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SYSTEMATIC SELECTION OF OFF-GAS TREATMENT AT THE SAVANNAH RIVER SITE (U)

by

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SYSTEMATIC SELECTION OF OFF-GAS TREATMENT AT THE SAVANNAH RIVER SITE

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ABSTRACT

The Savannah River Site (SRS), which has been in operation since the 1950s, is a 3~~1~~00-square mile reservation that produces nuclear materials for the national defense program. The Site is owned by the U.S. Department of Energy and operated by the Westinghouse Savannah River Company. From 1958 to 1985, effluent waste from the reactor fuel and target rod fabrication area (M-Area) was discharged to a settling basin. In 1981, monitoring wells detected groundwater contamination, specifically trichloroethylene and tetrachloroethylene, in the immediate vicinity of the basin.

Remediation of the M-Area contamination plume is driven by the Resource Conservation and Recovery Act (RCRA), administered by South Carolina Department of Health and Environmental Control (SCDHEC). Under the auspices of RCRA, the M-Area contamination must be addressed by a corrective action program until the volatile organic compound (VOC) concentrations reach Drinking Water Standards. This was initiated in 1985 with startup of a full-scale pump-and-treat air stripper system. Recently, remediation efforts have focused on vacuum extraction to treat vadose zone contamination not addressed by the original recovery wells, and additional pump-and-treat systems to achieve hydraulic control of the plume. Regulatory requirements allowed for discharge of VOCs to the atmosphere when the original remediation system was installed; however, 1990 amendments to the Clean Air Act will eventually require treatment of VOC contaminated air prior to discharge. This has ramifications to systems currently being designed, as well as the existing systems. To avoid future project work and additional regulatory approval, it is prudent for SRS to design off-gas treatment systems for use in both new and existing remediation systems. Consequently, SRS is faced with assessing available technologies to determine the optimum system for treating air emissions.

In response to the 1990 Clean Air Act amendments, SRS initiated a study to assess commercially available off-gas treatment technologies. These included carbon adsorption, thermal incineration, catalytic oxidation, absorption, condensation, and UV/peroxide destruction, and xenon flashlamp. Criteria used to evaluate the technologies were the thirty (30) year life cycle cost, permitting considerations, and manpower requirements. The study concluded that catalytic oxidation provided the most desirable combination of these elements.

INTRODUCTION

The Savannah River Site (SRS) is a Department of Energy (DOE) facility that produces nuclear materials for the national defense program. The SRS, which has been in operation since 1953, was placed on the National Priority List on December 21, 1989. Over 400 distinct locations within the Site boundary have been identified for investigation under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund. However, the Resource Conservation and Recovery Act (RCRA) has historically been the main driver for the corrective action program in the Administrative and Reactor Materials areas (A/M areas) of the Site. The corrective action program stems from the closure of a settling basin that received effluent waste from the reactor fuel and target rod fabrication processes. Organic contamination, primarily trichloroethylene (TCE) with smaller amounts of tetrachloroethylene (PCE), was found in the ground water surrounding the basin in 1981. In 1985, release to the basin was discontinued when the M-Area Liquid Effluent Treatment Facility was brought online. At the same time, full-scale cleanup of the contaminated groundwater began with the application of pump-and-treat using air stripping.

Schedules and activities described in the RCRA Post Closure Care Part B permit are the current drivers for the corrective action program. Projects to add three air strippers and four soil-vapor extraction units are currently in the design phase. 1990 Amendments to the Clean Air Act were signed into law at approximately the same time pre-project activities were started for the new systems. As a result, engineering studies now include assessing the need for off-gas treatment systems, as well as identifying the most appropriate treatment technology. The purpose of this paper is to describe results of the study performed to address these issues.

BACKGROUND

Air stripping and soil vapor extraction, as stand alone treatment processes, transfer VOCs to the atmosphere where they are dispersed, diluted, and subsequently degraded by reaction with hydroxl radicals. The treatment systems in the A/M areas of SRS are not considered major emission sources under South Carolina Department of Health and Environmental Control (SCDHEC) regulations, and therefore do not require emission control. The Air Quality Control Bureau of SCDHEC currently regulates emissions from the systems on a tonnage/year basis.

The 1990 Clean Air Act amendments identify TCE and PCE as two of 189 hazardous air pollutants that will require emission control in the near future. The Environmental Protection Agency (EPA) must establish categories of sources that emit hazardous air pollutants, and then promulgate regulations to control emissions by source category. This approach marks a shift from the risk-based approach of the National Emission Standards for Hazardous Air Pollutants (NESHAPs) program, Section 112 of the Clean Air Act, to a technology-based approach. As Hazardous Air Pollutants (HAPs), the TCE and PCE will be subject to what is called a Maximum Achievable Control Technology (MACT), defined as the average emission limit achieved by the best-controlled 12 percent of existing sources. MACT standards are to be instituted on major existing, new, and area sources that emit HAPs. Major emission sources are defined as any source emitting 10 tons/yr of a single HAP or 25 tons/yr of any combination of HAPs.

Air stripping was first demonstrated in M-Area in 1982. A pilot-scale unit verified the removal efficiency of the technology at greater than 99.99%, and as a result the technology was further pursued. A prototype unit was placed in operation in 1984 to acquire data needed for the design of a full-scale system. The original project activities were culminated in 1985 when a full-scale system was brought on-line. A separate plume of organic contamination was identified near the Site Admininistrative area (A- Area) and the Savannah River Laboratory in 1987. To address the plume in a timely manner and make efficient use of existing resources, the prototype unit used in the M-Area experimental program was relocated to A-Area and brought on line in March 1992.

DESCRIPTION OF TECHNOLOGIES

Thermal Incineration

Thermal incineration is a very simple, clean method for destroying VOCs. The contaminated gas stream is contacted with a fuel such as methane or propane and is combusted. The high temperature of combustion (typically about 1200 - 1500 ° F) is sufficient to convert the VOCs to carbon dioxide and water; conversion efficiencies must be at least 99.99% per SCDHEC regulations. Chlorinated VOCs such as TCE and PCE will also form HCl in the exhaust stream, and the process equipment must be protected from acidic corrosion. If the levels of HCl are high enough to exceed SCDHEC emission limits, currently four pounds per hour, a caustic scrubber must be added to neutralize the HCl. An alternative method would be to operate the unit at a lower flow rate to make sure that the permitted HCl emission rate is not exceeded. Based on the long remediation times at most locations, a limited treatment rate was not considered an appropriate alternative for this study.

Thermal incineration systems have a relatively low capital cost compared to other available treatment methods. However, the operating costs in thermal systems are high due to the amount of fuel which must be used to heat the air to the combustion temperature. The addition of a scrubber also adds considerable

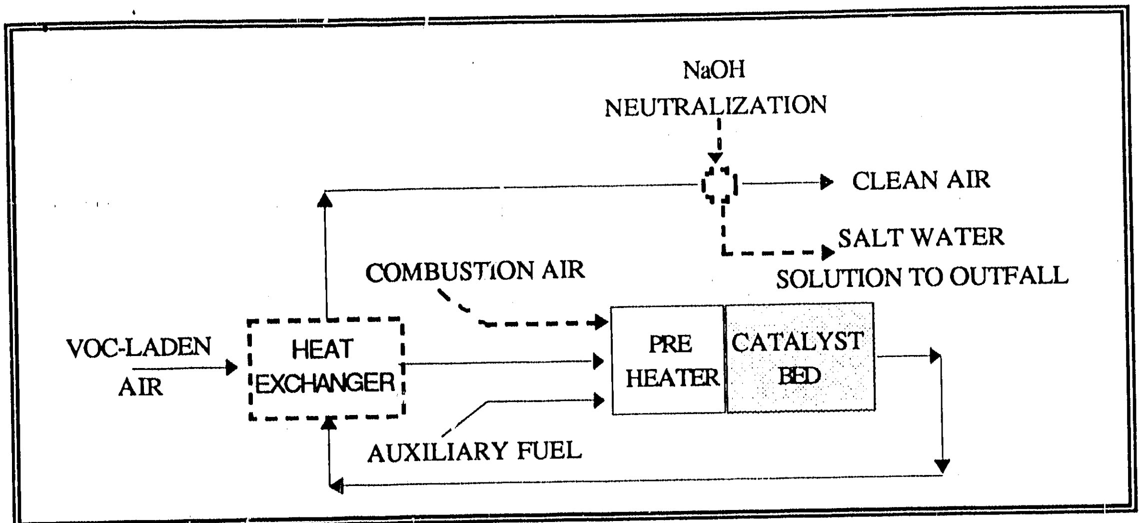

Figure 1. Catalytic Oxidation Process Diagram

cost and should be avoided if permit limits allow other alternatives. Maintenance costs are relatively low, and a thermal incineration system should be one of the least demanding systems to operate and maintain.

A heat exchanger is a highly recommended alternative to reduce lifetime operating costs. The cost of the heat exchanger can usually be recovered in one to two years. Typical conventional heat exchangers can obtain 40 to 70 percent heat recovery. This energy savings will greatly lower the life cycle cost of a thermal incineration system. Regenerative thermal incineration systems use a heat exchanger system that is claimed to recover up to 95% of the combustion energy. Some manufacturers offer a system that contains several beds of ceramic material that act as heat sinks. The process is operated by alternating treatment between the beds. When the beds are switched, the VOC stream is preheated by passing it through the recently heated bed before it is combusted. This method of recovering heat could result in the lowest cost system depending on the VOC concentration and the amount of air to be treated.

Catalytic Oxidation

Catalytic oxidation is a method that lowers the high energy costs of thermal incineration by lowering the reaction temperature. A schematic diagram of the process is shown in Figure 1. Normally, a gas fueled preheater provides heat and combustion air to the system. The hot gases are then mixed with the VOC laden air stream to the required temperature, and the heated stream is fed to the catalyst bed where the oxidation reactions occur. Certain noble metals (platinum, palladium, etc.), typically supported by a ceramic matrix, act as catalysts to enhance the reaction rate and lower the reaction temperature (600 - 800 °F). These two factors reduce the energy requirements for catalytic oxidation considerably below thermal incineration. The overall operating costs, however, are not reduced by the full amount of this energy savings. The catalyst bed must be replaced, on average, every three years. One potential problem with the technology is the fact that many noble metals are poisoned or masked by chlorides, sulfur, lead, silicones, or phosphorous containing compounds. The presence of these substances could greatly shorten the life of the catalyst used. A limited number of manufacturers now make catalysts which are resistant to chloride poisioning problems. A heat exchanger is also recommended for use with a catalytic oxidation system. While the cost savings are not as dramatic as those for a thermal system, the cost of a heat exchanger can still be recovered in approximately two years.

Carbon Adsorption

Carbon adsorption typically uses a granular activated carbon (GAC) bed to adsorb the VOC onto the carbon. A schematic of the process is shown in Figure 2. This method of VOC removal has been used for years in a number of

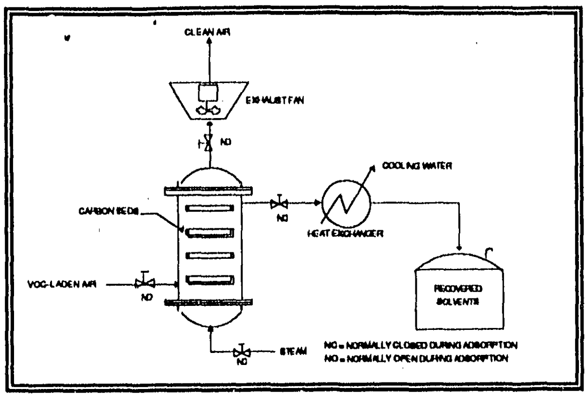

Figure 2. Carbon adsorption process

industries and is probably the best known method for removing VOCs from either a liquid or gas stream. Carbon adsorption does not destroy the VOCs but rather concentrates them for disposal or reuse. The organic pollutants are either adsorbed on the carbon particle's surface or are trapped in the extremely tiny pores. When the GAC bed becomes saturated with VOCs, the bed must be disposed of or regenerated. Regeneration is performed by raising the temperature of the GAC bed by introducing heated air or low pressure steam. The VOCs will release from the carbon and enter the air stream. The concentrated VOCs are then removed from the air stream through the use of a condenser and liquid separator. The VOCs are typically reused, thus saving the cost of purchasing new solvents for routine operations. For this study, several methods were considered for regenerating the bed. These included in-situ steam regeneration, in-situ hot gas regeneration, on-site combustion, off-site regeneration, and off-site combustion.

Absorption

This method is used primarily to recover large amounts of expensive VOCs from highly saturated gas streams for reuse of the VOC. The VOC is dissolved in a suitable liquid in a packed tower (absorber). This liquid is then passed through another packed tower (stripper) where the temperature and pressure have been adjusted to cause the VOC to become much less soluble in the liquid. The vapors are then condensed and taken out of the process. Efficiencies of 90-99% are typical of this technology. This system is not well suited to low VOC concentrations and was considered too expensive for this application.

Condensation

Condensation involves cooling the entire gas stream to below the VOCs dew point so that the VOC condenses as a liquid. This technology is typically used when the VOC is very expensive and in high concentrations (at least 10,000 ppm) in the air. Removal efficiencies can exceed 99%, but this method was not considered suitable for this application since the low concentration of the VOCs would make the operation prohibitively expensive.

UV/Peroxidation

Peroxidation is a relatively new technology that processes the groundwater directly rather than the VOC-laden air stream. Ultraviolet (UV) light is used in conjunction with hydrogen peroxide to catalyze the chemical oxidation of the organic contaminants. Many organic compounds absorb UV light and may undergo changes in their chemical structure or simply become more reactive to chemical oxidants. Hydrogen peroxide reacts in the presence of UV light to form hydroxyl radicals. These very powerful chemical oxidants then react with the organic contaminants to produce water and carbon dioxide. Chlorides present in the VOCs would again form HCl and lower the pH of the discharge water. Specific permit limits would determine if neutralization would be required before disposal of the wastewater stream. Additional maintenance required for this system would include servicing of the hydrogen peroxide source and replacing the UV bulbs.

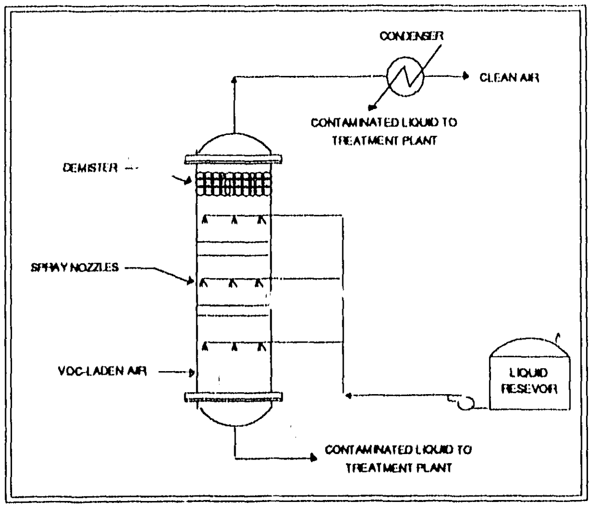

Figure 3. Absorption Process Diagram

Xenon Flashlamp

This is also a relatively new and unproven technology. The system uses a pulsed Xenon lamp to oxidize the organic contaminants in the liquid stream without the addition of hydrogen peroxide. HCl would still be formed in the waste water stream if the contaminant is chlorinated. Again, specific permit limits would determine the need for neutralization, although it is expected that the pH would not be low enough to require this additional step. A field demonstration of the technology is being conducted during the first quarter of 1992 at Lawrence Livermore National Laboratories. The demonstration will compare the xenon flashlamp technology with thermal incineration, catalytic oxidation, and granular activated carbon systems.

COST ANALYSIS

A cost analysis and advantage/disadvantage comparision listing of all the technologies is given in Table 1. The present value cost calculations used in this report are not meant

Technology	Advantages	Disadvantages	Capital Cost ($K)	Operating Cost ($K)	Total Cost ($K)
Thermal Incineration w/o Heat Exchanger	Low capital cost Low maint cost Low manpower Destroys VOC	Very high energy cost HCl producee Requires fuel source	76	343	419
w/ HE	Uses less fuel	Higher capital cost			
Catalytic Oxidation					
Electric, w/o HE	Low manpower Destroys VOC	High energy cost HCl produced Must replace catalyst	112	1,164	1,276
Electric, w/ HE	Uses less energy	Electricity expensive	137	500	637
Propane w/HE	Propane cheaper than electricity		88.5	186	274.5
GAC	Low capital cost Proven tech.	High oper cost High maint cost Manpower intensive High cost to ship or dispose of solvent	160	92	252
UV/Peroxidation					
Purchase	Mod cap cost Destroys VOC	Relatively unproven High oper cost Requires raw mat'l HCl produced	97.5	676	773.5
Lease			5	1.175	1.180
UV/Xenon	Mod cap cost No add'l mat'ls Destroys VOC Low manpower	Relatively unproven HCl produced	80	311	391
Absorption	Saleable product Simple to operate	High op cost Requires add'l solvent	-	-	-
Condensation	Saleable product Simple to operate	High op cost High maint cost	-	-	-

Table 1. Technology Comparison

to represent the total costs involved in design, construction, or operation of a given system. These values are to be used only to compare relative costs for the equipment required for each system. Costs such as providing utilities to a site, monitoring the air emissions, and preparing the site are not included in this comparison as they are considered equivalent for each option. The manhours required for each system are assumed to be the same, namely one operator per day. In should be noted that in practice each system will require differing amounts of effort for operation. The actual hours required are difficult to estimate without actual operating experience. General statements as to the probable labor required are made in the Advantages and Disadvantages section of Table 1.

The present value calculations assume a 30 year operating life, a 5% annual inflation rate, and a 10% cost of capital. Factors used for the calculations were derived from Reference 1. The factors were the average of the values obtained at the start and end of a particular year. Nominal equipment size was 600 scfm, and VOC concentration was 20,000 µg/L. The incoming temperature of the contaminated air was assumed to be 60 °F, and the operating temperatures of the catalytic and thermal systems were 700 and 1500 °F, respectively. Electricity costs were averaged at $ 0.06/kW and propane costs at $ 0.60/gallon. Peroxide usage was set at $12,000 for the first year, allowing for inflation each year thereafter. The purchase of the equipment was assumed to be 100% at time zero. The energy costs began immediately at this point. While it is likely that payment terms will vary and the equipment will not operate as soon as it arrives, these assumptions were made to simplify the basis of comparison between the various alternate methods.

DISCUSSION OF TECHNOLOGIES

Thermal Incineration

The energy input necessary to achieve the operating temperature of 1500 °F made the present value of thermal incineration much higher than catalytic oxidation. Although capital costs and manpower requirements are low for the system, the energy costs during the 30 year lifetime outweighed any upfront savings. Thermal incineration is also at a disadvantage due to the stringent destruction efficiencies and monitoring requirements imposed by SCDHEC regulations. Time costs were considered to be high for this technology due to the complexity of the permitting process.

Catalytic Oxidation

Catalytic oxidation technology provides a low capital cost system with a very low operating cost. Since the remediation operation is expected to continue for 30 years, the low operating cost becomes extremely important. The present value cost for a system using propane as the fuel and a heat exchanger for energy recovery was second only to the GAC costs. There should be a relatively low amount of maintenance required for this system as compared to some of the other methods. Catalyst beds would need to be changed out every 3 years, on the average. While catalyst poisoning or masking is a concern, many catalyst manufacturers are making chloride resistant catalysts. The catalytic oxidation unit also has an advantage over the GAC process due to the fact that the VOCs are destroyed and cannot become a future liability.

The catalytic oxidation system operating on electricity and using a heat exchanger for energy recovery had the next lowest present value cost. The use of electricity lowers the capital cost as no propane tanks are needed. However, the higher energy cost of electricity versus propane makes an electrical system feasible only in areas where propane cannot be used for safety reasons, or for short term projects where the energy cost of electricity does not add significant lifetime cost.

One useful alternative in choosing a catalytic oxidation unit comes from the fact that most systems are designed to allow removal of the catalyst module. This versatility could serve as a backup to convert the system to an incinerator. If, for any reason, the catalyst did not perform as expected, the system could be converted to a thermal incineration system by removing the catalyst module and operating the unit at the higher incineration temperatures.

Carbon Adsorption

The Granular Activated Carbon technology with in situ steam regeneration had the lowest present value cost of all options considered. GAC would be a feasible technology for this application since it has been shown to be capable of removing 99% of the VOC provided the bed is sized properly. As the bed ages, the removal efficiency will drop and bed replacement would be necessary. The GAC system has some hidden costs not identified in the cost comparison which would make it more expensive than catalytic oxidation. These systems require a steam regeneration step at least once per day. This requires that the system include a boiler, which would add a considerable amount of maintenance and manpower costs to the system.

One advantage of the GAC system is that it does not produce HCl in the exhaust stream. However, since it does not destroy the VOCs, a re-use must be identifed or disposal of the reclaimed solvent would be necessary. Collection, drumming, and loading adds significant manhours to this method. Although there are vendors willing to buy the reclaimed solvent, the additional manhours are estimated to cost more than the income provided. A major problem with this method is that the company generating the solvent could still be held liable for spills, accidents, or any illegal acts performed by unscrupulous recyclers. These extra risks, as well as additional manhour requirements, make this technology less desirable than catalytic incineration.

Other methods of regenerating the carbon bed, such as regenerating off-site or combustion off-site, were the most expensive methods of all and were not given further consideration.

Absorption

Absorption has typical removal efficiencies in the 90-99% range. Due to the high cost of desorption, this technology is limited to uses where the liquid absorbent can be used directly without removing the absorbed VOC. This virtually eliminates the use of this technology for groundwater remediation.

Condensation

Condensation is usually not used unless the VOC exceeds about 25% of the lower explosive limit (LEL). Due to economics, the application of this process is also limited to rather expensive solvents. These constraints restrict the use of this technology to a very limited number of applications. Efficiencies of 99% are achievable.

UV/Peroxide

The UV/Hydrogen Peroxide system had the second lowest present value cost, but was still nearly three times the cost for the catalytic oxidation system. The technology was not entirely suitable for this application since air strippers were already in place and the stream to be treated was a gas. The unproven nature of the technology also was considered a disadvantage that removed it from consideration. Some manufacturers offer a full service contract option in which there is no capital cost involved. This option, however, adds substantially to the present value cost and was considered prohibitive due to the difficult logistics involved with bringing a vendor on-site for work.

The strong point of this technology is the elimination of two systems to treat the contamination. Cost estimates may show that when vapor emission control is required from a system such as an air stripper, the single UV/peroxide system is more economical. Further investigation is needed to ensure that this system can give efficient and reliable destruction of VOCs at a low cost.

Xenon Flashlamp

The Ultraviolet Light process using Xenon Flash Lamps may show promise for the future. Its present value cost was the third lowest, and manpower and permitting requirements are perceived to be low. There are no current installations that demonstrate the operating characterisitcs of this system. Reports comparing this technology with GAC and catalytic incineration are to be written before the end of the year, and the technology may be tested at the SRS as part of the DOE Office of Technology Development Integrated Demonstration. This process could not be recommended with any confidence at this time, but will be strongly considered for future applications.

CONCLUSIONS

The treatment system recommended as a result of this study is catalytic oxidation. The system should include a heat exchanger to recover energy and propane as the fuel source. The addition of a heat exchanger is recommended since the savings in fuel consumption will pay for the heat exchanger in less than two years. Natural gas would be less expensive, but would require the installation of gas lines to these locations, versus a relatively simple tank installation for a propane system. Electricity is considerably more expensive than propane and should only be selected for short term projects or for areas where propane would not be acceptable. The catalytic oxidation system has a present value cost very close to that of the GAC steam regeneration in situ system. Since the VOCs are destroyed rather than collected for recycling, there is no possibility of further liability to the SRS. The additional handling and manhours required for the GAC in situ steam regeneration system is considered to push the actual present value costs higher than those of the catalytic system.

PATH FORWARD

The EPA published an initial list of approximately 350 hazardous air pollutant source categories in November 1991. By November of 1992, the EPA must publish MACT regulations for the first forty source categories, plus a schedule for establishing MACTs for all remaining categories. Remaining categories will be phased in 25% at a time every three years, with all category MACTs established by the year 2000. Once a MACT regulation is published for a source, the owner of the source has three years to comply. Based on this schedule, the first compliance date that a source could be subject to is November 1995. After MACT regulations are promulgated, they will be compared against the risk-based NESHAPs program to determine the need for additional control.

WSRC is currently investigating technologies that will meet and exceed the MACT guideline. As a result of the alternative study described in this paper, designs for the new air stripper and soil vapor extraction systems include catalytic oxidation units. Personnel from the Savannah River Laboratory are currently working in conjunction with the DOE Office of Technology Development to develop new off-gas treatment technologies. A demonstration of new technologies is scheduled to begin in spring 1992 and run for one to two years. Results of this testing will be used in designing new emission control systems in the future. SRS is being proactive with respect to the CAA implementation schedule outlined above to avoid the need for additional project work, design changes, and regulatory approval. Future projects will also address the treatment of gas-phase contaminants.

ACKNOWLEDGEMENT

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