INDIRECTLY-HEATED HIGH-TEMPERATURE HIGH-VACUUM ROTARY RETORT FOR THE DECONTAMINATION, VOLUME REDUCTION AND CONVERSION OF MIXED WASTE INTO LOW LEVEL WASTE

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The indirectly-heated, high-temperature, high-vacuum rotary retort system patented by SepraDyne Corporation has been commercialized and offers numerous advantages over the currently employed waste volume reduction and decontamination techniques. Numerous laboratory and pilot-scale treatability tests have been performed on a variety of solids, sludges and slurries and a commercial scale operation is ongoing at a large smelter to remove and recover mercury from air pollution control sludge. Full-scale evaluation of the system capabilities at one of the national laboratories on a wide range of radioactive and mixed wastes is planned for the near future. This unique process offers the potential to fulfill the primary goals of regulatory agencies, generators of wastes and environmentalists by economically separating "wastes" into several reusable product fractions without significant releases to the environment or generation of significant volumes of secondary wastes. The volatile portion of the "wastes", substances with boiling points below 8000 C, are converted to vapors within the inert high vacuum environment in the retort and continuously diffuse into the off-gas treatment system. There they are separated and recovered as liquids or solids. Resources could potentially be preserved and reused rather than burned or buried. Virtually all process off-gases can be condensed, thereby reducing to the lowest practical level any potential for air pollution. Depending upon the radioactive substances present, mixed wastes contaminated with polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organics, sulfur, water, arsenic and mercury and their compounds are converted to a smaller volume of solid radioactive waste and low level to free release liquids. All substances exerting significant vapor pressures at ambient temperatures are removed leaving only an inorganic granular to powder-sized material for follow-up stabilization processes. The low level or free release liquids, the vast majority of which is usually water, can often be disposed of inexpensively. The process is extremely versatile and has the capability of removing not only volatile and semi-volatile contaminants from any kind of solid, but also from any radioactive inventory material found at Department of Energy (DOE) and nuclear facilities as well as many highly flammable, explosive and thermally unstable materials. This paper will describe the SepraDyne process and its application to mixed waste.

INTRODUCTION

Mixed wastes, materials that are both radioactively contaminated and a RCRA waste, present a difficult disposal challenge. The long-term storage of these wastes requires the waste to be converted to a very stable form that minimizes potential future releases to the environment. Many stabilization processes have been developed that lock the constituents of concern within a solid matrix such as glass or plastics. However, the stability of these final waste forms is often affected by the concentration of substances that exert a significant vapor pressure at ambient temperatures. Therefore, the removal of as much of these substances as possible from the waste prior to stabilization is normally required. In addition, due to the high cost of treatment and disposal options for mixed waste, a low cost process is needed to reduce the volume of the waste

requiring final disposal and to convert the mixed waste into low level waste. With these goals in mind, research has been directed at various ways to remove volatiles from mixed wastes before stabilization and minimize final stabilized waste form volumes. Many of these processes are detailed in papers presented at this and previous Waste Management conferences. SepraDyne's approach to solving these problems is different and employs sustainable development concepts and the use of manufacturing techniques as opposed to strictly remediation technologies. Mixed waste is radioactive because it usually contains a small amount of radioactive substances and is hazardous waste because it contains a somewhat larger concentration of hazardous waste substances. Normally, the vast majority of the mixed waste is neither radioactive nor hazardous. If all of the substances of concern could be economically separated from each other and collected in their "pure" form or just separated from the bulk inert material, then the radioactive and/or hazardous waste left would be highly concentrated and the volume dramatically reduced. Pursuing this line of reasoning led SepraDyne to modify its mercury decontamination process to accomplish at least some of these desired separations.

THE SEPRADYNE APPROACH TO CONVERSION OF MIXED WASTE INTO LOW LEVEL RADIOACTIVE WASTE

SepraDyne's patented indirectly-heated, high-vacuum, high-temperature rotary retort used for removal and recovery of mercury and mercury compounds from various waste solids and sludges appeared to be capable of performing the primary separation of volatile from non-volatile substances. Because of the wide variety of existing liquid and gas separation technologies, modifications of the SepraDyne off-gas and liquid treatment systems to incorporate various configurations of these processes offered the potential of performing the remaining separations of the volatile components to produce one or more feedstocks. The ultimate goal was to retain the radioactive species, which normally had relatively high melting and boiling points, within the non-volatile solid fraction left in the retort after processing and collect and separate the volatile species as free release liquids.

At the very least, SepraDyne wanted to separate those substances with boiling points below 8000 C from those with boiling points substantially above 8000 C. This would reduce the volume of the radioactive portion of the waste and permit the relatively easy production of a very stable waste form of this solid fraction by methods such as vitrification, plastic encapsulation or grout. If the initial mixed waste only contained hazardous waste organics, PCBs, arsenic and mercury, the removal of these volatile species would permit the reclassification of the retort residue solids from mixed waste to low level radioactive waste. The degree of concentration of the radioactivity in the solid phase could be controlled to prohibit the waste from becoming high level radioactive waste. If the mixed waste also contained sufficient concentrations of non-volatile hazardous waste substances, such as chromium and lead, the waste might still remain classified as mixed waste. However, the solid process residue would be reduced in volume and properly conditioned for long-term stabilization. The substances that volatilized in the retort would diffuse out of the retort into the off-gas and liquid treatment system where they would initially be condensed to liquids or dissolved in various solutions. These liquids would undergo further separations through methods such as distillation and decantation to produce more desirable fractions for recycling or low volume disposal. Distillation processes coupled with ion exchange can be

tailored to remove radioactive species from the aqueous condensates so that the processed liquids can be classified as free release. Organic fractions that can not be reused can be oxidized to carbon dioxide and water and the water condensed and passed through an ion exchange column to remove the radioactivity prior to a free release discharge. The SepraDyne system is also capable of ramping up the retort temperature under a high vacuum so that the most volatile species are evaporated first at lower temperatures. This would permit the almost complete removal of some substances at low temperatures so that when the temperature was raised, these low-boiling-point compounds would not be present in the vapor phase when the higher-boilingpoint compounds were evaporated. Because most of the radioactive substances have relatively high melting and boiling points, these initial low-boiling-point condensates are the most likely to be free of radioactivity without the need for further treatment by methods such as distillation and/or ion exchange. For example, benzene could be removed from the mixed waste at 800 C under a system pressure of 50 torr. The retort temperature could then be increased to perhaps 2500 C. At this temperature, the vapor exiting the retort would not contain significant concentrations of benzene. The preliminary separations performed in this manner will simplify the additional separations performed in the off-gas and liquid treatment systems.

SEPRADYNE ROTARY VACUUM RETORT RESOURCE RECOVERY SYSTEM

The SepraDyne system is designed to efficiently remove and recover volatile metals and inorganic substances and all organic compounds from soils, slurries and solid wastes through the application of indirect heat and high vacuum in a rotating retort.

Substances with boiling points below 8000 C are quickly volatilized within the retort and transferred to the off-gas treatment system by rapid diffusion through a pressure gradient. The degree of thermal decomposition of specific compounds can be controlled to some degree through the varying of the temperature program and vacuum level. Most compounds will volatilize under a high vacuum at a temperature significantly below its boiling point and thermal decomposition temperatures. If the temperature is not increased too rapidly, these compounds can be converted to vapors and removed from the retort before decomposition. In the off-gas and liquid treatment systems, the various gases can be reacted with other chemicals to produce products or can be converted to liquids and separated for recovery and reuse using any of a number of commercially available separation technologies. The retort exhaust gas and liquid treatment train incorporates, as needed, filters, scrubbers, condensers, reaction chambers and activated and/or chemically impregnated absorbents.

The general operating parameters and processing sequence of the SepraDyne system are as follows. Solid or semi-solid waste is fed into the retort through a hopper/feeder assembly. For batch operations, once the unit is loaded, the vessel is sealed, a vacuum is established and the retort is set into rotation. An inert gas can be added to displace substantially all of the atmospheric oxygen and ensure an inert environment at the onset of the process. Heat is indirectly applied within an insulated firebox by an arrangement of burners fueled by diesel oil, natural gas or similar fuel. Alternatively, electric heating can be employed in highly sensitive environmental settings. The waste is initially heated to about 800 C to remove the moisture and low boiling point substances. Due to the high vacuum environment, the very low volume and velocity of produced vapors, the elimination of non-condensable gases and proprietary equipment

there is very little carryout of particulates from the retort. The small amount that is exhausted is readily captured in the scrubber solution. The steam and other low-boiling-point gaseous compounds are normally condensed in the off-gas treatment train or scrubbed into a suitable solution. The chemistry of the solution can be varied to selectively absorb specific compounds. For example, a two-phase immiscible solution can be used, one aqueous and one organic so that some degree of partitioning of the organic substances into the organic phase will occur. If very low boiling point organics are produced through thermal cracking, cryogenic cooling can be employed to condense these chemicals. Alternatively, gaseous reactants can be introduced to convert the retort off-gases into useful products or substances with more desirable separation and recovery properties. Water is separated from organic liquids. The water is processed with commercially available technologies to remove suspended, dissolved and radioactive substances. The cleansed water is then discharged. The organic liquids that can not be economically purified for reuse can be oxidized to produce non-radioactive gases, such as carbon dioxide, for free release and water, which can be processed with the aqueous fraction as just described.

Once the waste is dried, the waste temperature is ramped up to the target value, usually 4000 C to 7500 C, under a reduced pressure of 50 torr or less and held at the target temperature for 15 to 30 minutes. All additional chemicals that will volatilize under these conditions, which include semi-volatile organic compounds, heavy tars and all compounds of mercury vaporize and are condensed and captured in the off-gas treatment train. Any trace amounts of hazardous vapors that have passed through the low temperature off-gas system are removed in the absorber section. The condensed concentrated liquids, some of which may be valuable feedstock materials, are collected in separate containers for shipment to off-site recyclers, returned to the generator for incorporation into the process, recovered for heat value, purified or converted to substances that can be sold or economically disposed. The waste is maintained at the target temperature until system monitoring indicates that the contaminants of concern have been removed. After processing, the burners are turned off and the vacuum released. The processed material is then cooled and conveyed via a screw feeder into a receiving vessel fitted with particulate air control equipment.

UNIQUE AIR POLLUTION CONTROL CAPABILITIES OF THE SEPRADYNE SYSTEM

The use of thermal technology to vaporize hazardous and radioactive substances is always challenged by the public and regulators due to their concerns regarding chronic long-term adverse health and environmental effects from air pollution emissions and the potential of periodic catastrophic hazardous and radioactive releases. To combat these fears industry has developed more and more sophisticated and efficient air pollution control devices. In all cases, these devices are designed to remove substances of concern, whether solid, liquid and/or gaseous, from a gas stream that is to be ultimately exhausted to the atmosphere. SepraDyne's unique process permits a different approach that is capable of eliminating virtually all emissions of substances of concern to the atmosphere. The only gases of any appreciable volume released are the atmospheric gases removed from the retort prior to high temperature processing of the waste. One of the major reasons traditional air pollutant is because there are relatively large volumes of gases passing through the control devices and transporting the pollutants with them.

If this carrier gas stream, which is predominately composed of oxygen, nitrogen and/or carbon dioxide, were not present, then the corresponding driving forces to transport pollutants through the air pollution control system would also be eliminated. There would be no stripping action if the vapors in the retort off-gas stream could all be condensed and/or dissolved in a scrubbing solution. By incorporating cryogenic cooling at the back end pressure side of the off-gas and liquid-treatment systems just before any absorption columns, the small amount of vapor that does pass through the condensing/scrubbing system can readily be condensed and prevented from release to the atmosphere.

SepraDyne eliminates the atmospheric gases that cause the transport/stripping problems by employing a high vacuum and preventing the influx of air during processing. The elimination of air from the system during processing is critical. In the SepraDyne system, the vacuum pumps can be turned off during processing and the system will remain under a high vacuum. As a comparative illustration, laboratories frequently perform chemical refluxing of solutions in which one or more of the components of the solution are volatilized within a flask connected to a glass cooling water condenser. The vapor rises, condenses and drips back into the flask. No air pollution control devices are needed because the system never pressurizes and there is no influx of air passing through the system. The SepraDyne system is similar except that a high vacuum is employed to lower the temperature needed to volatilize species and to prevent any possibility of the system pressurizing. The SepraDyne system is so efficient that a commercial unit operating at a smelter to remove and recover mercury from acid plant blowdown sludge only required an air pollution control permit for the burning of the natural gas to heat the outside of the retort. The entire permitting process required 5 months, the only testing requirement was a one-time opacity test and there was no public opposition to the unit. In 6 months of operation the system has processed over 500 tons of sludge in its small 2-ton batch unit and reduced the mercury content of the sludge from approximately 2500 mg/kg to an average of less than 8 mg/kg. SepraDyne believes that it can use its process to treat virtually any kind of solid mixed waste that contains substances with boiling points below 8000 C and reduce the release of substances of concern to the atmosphere to levels far below those currently achievable with competing technologies.

ADVANTAGES OF THE SEPRADYNE PROCESS

The disadvantages of most commercial thermal treatment systems are largely overcome by the use of a high vacuum and an inert gas to economically produce a completely inert environment within an indirectly-heated rotary retort and to recover the produced vapors through condensation and/or scrubbing (See Figure 1). The technology was specifically designed to decontaminate non-volatile materials by volatilizing the constituents of concern with as little thermal decomposition or chemical reaction as possible and separating and recovering the volatile substances for further refining and reuse. The off-gas treatment system is simplified because only condensable gases and a minimal amount of solids exit the retort during processing. The process does not require the use of cyclones, bag houses or electrostatic precipitators. By eliminating non-condensable gases from the retort and prohibiting the influx of air, the volume of gas to treat is minimized, and there is no stripping action to transport condensable gases through the condensing system. The resulting contaminant capture efficiency is extremely high compared to traditional air pollution control technology. Among the benefits of this system are:

The high vacuum rotary system is a non-incineration thermal processing unit due in part to its ability to reduce oxygen to very low concentrations during processing. A small amount of thermal oxidation may potentially occur if oxygen is liberated from the thermal decomposition of oxygen containing compounds. The system is capable of nearly complete elimination of retort off-gas emission releases to the atmosphere during processing at elevated temperatures due to its removal of non-condensable atmospheric gases at low temperature and its ability to condense and recover nearly all retort off-gases generated at elevated temperatures. Cryogenic cooling can be employed to condense the small amount of low-boiling compounds that might be produced by thermal cracking.

A rotary system quickly and uniformly distributes the heat to the waste and constantly tumbles the waste while heating so that volatilized chemicals can readily separate from the waste and exit the retort rather than readsorb onto other waste particles as occurs with passive systems. Systems using mixing paddles or screws inside a stationary vessel normally use lower temperatures to minimize structural damage to their vessels due to uneven heating and volatilizing contaminants can readily readsorb onto the solid substrate, elongating processing. Products of incomplete combustion (PIC) formation should be dramatically reduced within the system because of the absence of significant amounts of oxygen in the high vacuum environment; however, some amount of thermal cracking could produce low-boiling-point compounds. The degree of thermal cracking can be increased or decreased to some degree to produce desired products by varying the temperature program and vacuum level. If necessary, the complete elimination of atmospheric oxygen is accomplished by the patented design of the unit and the introduction of a small volume of inert gas to displace any remaining oxygen. Some oxygen could be liberated during the small amount of thermal cracking of oxygen-containing compounds that could occur and some of this oxygen might be available for some degree of thermal oxidation reactions prior to exiting the retort.

This system can use high temperatures, up to 8500 C, combined with a high vacuum, down to a pressure below 50 torr, in a batch or continuous rotating retort to increase the volatilization rate, decrease processing time, increase throughput rate and decrease the concentration of residual contaminants.

The combination of a high vacuum and an indirectly-heated rotary retort significantly reduces operating and capital expenditure costs by:

- a. Increasing the throughput rate as previously described
- b. Decreasing the size and complexity of the off-gas system, because only those vapors generated from within the retort need to be treated and particulate carryout from the retort is reduced to a minimum

Simplifying the permitting process because the technology is classified as a recycling or resource recovery process, not incineration, and toxic air emissions are reduced to the lowest practical level.

The heat transfer efficiencies of a high vacuum rotary system can approach and even exceed

those of direct-fired incinerators. This is because the heat of the combustion gases, normally lost in the off-gas treatment system, can be recovered to dry the incoming waste and preheat the air used for combustion of the fuel.

This process is designed to be a chemical separation process instead of a chemical conversion process such as in incineration processes, and as such, is a true resource recovery operation. Most chemicals present in the waste with low enough boiling points are not changed, but merely volatilized so that they will separate from the non-volatile waste and be condensed into a low temperature concentrate for further treatment or reuse. If a condensate stream can not be economically purified and reused, at least it has been dramatically reduced in volume for alternative disposal.

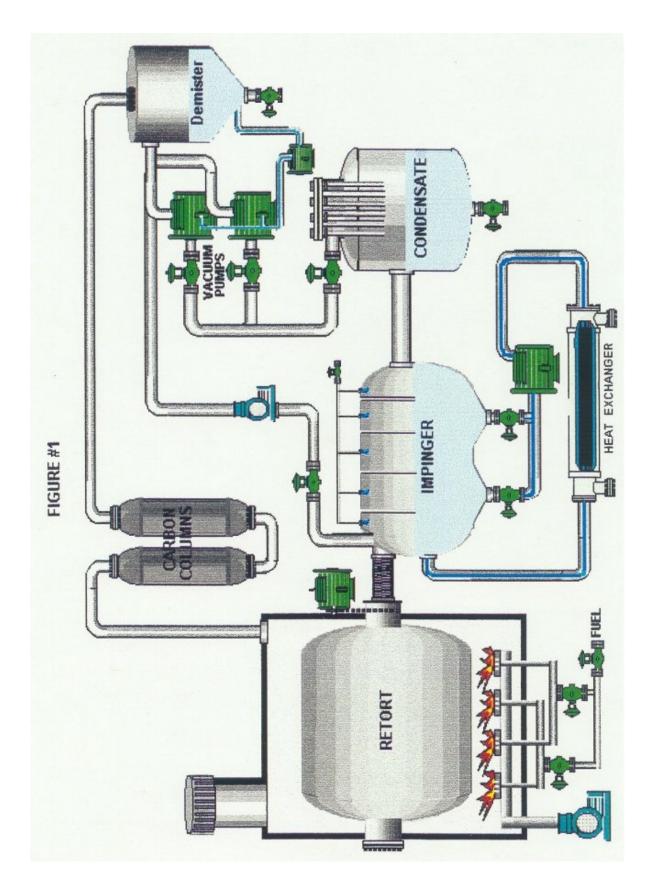
The high vacuum employed prohibits the release of untreated retort gases to the atmosphere. Any breech in the system simply results in a decrease in system vacuum, not a pressurization of the system that could occur with systems operating under a slight negative pressure.

Because the system operates under a high vacuum in an inert environment, explosive and highly flammable materials can potentially be safely volatilized and separated at lower temperatures.

The high vacuum rotary system can be heated electrically to eliminate the on-site production of combustion gases. The use of a high vacuum permits the rapid volatilization of substances at lower temperatures, thereby improving fuel efficiency.

CONCLUSIONS

The patented SepraDyne system offers the potential to convert a wide range of solid mixed wastes containing organics, PCBs, water, sulfur, arsenic and mercury and their compounds into a smaller volume of low level radioactive solid waste suitable for long term stabilization by vitrification, plastic encapsulation or grout. That portion of the mixed waste that will volatilize below 8000 C at a reduced pressure of approximately 50 torr can be condensed and/or dissolved in scrubbing solutions and separated into various fractions. Some of these fractions may be recycled and the water free released to the sewer, recycled or evaporated. Air pollution permitting, if needed at all, is greatly simplified because emissions of substances of concern are reduced to their lowest practical concentration by a combination of the elimination of non-condensable gases and the condensation and/or scrubbing of retort vapors.



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