatment cell by passing steam through the cell jacket.

- **Metal Debris**

Metal debris can be pre-treated with one of two processes. One is cutting into small pieces and the second is washing to flood the metal pieces with ammonia. The ammonia dissolves all of the organic contaminants including PCBs and can be transferred to the treatment cell after it is used to wash the metal parts. The metal is free of organic contaminant and can be reused or disposed.

- **Ceramic/Brick/Concrete Debris**

Porous solids such as concrete, brick, ceramic and rock can be treated as is by allowing for grinding by the mixer in the treatment cell during the slurry process or they can be size reduced prior to treatment if the pieces are to large to be placed in the treatment cell. This can be accomplished by crushing and sieving before the matrix is placed in the treatment cell.

- **Paper/Rags/Plastic/Rubber**

Paper, rags, plastics, and rubber can be treated after shredding. Shredding is usually required to prevent the materials from winding around the rotating parts of the treatment cell. Once the material is shredded, it can be placed in the treatment cell and treated with solvated electrons.

- **Organic Debris**

Most organic debris such as in-homogeneous oils, greases and non-aqueous liquids do not require pre-treatment. However, if the material contains non-organic debris, this debris may have to be removed by screening. The debris may interfere with the handling of the matrix if not removed. The debris can be subsequently treated by washing with ammonia prior to treating the ammonia.

- **Mixed Debris**

Low-level radioactive material does not interfere with the SET process and most mixed debris can be treated as is. Heterogeneous mixed debris may require screening out of the larger pieces of material. These pieces can be handled as discussed above.

- **Heterogeneous Debris**

A major benefit of the SET process is that it can treat a heterogeneous matrix. The matrix must be able to fit into the treatment cell as discussed above but the fact that it is heterogeneous by itself does not preclude treatment by the SET process. Examples of heterogeneous debris successfully treated include paint chips, greases, cutting fluids with metal filings and PPE.

- **Aqueous Waste**

Aqueous waste streams can be treated but they will require high levels of solvated electrons and will require large quantities of sulfuric acid for pH adjustment. It is usually helpful to remove the water by drying prior to treatment with solvated electrons.

Post Treatments

Most solvated electron treated waste requires post-treatment.

- **Ammonia Recovery**

The first post treatment involves removing and recovering ammonia from the matrix. This is accomplished by passing hot water or steam through the jacket of the treatment cell and condensing the ammonia for re-use.

- **pH Adjustment**

Materials treated with solvated electrons have a relatively high pH if they are not pH adjusted. Without a pH adjustment the treated waste would be a characteristic RCRA waste. This characteristic can be removed by adjusting the pH of the matrix with dilute acid. A description of this process is given above. The material can be disposed in a non- PCB waste landfill or waste disposal site handling radioactive material. In most cases, the radioactive species remains in the matrix for subsequent disposal.

VOLUME REDUCTION

Considerable volume reduction is accomplished through the action of the rotator paddles in the treatment cell. These paddles size reduce many materials such as PPE and absorbent materials. By creating a smaller particle size, the solid matrix being treated is more compact resulting a smaller volume. Figure 4 is of material prior to treatment and Figure 5 is treated material. These figures illustrate the size reduction process.

Fig. 4: Prior to Treatment

Fig. 5: Treated Material

Volume reduction of solids can also be accomplished in the SET process during pre-processing. Metal parts, plastics, PPE, and other solid materials can be shredded or cut prior to placement in the treatment cell. The net effect of this step is to reduce the volume considerably. The volume of these solid materials is further reduced by compaction after the treatment process as discussed above. While the volume of these materials is reduced, the weight of the treated material does increase by approximately 10-20 percent due to the sodium and acid added during the processing. The overall volume reduction that can be obtained with the SET process and pre-treatment techniques can exceed 60%

The volume of aqueous liquids and oils is not reduced, however, material handling is improved. These liquids are usually converted to a solid or semi-solid salt mixture. This occurs because water reacts with solvated electrons to produce solid sodium hydroxide, which is subsequently converted to solid sodium sulfate during pH adjustment. This is especially useful for disposal of radioactive wastes because most radioactive waste sites cannot accept liquid waste.

SECONDARY WASTE REDUCTION

The SET process produces very little secondary waste products. The waste generated is primarily the reaction product of solvated electrons with the organic contaminant such as PCBs. The reaction products remain with the matrix for subsequent disposal. The SET process utilizes solvated electron solutions to destroy hazardous contaminants. In the process, contaminants are destroyed by a chemical reduction mechanism, whereby the functional organic compounds are converted to petroleum hydrocarbons and metal salts. The reaction products will vary depending on the contaminant being destroyed.

In the case of a PCB molecule, the halogen atoms are stripped from the halogenated organic compound and converted to sodium chloride; the biphenyl functionality is also destroyed. The carbon skeleton is converted to non-conjugated hydrocarbons. After treatment, the soils will pass all TCLP tests for organics and TPH (Total Petroleum Hydrocarbon). The resultant soil can be returned to its original location.

Incineration of PCB wastes can produce dioxins as a secondary waste product. It is important to point out that the SET process does not produce any dioxins. In fact, the process is very effective at destroying dioxins. In many cases, dioxins accompany PCB contamination and the SET process destroys these dioxins along with the PCBs.

Solvated electrons that react with moisture in the waste produce sodium hydroxide and hydrogen. The amount of hydrogen that is produced in any one batch is a relatively small amount, well below hazardous quantities. The hydrogen is removed by purging the system through the scrubber/HEPA system. The acid in the scrubber scrubs any ammonia in the purge vapor and the hydrogen is diluted by the air in the scrubber and released to the atmosphere. There are no volatile organic compounds (VOCs) in this vapor purge.

Water is usually added to soil treated with solvated electrons, after the reaction is complete. The addition of water produces sodium hydroxide. If the soil is to be land filled or replaced, a pH adjustment is necessary. Sulfuric acid, phosphoric acid or ammonium sulfate are used to accomplish the pH adjustment. The net effect is that sodium hydroxide is converted to sodium sulfate or sodium phosphate.

The only other waste generated is pH-adjusted water from the scrubber system. The purpose of the scrubber is to prevent ammonia from being released to the environment when equipment valves are opened to vent non-condensable gases. When these valves are opened, the ammonia vapor is transferred to a scrubber containing pH-adjusted water. This scrubber water is generally disposed of, after treatment campaigns, by sending it to a permitted TSD facility.

HYPOTHETICAL EXAMPLE

A sandy soil containing 500 ppm of PCBs may require approximately 4% by weight sodium for complete destruction of the PCBs. After treatment and pH adjustment, this treated soil will contain 447 ppm sodium chloride, 61,700 ppm sodium sulfate, and additional TPH of 10-100 ppm. The soil will pass TCLP tests, contain no VOCs or Semi VOCs and be suitable for replacement or landfill. Once in place, the sodium sulfate will be reduced, over time, by sulfate reducing bacteria. PCBs treated with SET produce non-toxic hydrocarbons, sodium chloride, and sodium hydroxide or sodium sulfate.

FINAL WASTE FORM AND CHARACTERISTICS

The final waste form is dependent on the form of the waste treated. For solids such as soils, the waste has the same general characteristics as the waste prior to treatment. Figure 6 is a photograph of soil after treatment by the S-10.

Fig. 6

Treated liquids usually have a changed characteristic. Oils may become more viscous. Aqueous liquids will become solids or semi solids. Most organic liquids will become oily semisolids. The pH of the waste will be adjusted to below 12.5.

SHIPMENT OF WASTE

Waste treated by SET which has been pH adjusted is suitable for shipping in 55 gallon drums or fiberboard containers

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