Los Alamos
NATIONAL LABORATORY
memorandum

Nuclear Materials and Reconfiguration Technology
Rocky Flats (NMRT/RF)

To/MS John Hopkins, EG&G, B080
Dave Struckman, EG&G, T130 C
Thru Tony Muscatello, NMRT/RF, T 130 A ACM
From/MS Glenn Escobar, NMRT/RF, T 130 A GAE
Phone (303) 966-3478
FAX (303) 966-4933
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Subject **Deliverable for Granular Activated Carbon-Phase 1· System Evaluation**

The enclosed report constitutes the final deliverable for the system evaluation of a granular activated carbon (GAC) treatment technology (WP# 12190-3)

This report proposes low temperature (200° C) regeneration followed by non-thermal plasma destruction for the approximately 74 tons of Rocky Flats GAC Our assessment concludes the bio-mass accumulation can be accommodated and that the technology is technically sound In addition, a preliminary regulatory analysis of the pondwater and OU-2 GAC was performed, and a conceptual design of a full scale system suitable for operations at Rocky Flats was completed

Based on these results, Los Alamos proposes further investigation of this technology and initiation of Phase 2 of this project--fabrication and testing of a prototype system

If you have any questions, please contact me or John Coogan (505/665-0186)

Enc a/s

Cy Duane Catlett, NMRT/RF, T 130 A ACM-for
Dave Moody, NMRT/RF, T 130 A
Tom Norris, NMRT/RF, T 130 A
Tim Burns, NMRT/RF, T 130 A
Author File
File

Granular Activated Carbon - Phase 1: System Evaluation

(EG&G Workpackage Number 12190-3)

Progress Report to
EG&G Rocky Flats Environmental Technology Site
for Activities from April 20 to May 31, 1995

by
John J Coogan, Kurt R Anast, and Stephanie Stoddard
Technical Contributors
Chemical Science and Technology Division

The Alternative Combustion Laboratory
Los Alamos National Laboratory
CST-18, Mailstop E525
ph 505-665-0186
FAX 505-665-8441

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Executive Summary

We have proposed that LANL demonstrate a treatment technology to remove and treat hazardous organics from spent granular activated carbon (GAC) Approximately 74 tons of GAC, used for pond water decontamination and OU2 remediation activities, are now stored at RFETS awaiting treatment for disposal or reuse Existing steam reforming techniques (e g Synthetica) while able to volitilize entrained organics, are unable to destroy them, and produce large quantities of secondary waste water What is needed is a technology that can both separate the hazardous compounds from the GAC matrix and destroy them while producing a minimum of secondary waste Additionally the technology must be able to handle the trace amounts of radioactive materials present and respond to local stakeholder concerns The technology proposed combines conventional carbon regeneration with a novel off-gas treatment technology based on plasma produced "cold-combustion" This report summarizes activities under phase I of the program This work includes a technical review to determine the applicability of the proposed technology to the specifics of the RFETS GAC, a preliminary regulatory analysis of the pondwater and OU2 GAC, and a conceptual design of a full scale system suitable for operations at RFETS A brief summary of these findings follows

System Design The proposed technology, low temperature (200°C) GAC regeneration followed by non-thermal plasma destruction, is technically sound Bio-mass accumulation can be accommodated Analytical data provided by RFETS on the compounds contained in the GAC show no technical show stoppers within either the regeneration or plasma stages The key technical issue that can be resolved in phase 2 is the efficiency of the system

Regulatory Analysis A survey of the regulatory drivers has identified several key questions that need to be answered before a final analysis can be made A real determination by CDPHE and possibly EPA must be made concerning which, if any, of the GAC is controlled under RCRA RFETS might successfully argue that the treatment units at A-4 (outfall 005), B-5 (outfall 006) and C-2 (outfall 007) are regulated under the Clean Water Act With regard to the 70 ton pond GAC, RCRA exclusions exist for waste water discharge upstream from Pond B-5 Arguments can be made that the GAC used to treat these wastewaters is RCRA exempt However, the same GAC was also used to treat surface water flow originating in Operable Units If CDPHE or EPA decide to regulate this surface water as contaminated media, all or part of the GAC may be designated as listed hazardous waste A ruling along these lines could potentially impact the status of wastewater discharge from RFETS Interagency Agreements may override these RCRA designations Preliminary examination of analytical results indicate that the GAC meets LDR treatment standards for hazardous waste found at 40 CFR 268 40, although no evaluation was made regarding the validity of the results Additional testing may be required A preliminary waste code of F001 has been identified by RFETS for the 4 tons of GAC generated from OU2 activities Our preliminary assessment is that the 4 tons are likely to contain other listed constituents Preliminary examination of analytical results indicate that all the GAC may meet LDR treatment standards for characteristic waste found at 40 CFR 268 40 Additional testing may be required In accordance with 40 CFR 261 3(c)(4) regenerated GAC can be reused without further RCRA Subtitle C regulation until it becomes spent material that must be regenerated again or disposed of

Conceptual Design. The siting requirements are reasonable and a trailer mounted system is feasible Estimated costs for a 100 lb/hr system are 263k$ capital and 261k$ operating No unusual utilities are required and the estimated footprint is 1000 to 1600 sq ft With adequate support, a working system can be delivered to RFETS in FY96

I Introduction

The proposed system combines a well characterized and commercially available technology to regenerate spent granular activated carbon (GAC), with an emerging and environmentally friendly advanced oxidation technology (AOT) to treat off-gases It is our design philosophy that is advantageous to destroy any hazardous vapors as they are generated, and without the addition of any fuels or oxidants The use of commercially available "low-temperature" carbon regeneration allows for cost effective and dependable processing of the spent GAC GAC throughput, system costs and the demonstrated ability of this technology to handle "bio-fouled" carbon reduce risk Non-thermal plasma (NTP) off gas treatment offers several advantages 1- It is a robust technology, requiring no added fuel, minimizing secondary waste Toxic off-gases generated from the GAC regeneration process are immediately treated, simplifying disposal and removing storage and transportation expenses 2- Since significant water remains in the GAC canisters, the efficiency of thermal treatment units is reduced, this water will enhance removal rates within NTP reactors since the water is dissociated to form useful OH radicals 3- The NTP system can function in a wide range of off-gas conditions from an oxygen rich (air-like) to an "inert" gas matrix, increasing system flexibility and simplifying the possible implementation of a closed-loop design NTP has demonstrated efficient destruction of VOCs to levels below 20 ppb 4- Ongoing demonstration of low temperature thermal desorption (at RFETS) and soil vapor extraction (at industrial and DoD sites) using a LANL NTP reactor will assist in cost effective prototyping and if necessary, since the Colorado Department of Public Health and Environment (CDPHE) has already been briefed on NTP, reduced permitting times

A two phase project has been agreed upon by EG&G and LANL Here we describe the results of phase I This preliminary analysis, or reality check, of both technical and regulatory issues has demonstrated that the technology is capable of treating the spent GAC now stored at RFETS The figures referenced in this report correspond to the presentation graphics (i e transparencies) distributed to RFETS earlier

II Regulatory Issues/ Needs

We currently believe that there are three RCRA related issues First, does the GAC currently meet Land Disposal Restrictions (LDR) standards? Second the specific characteristics of the pondwater (70 tons) and OU2 (4 tons) GAC And third, are there any impediments to reuse?

II-1 Land Disposal Restrictions (LDR) Issues

In order to evaluate whether or not the granulated activated carbon (GAC) meets the LDR standards, one must consider first how the GAC could become regulated under the Resource Conservation and Recovery Act (RCRA) Once it is established that the GAC is indeed regulated under RCRA, all applicable waste codes must be assigned to the waste in order to determine which LDR standards apply Of the 74 tons of GAC in question, some was used to treat environmental media (OU-2 GAC) and some was used to treat environmental media and/or effluent from the Sewage Treatment Plant (70 ton GAC) Applicable regulations include

EPA's Contained-In policy
The contained in policy covers environmental media which has been contaminated with RCRA waste Both surface water runoff and groundwater are considered by the Environmental Protection Agency (EPA) to be environmental media (57FR 986, 1/9/92), 65FR 63850, 12/5/91, 57FR 61497, 12/24/92) Environmental media contaminated with a RCRA hazardous waste must be managed as if the media were a hazardous waste until it no longer "contains" the hazardous waste Environmental media containing a characteristic hazardous waste remains a characteristic waste

until it no longer exhibits the characteristic Environmental media containing a listed hazardous waste remains a listed waste until it no longer contains the listed waste Surface water runoff into the A, B, and C series ponds and OU -2 seep collection pond will be considered to be contaminated media if it is determined that the water contains a listed waste or the water is in itself characteristically hazardous

The Derived-from rule 40 CFR 261 3(c)(2)(i) Any solid waste generated from the treatment, storage, or disposal of a hazardous waste is a hazardous waste Residues (e g GAC) derived from the treatment of characteristic wastes are only hazardous if they continue to exhibit a characteristic Residues derived from the treatment of listed wastes remain listed wastes

The Mixture Rule 40 CFR 261 3(a)(2)(iii-iv) In general, a solid waste that is mixed with a characteristic hazardous waste remains hazardous only if it continues to exhibit a characteristic If a solid waste is mixed with a listed waste, the resulting mixture will remain listed

II-2 Overall Approach to Waste Characterization

40 CFR 262 11 requires a generator of a solid waste to determine whether or not the solid waste is a hazardous waste according to a specified hierarchy The generator must determine if the waste is

1 excluded from hazardous waste regulation,
2 listed in Subpart D of 40 CFR 261 (listed waste), and
3 listed in Subpart C of 40 CFR 261 (characteristic waste)

The generator can determine if the waste is characteristic by applying knowledge of the hazardous characteristic of the waste or by testing utilizing specified methods This hierarchy will be used to evaluate the regulatory status of the GAC as follows

II-2-A 70 Ton GAC Hazardous waste determination for residue resulting from wastewater treatment

Exclusions

The following exclusions could be used by RFETS to prevent the application of hazardous waste listings via the mixture rule to A and B series GAC from waste water treated at the sewage treatment plant If these exclusions apply to the wastewater, then the exclusions will apply to the treatment residue (GAC)

Domestic Sewage Exclusion

40 CFR 261 4(a), Materials which are not solid wastes "Any mixture of domestic sewage and other wastes that passes through a sewer system to a publicly-owned treatment works for treatment "Domestic sewage" means untreated sanitary wastes that pass through a sewer system "

In the Federal Facility Compliance Act of 1992, Congress amended RCRA such that the domestic sewage exclusion applies to Federally Owned Treatment Works (FOTW) as long as

1 the sewer contains untreated sanitary waste
2 the facility complies with applicable pretreatment standards (If there are no pretreatment standards, the waste must meet Land Disposal Restrictions prior to entry into the sewer)
3 each generator of the hazardous waste (defined as "person" or "household") adds to the waste stream no more than 100kg/mo or 1kg/mo of acutely hazardous waste

The Act language also states that it is unlawful to introduce a hazardous waste into an FOTW One could argue that as long as numbers 1-3, above, are adhered to, hazardous waste introduced to an FOTW would cease to be solid waste and therefore could not be hazardous waste

The codified language at 40 CFR 261 4(a)(1)(ii) defines "domestic sewage" to mean "untreated sanitary wastes that pass through a sewer system " However, a judge in Federal District Court (Puerto Rico) ruled that domestic sewage must come from residences in order for this exemption to apply On the other hand, Pantex has found a way to use this exclusion RFETS will have to make a determination regarding the utility of this exclusion in light of waste streams generated and overall waste management strategies at the plant

Wastewater Discharge Exclusion

40 CFR 261 3(a)(2)(iv) Definition of a hazardous waste "A solid waste, as defined in 261 2, is a hazardous waste if it is a mixture of solid waste and one or more hazardous wastes listed in subpart D [unless] the generator can demonstrate that the mixture consists of wastewater the discharge of which is subject to regulation under either section 402 or section 307(b) of the Clean Water Act "

The Preamble to the May 19, 1980 Federal Register (Part III, Identification and Listing of Hazardous Waste) discusses application of the wastewater discharge exclusion in light of the RCRA statute and legislative history (45FR 33098) EPA defends RCRA jurisdiction over industrial wastewaters prior to discharge and defines "discharge" as a term of art under the Clean Water Act (CWA) referring only to "the addition of any pollutants to navigable waters "

It appears as though this wastewater exclusion could be used to eliminate potential listed waste codes from the 70 Ton GAC only if the A-series and B-series ponds are considered navigable waters of the United States

Listed Waste Determination

RFETS Surface Water and Sanitary Waste Operations groups enforce administrative controls to prevent introduction of hazardous waste into the Sewage Treatment Plant Assuming RFETS chooses not to utilize either of the exclusions discussed above, to determine if any listed waste codes could be applied to the 70 ton GAC from the STP waste water effluent, RFETS could rely on in-place administrative controls to argue that no hazardous wastes are treated in the STP Otherwise, RFETS must evaluate potential listed waste streams (such as P or U wastes) and test the 70 ton GAC for the specific regulated hazardous constituent(s) found at 40 CFR 268 40 for each listed waste Under RCRA, any known introductions of listed waste into the Sewage Treatment Plant must be applied to the GAC

Characteristic Waste Determination

Analytical results show that the 70 ton GAC meets LDR standards for TC characteristic waste (D004-D043) A process knowledge determination for the characteristics of ignitability, corrosivity, and reactivity should be sufficient to eliminate a D001, D002, or D003 waste designation

Conclusion With respect to the portion of the 70 ton GAC used to treat waste water effluent from the Sewage Treatment Plant, it meets the LDR standards for characteristic wastes If RFETS maintains that administrative controls are sufficient to eliminate introduction of listed waste into the Sewage Treatment Plant and there have been no accidental discharges of listed wastes into the plant, then the portion of the 70 ton used to treat wastewater effluent does not need to meet any of the LDR standards for listed wastes

II-2-B 70 Ton GAC Hazardous waste determination for residue resulting from treating contaminated media

Surface water runoff into the A, B, and C series ponds will be considered to be contaminated media if it is determined that the water contains a listed waste or the water is in itself characteristically hazardous

Exclusions

None applicable

Listed waste determination

A technical verification is needed whether or not listed constituents from IHSS's could have impacted the contaminated media collected at the ponds If CERCLA investigations indicate that listed constituents were present in the pond water, then RFETS must test the 70 ton GAC at a minimum for the specific regulated hazardous constituent(s) found at 40 CFR 268 40 for each listed waste EPA/DCHPE could require application of the F039 waste code to GAC if more than one listed waste is identified This waste designation could prove problematic from the stand point that environmental media (not the GAC) could easily remain subject to RCRA regulation after it passes through the GAC unit because the GAC cannot remove F039 constituents The F039 waste designation requires analysis for a large (up to 200) number of constituents

If the results of the technical evaluation indicate that no listed waste impacted the pond water, then the GAC is subject to characteristic waste determination only As stated below, the GAC meets the LDR standards for characteristic wastes However, as for any process knowledge/acceptable knowledge determination, RFETS must be correct, and keep at the facility documentation substantiating this determination

If the results of the technical evaluation are inconclusive, RFETS may go to EPA/CDPHE and request that the contaminated media be considered characteristic waste only (55 FR 8758)

characteristic determination

Analytical results show that the 70 ton GAC meets LDR standards for TC characteristic waste (D004-D043) A process knowledge determination for the characteristics of ignitability, corrosivity, and reactivity should be sufficient to eliminate a D001, D002, or D003 waste designation

conclusion If the technical evaluation shows no listed hazardous waste impacted the pond water, or The EPA/CDPHE determine the contaminated media can be managed as a characteristic waste, the 70 ton GAC meets LDR standards

II-2-C OU-2 GAC Hazardous waste determination for residue resulting from treating contaminated media

Exclusions

none applicable

Listed waste determination

RFETS personnel have indicated that the primary source of contamination of the OU-2 pond water is Pad 903 The site was used from 1958 to 1967 to store drums containing machine cutting oils and solvents A preliminary waste code of F001 has been applied to the OU-2 GAC Review of Approved Procedures and interviews with RFETS and LANL personnel confirmed the F001 listing, provided that 1,1,-trichloro-1,2,2,-trifluoroethane (a potential F002 listed waste) was not used for its solvent properties Small amounts of F003 listed solvents (acetone and methanol) were also used in cleaning operations

Analysis results provided showed levels of F001 constituents well below the LDR treatment standards However, F002 and F003 constituents were not analyzed RFETS must get a determination from EPA/CDPHE as to whether all regulated hazardous constituents listed in 40 CFR 268 40 for F001-F005 waste must be analyzed or if only those constituents attributed to the F001 and F003 listings are appropriate

Hazardous waste determination

Analytical results show that the OU-2 GAC meets LDR standards for TC characteristic waste (D004-D043) perhaps with the exception of D015 and D017 (This is not to say that the TCLP values were exceeded for these constituents These constituents may have been analyzed and reported under a different name) A process knowledge determination for the characteristics of ignitability, corrosivity, and reactivity should be sufficient to eliminate a D001, D002, or D003 waste designation

Conclusion At a minimum, F003 and perhaps F002 constituents should be analyzed If the analysis for the other constituents was performed by mass spec, the analytical laboratory may be able to reevaluate the analysis results against their library and report concentrations for the missing constituents It is likely that the analysis will show levels below the concentrations specified and the OU-2 GAC will meet LDR standards Secondly, further analysis may indicate that other listed constituents from IHSS's impacted the contaminated media If so, the F039 waste designation could be applied (see above)

II-3 Reuse of Carbon

There are regulatory advantages to onsite regeneration of the GAC40 for reuse CFR 261 3(c)(2)(I) states that materials reclaimed from solid wastes and are used beneficially are not solid wastes and hence are not hazardous wastes under the derived from rule unless the reclaimed material is burned for energy recovery or used in a manner constituting disposal Onsite regeneration for reuse therefore avoids many of the issues just discussed

In accordance with 40 CFR 261 1(c)(4) A material is "reclaimed" if it is processed to recover a usable product, or if it is regenerated Examples are recovery of lead values from spent batteries and regeneration of spent solvents Further, EPA defined reclaimed material as follows " We defined "reclamation" to constitute either regenerating waste materials or processing waste materials to recover usable products In essence, reclamation involves regeneration or material recovery Wastes are regenerated when they are processed to remove contaminants in a way that restores them to their usable original condition " (50 FR 633, 1/4/85) Regenerated GAC can be reused without further RCRA Subtitle C regulation until it becomes spent material that must be regenerated again or disposed of

This work directly addresses several Rocky Flats strategic objectives Obj #1 Rapid implementation of this technology will enable the timely disposal of wastes in a cost-effective and environmentally responsible manner The off-gas treatment system has already been granted a

RCRA waste treatment facility permit from the state of New Mexico, greatly reducing the time required for a local permit During public comment on this permit, feed back from local stakeholder groups about non-thermal plasma processes was very positive Obj #3 Public risks are reduced by the implementation of a closed-loop process design which eliminates uncontrolled stack emissions (including both hazardous chemical emissions and rad lofting) through the recycling of exhaust gases

IV GAC Regeneration Technology

The GAC regeneration sub-system will remove organic contaminants from the carbon matrix to either improve the effectiveness of the carbon for future use or prepare the carbon to meet land disposal restrictions Commercial systems are available that can handle both the chemical (target organics) and physical (water content, bio-mass) characteristics of the pondwater and OU2 GAC Several configurations are available, including rotary kilns, vertical furnaces and tray kilns (see FIGURES 10, 11, 12, 13), but all share the same basic layout First a feed mechanism delivers the GAC at a controlled rate This allows for steady state operation and simplifies the maintenance of a constant temperature Second, the GAC is moved through a heated chamber to vaporize the water and volitilize the organics Third the off-gases are vented, and the dry, clean carbon is collected The maximum required temperature is determined by the boiling point of the target organics Analysis provided by RFETS show the principle organic contaminants to have boiling points below 150°C One exception is pentachlorophenol, found in al least one sample, with a b p of 309 °C See table below

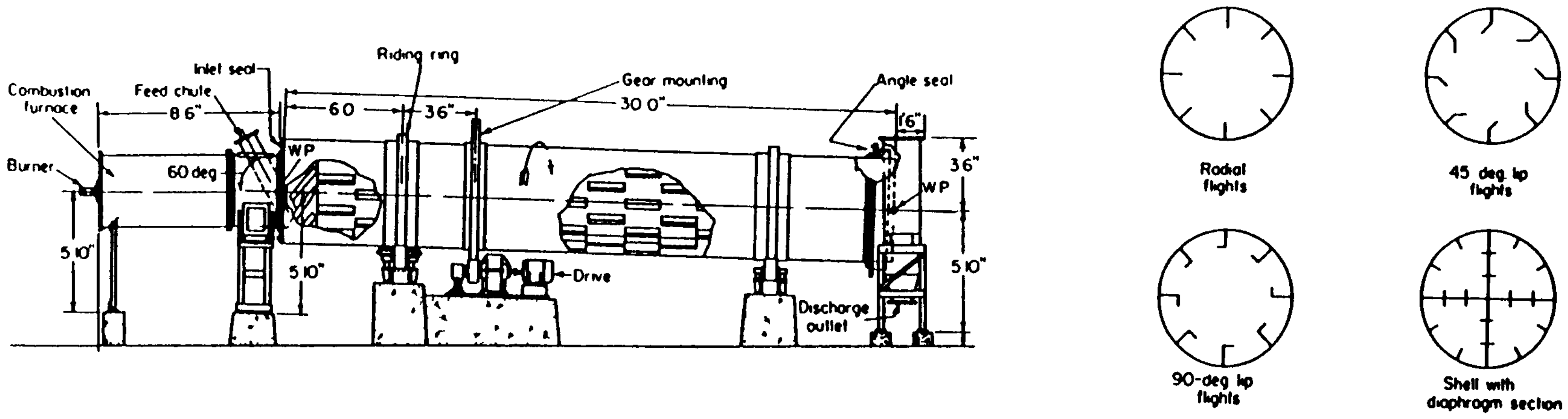
Compound	Boiling point (b p) °C	ppb in TCLP sample
acetone	57	1200
methylene chloride	40	150
1,2 dichloroethane	84	80
chloro phenylmethyl phenol	100	50
dodecanoic acid	131	50
pentachlorophenol	309	80
carbontetrachloride	77	none detected

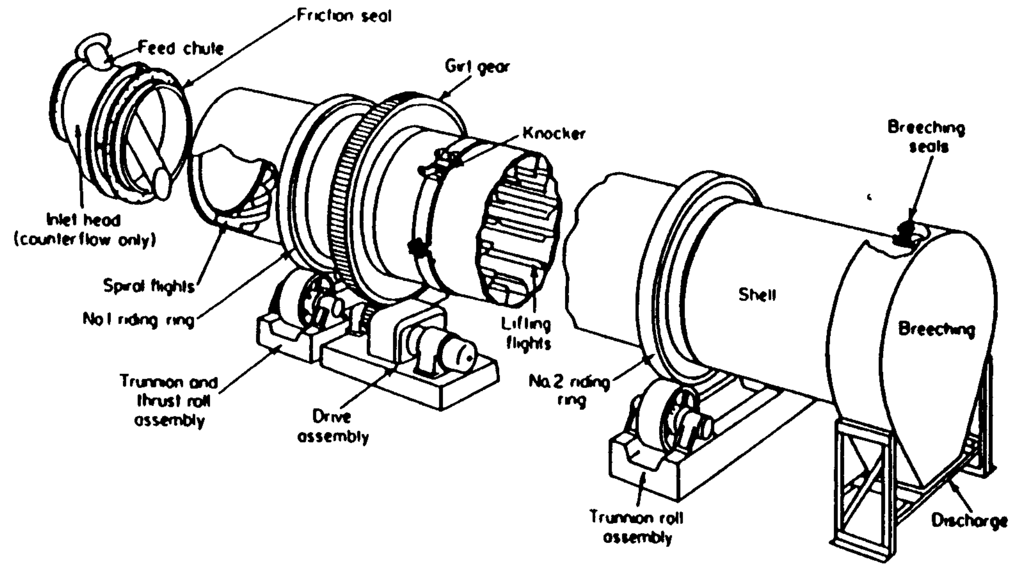
TABLE 1

Higher temperatures (600-700°C) are only required when one needs to "reactivate' the carbon This process selectively enlarges the pores of the carbon to increase its absorptive capacity After several low temperature regenerations the capacity of the carbon to trap organics will have decreased and it will be necessary to "reactivate" the cleaned carbon before it can be reused It is therefore desirable that the carbon regenerator have the capability to operate at a range of temperatures from 150 to 700°C While each of the 4 commercial units can be engineered to meet this specification, our recommendation is the lower cost rotary kiln A schematic of the proposed regeneration unit is shown in FIGURE 14

System throughput is easily calculated, see FIGURE 16 Since most of the off-gases are produced from volitilizing water into steam, the water content of the GAC is an important engineering parameter Data provided by RFETS show that water content varies from 40 to 42% (that is 60% solids) Therefore a 100 lb per hour system, operating at 175°C, will produce 40 lbs of steam (35 scfm) and 60 pounds of clean dry carbon per hour After the steam is treated in the NTP system, the water can be either condensed, resulting in an easily controlled exhaust stream of only a few slpm, vented up a stack, or our preferred option, recycled

GAC regeneration is a mature, reliable technology It is well established that it is able to handle both the chemical and physical properties of both the pondwater and OU2 generated GAC What


Combustion furnace
Burner
Feed chute
Inlet seal
8 6"
60 deg
WP
5 10"
6 0
Riding ring
36"
Gear mounting
30 0"
Drive
Discharge outlet
Angle seal
6"
36"
WP
5 10"
Radial flights
45 deg lip flights
90-deg lip flights
Shell with diaphragm section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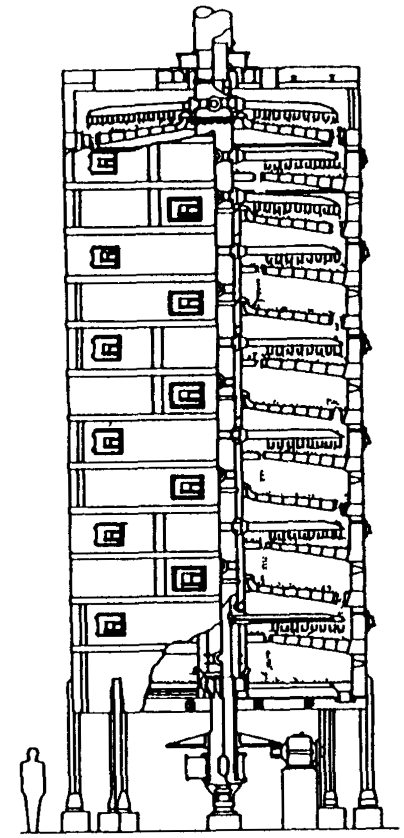
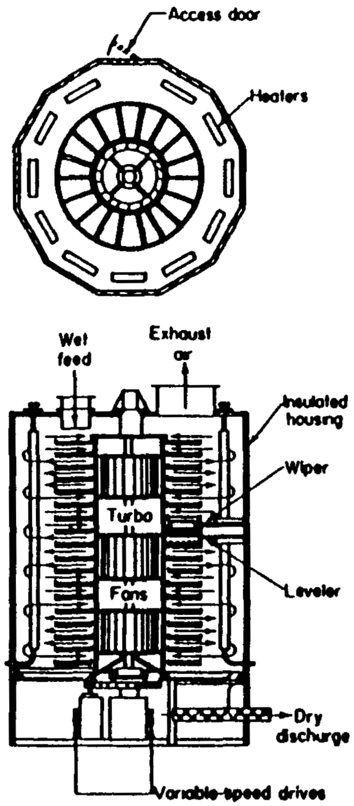
Friction seal
Girt gear
Knocker
Inlet head (counterflow only)
Spiral flights
No 1 riding ring
Trunnion and thrust roll assembly
Drive assembly
Lifting flights
No.2 riding ring
Trunnion roll assembly
Shell
Breeching seals
Breeching
Discharge

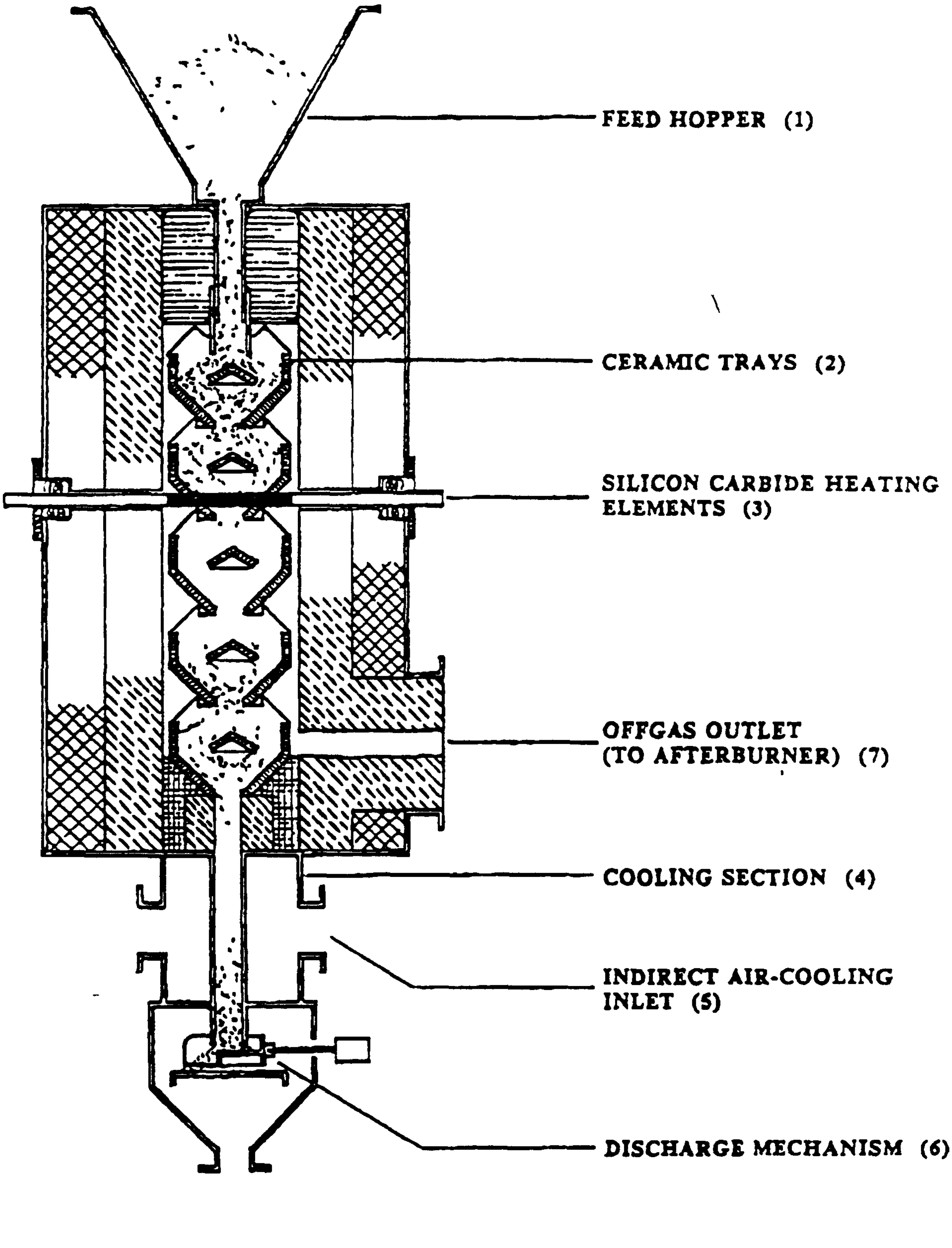
ROTARY KILN



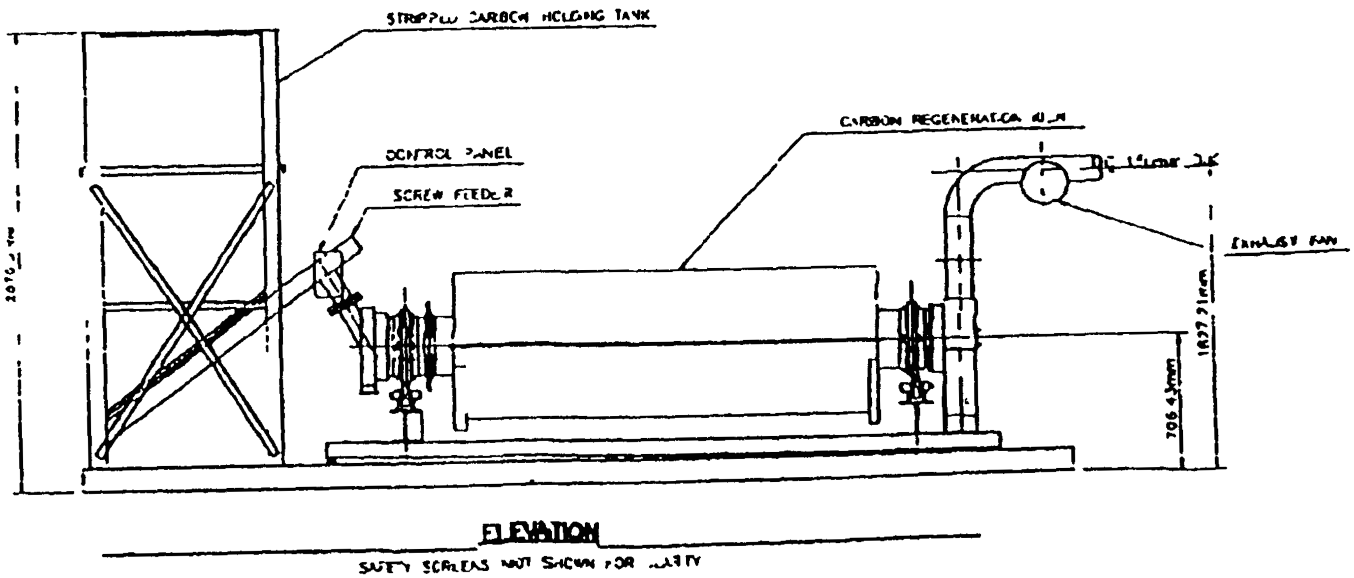
Pacific multiple hearth furnace



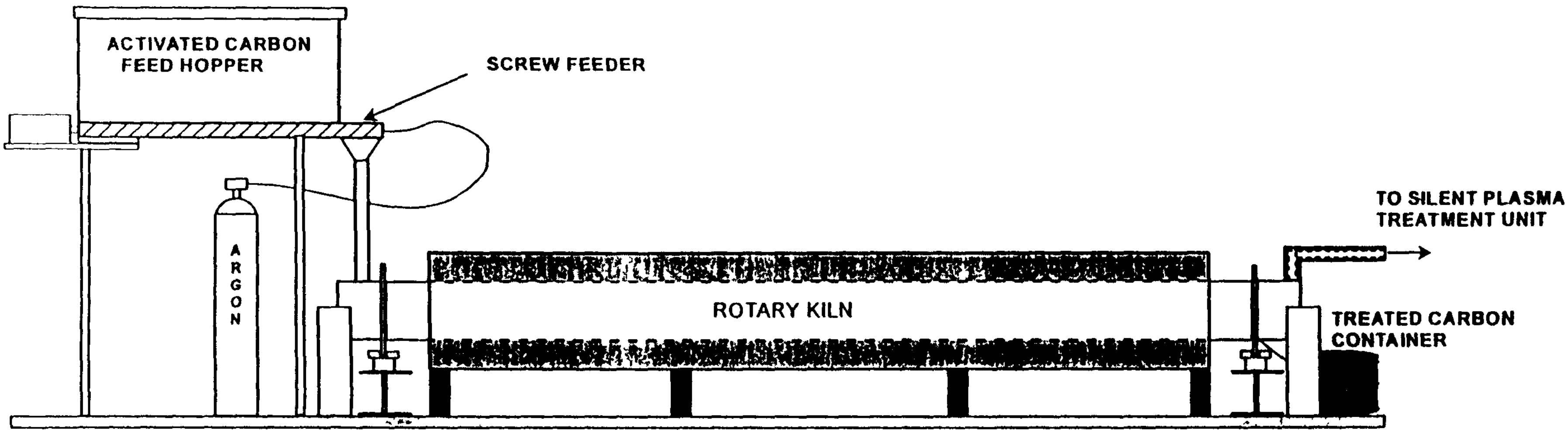
TRAY OR MULTIPLE HEARTH KILN



VERTICAL KILN


CARBON REGENERATION KILN
CONTROL PANEL
SCREW FEEDER
EXHAUST FAN
706.43mm
ELEVATION

ROTARY KILN



PROPOSED GRANULAR ACTIVATED CARBON (GAC) PRETREATMENT EQUIPMENT

ESTIMATED KILN FEED RATES & RESULTING GAS FLOWRATE TO SDP UNIT

	Activated Carbon Feed Rate			Estimated gas flow rate @ RF (cfm)												
water vap	50% solid	60% solid	70% solid													
Lb/hr	Lb/hr	lb/hr	lb/hr	150C				175C				200C				Outlet Gas Temp
				100	75	50	25	100	75	50	25	100	75	50	25	% H2O in Gas Stream
1 00	2 00	2 50	3 33	1	1	1	3	1	1	1	3	1	1	1	3	
2 00	4 00	5 00	6 67	1	2	3	5	1	2	3	5	1	2	3	6	
3 00	6 00	7 50	10 00	2	3	4	8	2	3	4	8	2	3	4	8	
4 00	8 00	10 00	13 33	3	3	5	10	3	4	5	11	3	4	6	11	
5 00	10 00	12 50	16 67	3	4	6	13	3	4	7	13	4	5	7	14	
6 00	12 00	15 00	20 00	4	5	8	15	4	5	8	16	4	6	8	17	
7 00	14 00	17 50	23 33	4	6	9	18	5	6	9	19	5	7	10	20	
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12 00	24 00	30 00	40 00	8	10	15	30	8	11	16	32	8	11	17	34	
14 00	28 00	35 00	46 67	9	12	18	35	9	12	19	37	10	13	20	40	
16 00	32 00	40 00	53 33	10	13	20	40	11	14	21	43	11	15	23	45	
18 00	36 00	45 00	60 00	11	15	23	45	12	16	24	48	13	17	25	51	
20 00	40 00	50 00	66 67	13	17	25	50	13	18	27	53	14	19	28	57	
25 00	50 00	62 50	83 33	16	21	31	63	17	22	33	66	18	24	35	71	
30 00	60 00	75 00	100 00	19	25	38	75	20	27	40	80	21	28	42	85	
35 00	70 00	87 50	116 67	22	29	44	88	23	31	46	93	25	33	49	99	
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45 00	90 00	112 50	150 00	28	38	57	113	30	40	60	120	32	42	64	127	
50 00	100 00	125 00	166 67	31	42	63	126	33	44	66	133	35	47	71	141	
55 00	110 00	137 50	183 33	35	46	69	138	37	49	73	146	39	52	78	155	
60 00	120 00	150 00	200 00	38	50	75	151	40	53	80	159	42	57	85	170	

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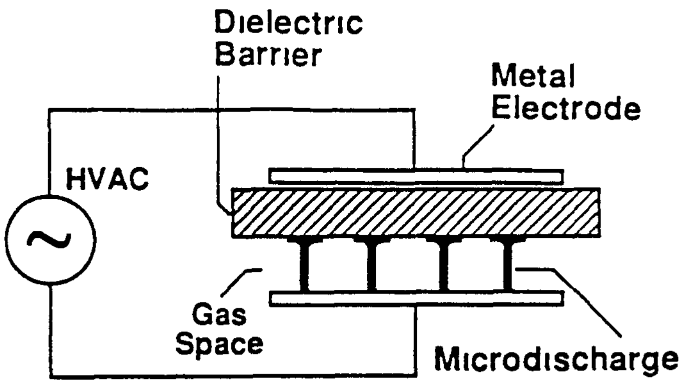
is lacking is an off-gas treatment system optimized for the high water vapor content gases generated by the regeneration process

V Introduction to Non-thermal Plasmas

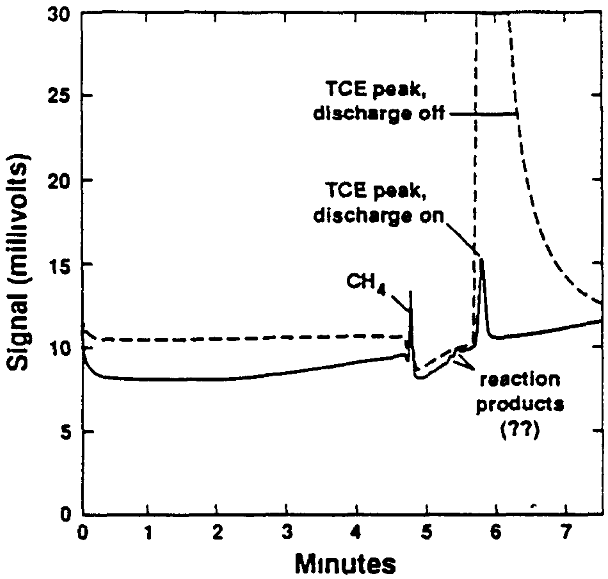
Non-thermal plasmas (NTP) have demonstrated destruction and removal efficiencies (DRE) from 95 to >99 999% for such ubiquitous solvents as TCE, TCA, and PCE during field demonstrations Laboratory tests (initially performed under a Rocky Flats incinerator alternatives initiative), have measured similar removal rates for a range of chlorinated solvents, PCB surrogates (dichlorobenzene), carbon tetrachloride, p-cumene, benzene, toluene, xylene (BTX), SOx, NOx, and CFCs Operating at ambient temperatures and pressures, NTPs generate copious quantities of highly reactive free radicals which rapidly and efficiently dissociate hazardous organics In humid air steams, for example, chlorinated solvents are oxidized to produce carbon dioxide, water and hydrochloric acid LANL's NTP reactor is the off-gas treatment sub-system within a two-stage technology which has received the first RCRA RD&D permit from the state of New Mexico (permit # NM0890010515-RDD1)

The use of plasmas can provide an efficient way to produce the free radical concentrations required for complete destruction of waste Plasmas can generate very energetic ("hot") electrons (typical energy range of 1-10 eV), which are very efficient at creating free radicals (including atomic oxygen and hydroxyls) without adding the enthalpy associated with very high gas temperatures Thus, reaction rates associated with temperatures of 10,000 K to 100,000 K can be realized while the actual gas temperatures remain near ambient These "cold plasmas" can be very energy efficient for waste destruction because most of the work goes into enhancing the chemistry without significantly raising the gas temperature and without adding additional fuel to the process Additionally, these system require no added fuel or oxidants The radicals are generated from the constituents already within the off-gas For GAC regeneration, steam provides the raw materials for the production of hydroxyl (OH) radicals which aggressively attack organic contaminants One of these "cold plasma" processes, the silent discharge plasma or SDP, offers superior treatment capabilities compared to other cold plasma techniques (corona for example)

Silent discharge cold plasmas are commonly produced with near-atmospheric pressure discharges called dielectric barrier or silent discharges Typically, one or both electrodes are covered with dielectric layers (e g , glass), which separate them from the gas (see FIGURE 20) This arrangement is an old one, first employed by Siemens in 1857, and still used today for the industrial production of ozone At gas pressures of 1-10 atmospheres and gap spacings of a few millimeters, without the dielectric a few localized intense arcs would develop in the gas between the metal electrodes With a dielectric and the application of alternating high voltages (50 or 60 Hz power frequency to tens of kilohertz), substantial quantities of plasma are created by a large number of "microdischarges" in the gas, which are statistically spread in space and time, filling the reactor volume Because of the short duration (a few nanoseconds) of the microdischarges and the low ion mobilities, electrical energy in silent discharges is principally coupled into electron channels - electrons, ions, and gas do not equilibrate - so the electrons are "hot", while the other species are "cold " This results in a very efficient transfer of electrical energy to electronic excitations of molecules and/or chemical processes in the plasma, while the temperature of the bulk medium remains at ambient temperature The ability to maintain a discharge does not depend highly on the composition of the feed gas (nebulized organic or aqueous/organic mixtures) and requires no added fuel Since most of the electrical energy goes into free radical formation and very little into heating the gas the process has demonstrated very high destruction efficiencies yielding very attractive economics of kilograms of waste destroyed per kW-hr of electricity consumed Secondary waste streams typically contain the completely oxidized products of the feed constituents, primarily CO_2 and H_2O, with HCl from chlorocarbon waste



TCE Destruction in the SDP Cell (100 x magnification)



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In field tests, conducted at DOE s Savannah River Site (FIGURE 21) the output from a vapor extraction system containing from 700 to over 4000 ppm of PCE, TCE and TCA was treated with DRE's ranging from 95% to 99 9999% Additional filed demonstrations are planned this summer at Tinker AFB, and this spring at a semiconductor fabrication facility The technology is cost-competitive, and will prepare for the advent of even more stringent air pollution regulations SDP has also been identified as an offgas treatment within the FFCA for DOE's EG&G Mound facility where SDP will be part of a facility treating a mixed PCB/tritium waste stream TSCA permits will be submitted next spring As part of the LTTD demonstration at RFETS, NTP has already been reviewed by the Colorado department of Public Health and Environment (CDPHE) (FIGURE 22) Additionally, upon completion of both technical and public reviews LANL's NTP system has received a RCRA RD&D permit from the New Mexico Environmental Department Recently a commercialization workshop identified industrial partners to begin production of this equipment The technology can help address Rocky Flats compliance needs in a timely, cost-effective manner

In phase II of this effort, several issues related to SDP treatment of off-gases generated from regeneration of activated carbon will be specifically addressed For steam based regeneration schemes, the behavior of the discharge with high concentrations of water vapor will be explored We predict very high production of OH radicals from the dissociation of H_2O, but specific measurements are required to specify a full scale system Similar tests could also be done using hot nitrogen regeneration schemes We predict less efficient volatilization of organics from the carbon, but other advantages, such as a simplified closed loop design, may mitigate this problem The metrics for final system design will be dependability, efficiency, and final waste form Rocky Flats ER and WM personnel will be consulted to ensure the final design meets their needs

V Conceptual Design of "full-scale" System

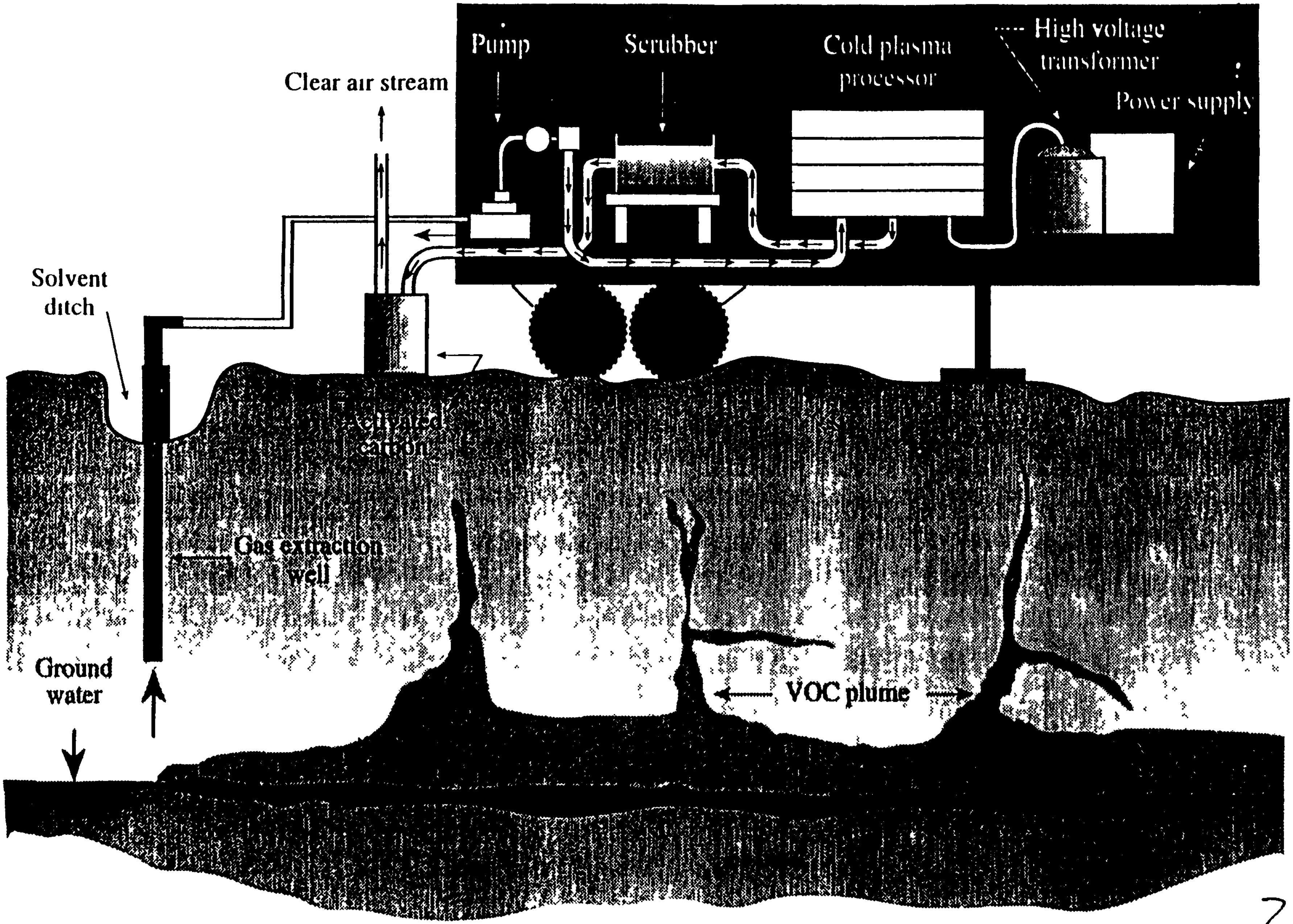
The following assumptions have been made

- 74 tons of feed material (GAC plus water)
- Thermal oxidation (i e incineration) is not acceptable
- Technology must meet stakeholder and RFETS concerns for on-site treatment
- Reasonable footprint and utility requirements
- Implementation within FY 96 or 97 (scale dependent)
- Acceptable to CDPHE (if permitting is required)

A flow diagram of the proposed system is shown in FIGURE 25 Spent GAC is fed from a storage bin into a rotary kiln operating at 125 to 250°C (dependent upon the target compound with highest boiling point) The kiln volitilizes both the water and the organics contained in the GAC Off gases composed mostly of steam are sent immediately into a non-thermal plasma system operating at the exit temperature of the kiln The organics are oxidized by the reactive hydroxyl radicals generated in the plasma from the water vapor already present No fuel of oxidants are added to the gas stream After treatment in the plasma chamber, water vapor is condensed and the byproducts of the cold plasma combustion are scrubbed out This water will be "cleaned" and can be sent through a conventional waste water treatment plant. Any remaining gases are sent back into the GAC storage bin An inert carrier gas may be used The cleaned, dry GAC is ready for reuse or disposal When high temperature reactivation is required, the dry GAC is again sent into the kiln This time it is treated at a higher temperatures to reactivate the carbon pores which trap organics As a precaution off gases from this process could again be treated within the plasma chamber

Given this it was determined that a 100 lb/hr system, operable for 24 hrs/day (8 hour days also possible, but less efficient), would meet RFETS needs This system would be able to treat the 74

Destruction Unit at Savannah River



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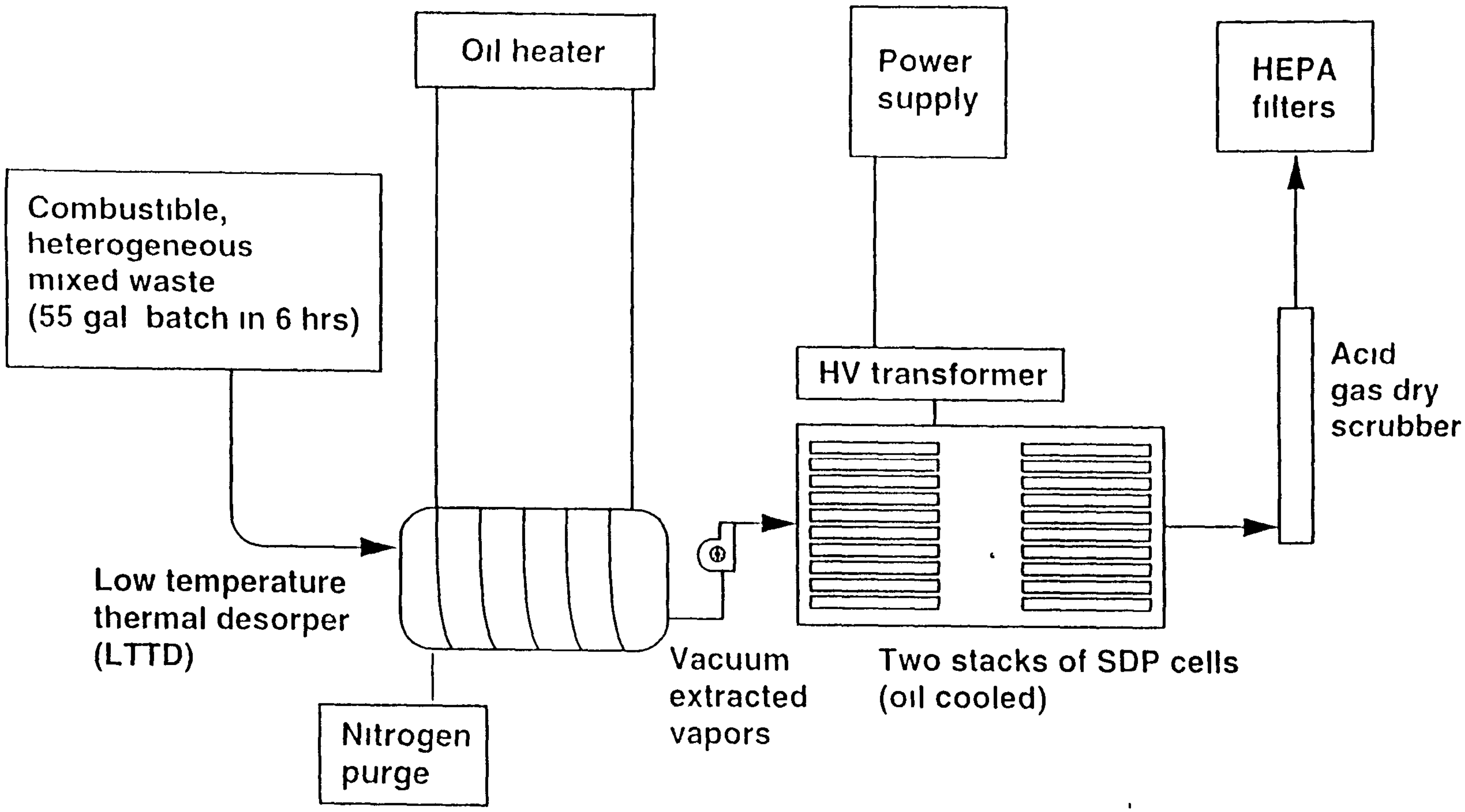
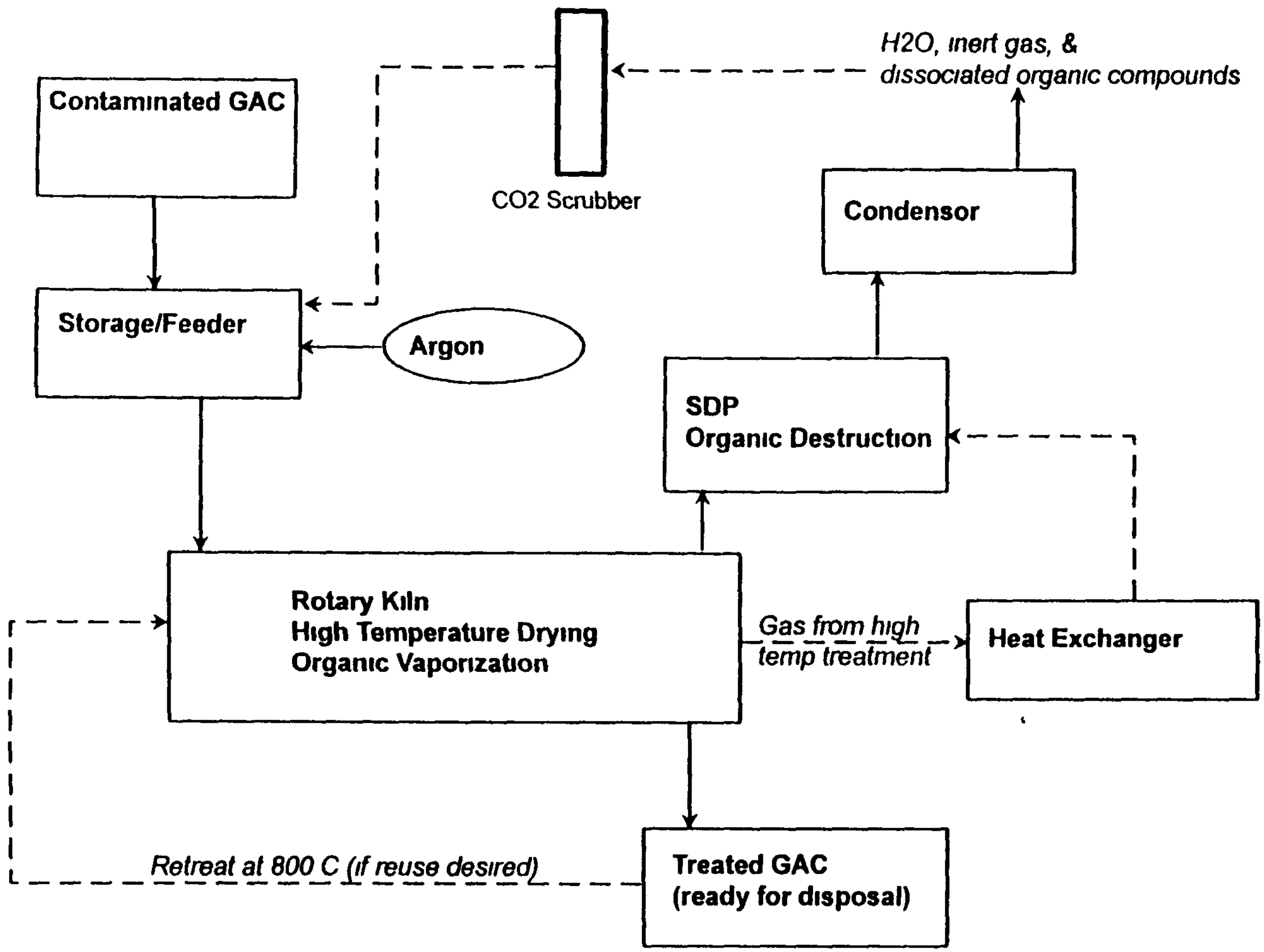
Desorber/nonthermal plasma system for treating vapors extracted from heterogeneous waste



Mixed waste is fed into LTTD unit where it is heated to ~125 F and flushed with nitrogen
Vapors are extracted through a vacuum pump, and treated within the SDP unit.



PROPOSED GAC TREATMENT FLOWSHEET

tons of spent GAC in a 12 month campaign The foot print of this system is shown in FIGURE 26 The estimated footprint of the complete system is 1000 to 1600 square feet If desired by RFETS, the system could also be trailer mounted and moved from site to site Power can be supplied by either 208 VAC 3 phase 200 amp, or 480 VAC 3 phase 100 amp services Scaling of the GAC unit, cost and footprint, is based on interviews with manufacturers of the equipment If useful, we can provide catalogs, company names and contacts A 5-7 ton chiller system is also required

NTP scaling uses the following method The approach that we have adopted for this work is to use the plasma energy per unit volume (or deposited electrical power divided by gas flow rate - P/Q) as the key parameter to determine the degree of removal of contaminants entrained in the gas stream fed to the SDP stage The target P/Q is likely to be in the range 200 - 500 J/std liter Energy density removal scaling relationships are described below

In many cases, the removal of a contaminant X can be approximated by an exponential decay

$$[X] = [X]_0 \exp(-E/b),$$

where [X] is the resulting concentration, $[X]_0$ is the initial concentration, E is the applied specific energy or P/Q, and b is the e-fold energy density Supplying one b of energy density to the reactor reduces the concentration by 1/e, two b's reduces it by $1/e^2$, and so on In an ideal case, when E is plotted versus $-\ln([X]/[X]_0)$, a straight line of slope b results Therefore, the b-value can be easily determined from data presented in such a removal plot For some cases, the removal plot is not necessarily a straight line, so such a slope-determined b-value is only an approximation Nevertheless, it is still quite useful over a limited range of e-folds

b-values are usually given in base e units It is also convenient to express b in base ten units because then it represents the energy density required to reduce the contaminant concentration by a factor of ten The removal, $1 - ([X]/[X]_0)$ is often expressed in terms of a destruction and removal efficiency (DRE) of so many "nines", e g , three "nines" removal (or 99 9%) is achieved by supplying the reactor with three base-ten b's For base ten units, the removal equation is

$$[X] = [X]_0 \exp(-E/a),$$

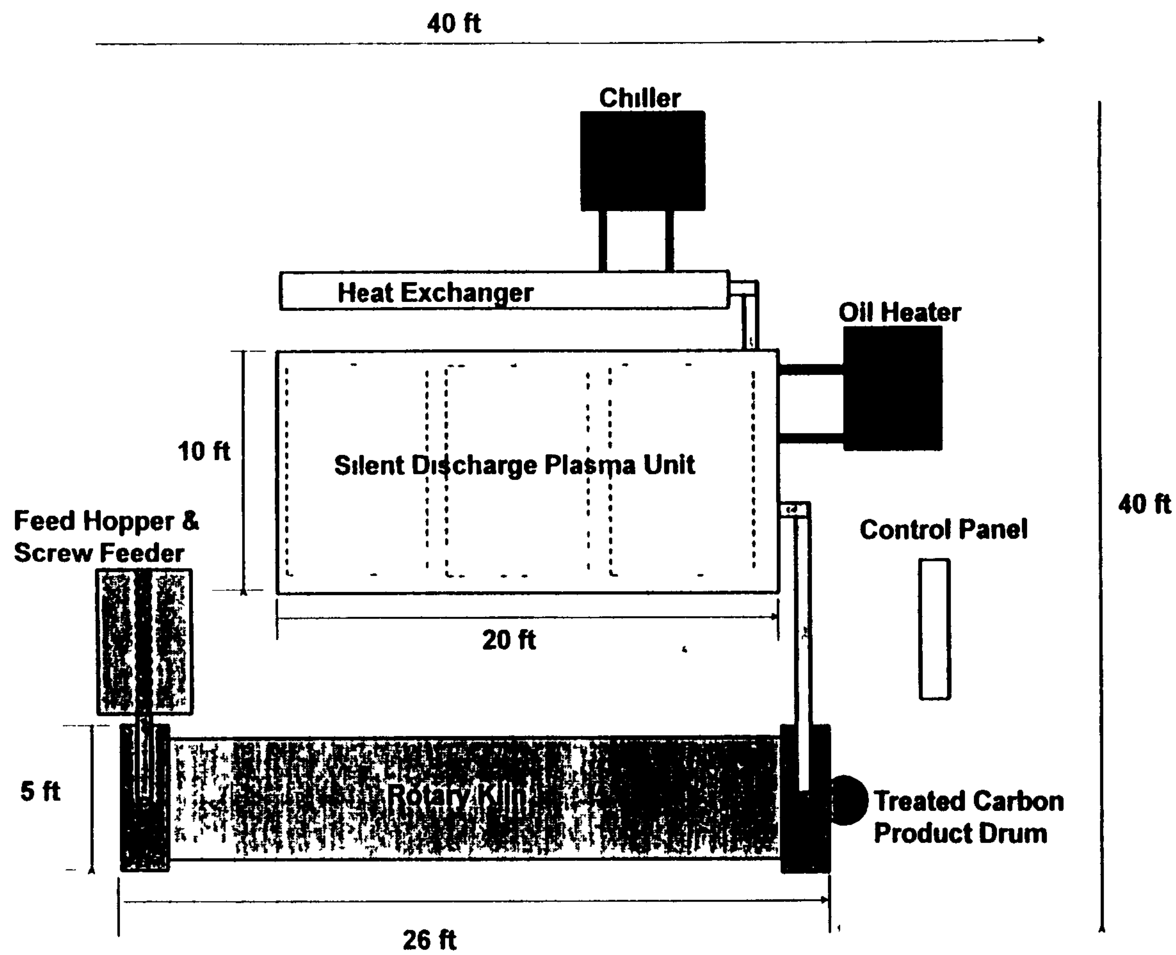
where the base-ten exponential-folding factor $a = -b \ln 0\,1 = 2\,3\,b$ This simple formula is the basis of an engineering model used to generate scaling factors for higher flow rates (FIGURE 29)

To increase the removal fraction $[X]/[X]_0$ for a given gas mixture, E must be increased Because E = P/Q, E can be increased by either increasing P or, equivalently, decreasing the flow rate Q for a given cell power This can be accomplished by directly increasing the power to the cells Alternatively, by dividing a given gas flow into several parallel cells, the overall energy density for the total flow can be effectively increased We prefer the second approach of modularization, whereby a cell of desirable properties is replicated many times Such modularization scaling of silent discharge cells has been previously demonstrated for the industrial-scale synthesis of ozone, where municipal water treatment plants frequently require the on-site generation of thousands of kilograms per day This also simplifies scaling as the flow per cell in a large system is the same as the flow per cell in the smaller, lab based system

The b-value depends on the particular compound, the gas mixture, and to some extent the concentration of the contaminant From the previous LANL work with spiked gases, the decadic energy density (i e , a-value) for acetone is estimated to be 150-200 J/std liter For the sizing of the equipment, we have assumed a more conservative value of 250 j/std liter and a target DRE of 99% This requires an energy density of 500 J/std liter Scaling to the target flow rate of 35 scfm,

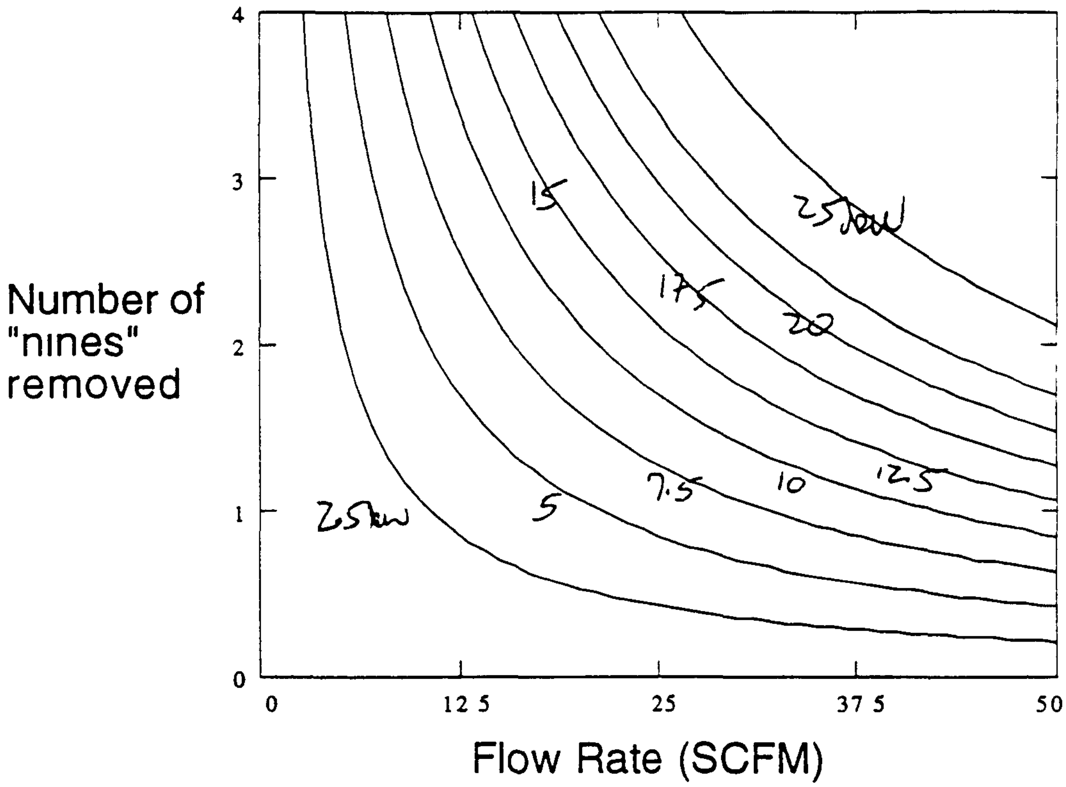
Equipment List

Feed Hopper	- 40 cu ft
3" Screw Feeder	- 1 hp motor
Rotary Kiln	- 26'L x 5"D ?? kw
Heat Exchanger	- 75,000 btu
SDP Unit	- 35 cfm 25 kw
Chiller	- 7 ton
Oil Heater	- 50,000 btu



FULL SCALE SYSTEM EQUIPMENT LAYOUT

Number of Nines Removed -vs- System Power



b2

see figure 29, provides the 10kW power required An important deliverable of phase II is the a value for table I compouds, within steam

At Los Alamos, we have had considerable experience with both laboratory bench-scale and field-deployed SDP units The basic concept recommended for the RFETS system is a parallel-gas-fed arrangement of simple, flat-plate, modular units The mechanical details of how the modules are held together, the secondary containment vessel design, and plumbing and electrical connections for the cells and feedthroughs for the secondary containment vessel are considered part of the detailed design and are not included in this document

A table of operating parameters for a 35-SCFM module is presented below The electrical power input will increase in proportion to the number of modules employed The sections that follow discuss specific aspects of the parameters or how these relate to system components

SDP Unit Operating Parameters

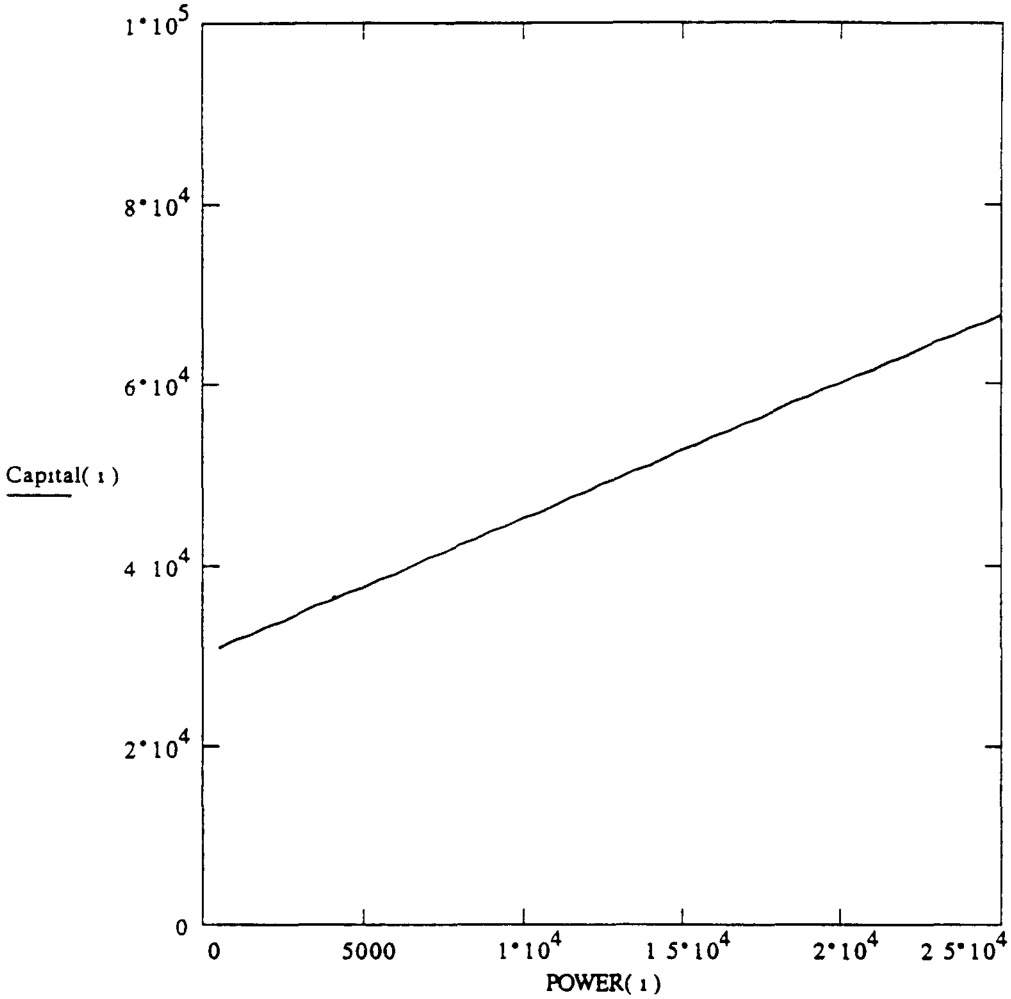
Parameter	Value or Range
Gas flow rate (through SDP module)	35 SCFM (987 std liter/min)
Plasma energy density in gas	250 J/lit (1 decade), 500 J/lit (2 decades)
Electrical power input	10 kW (1 decade), 20 kW (2 decades)
Cell voltage	20 kV rms
HV transformer step-up ratio	60 1
Cell gas pressure	Approximately ambient absolute pressure
Cell pressure drop	Negligible
Gas temperature (input)	120-150 C

The total number of cells will be chosen to give the design energy density and gas flow rate when the cells are operated in parallel Each cell will be operated at a flow of Q/N and a power density of (P/N)/A, where P and Q are the total power and flow, respectively, N is the number of cells and A is the active electrode area of each cell Previously demonstrated values of power density (power per unit area) will be used as the design basis

A 10 kW system will require 10 to 20 cells depending upon the power density A conservative design will use 20 cells These cells will be arranged in two stacks of 10 Each stack will be 14 5 inches wide and 27 inches long (the same size as dielectric plates) For forced liquid temperature control each stack, including press system, is 30 inches high The two stacks are assembled onsite within a secondary containment vessel approximately 4 feet wide by 6 feet long by 4 ft high The weight of the fully assembled system, excluding power supply, is less than 1000 lbs A 12 kW power supply will be approximately 3 feet by 2 feet by 5 feet and weigh 700 lbs Commercial systems can provide primary power for $0 80 to $1 00 per watt Estimated capital costs for the non-thermal plasma off-gas treatment system (cells, control system, power supplies, pumps, valves,) are given as a function of power in FIGURE 30

The power supply is usually an oscillator-power amplifier unit that is commercially available as a standard product item Suggested manufacturers are the Elgar company and California Instruments company Higher efficiencies are possible if a "simple" inverter circuit is used These power supplies can be built in-house or acquired through ozonizer manufacturers The high-voltage transformer and tuning inductor are individually-designed items made to designer specifications by electrical specialty firms (we have been satisfied with units from Stangenes Industries, Inc) The recommended transformer step-up ratio of 60 1 is based upon our experience with available commercial sinusoidal-waveform power supplies and their current ratings for driving a typical cell-stack capacitive load The value of the tuning inductance depends upon the desired operating repetition frequency and the cell and transformer capacitances The power supply, high-voltage

Capital Costs for Off-Gas System



transformer, and power factor correction inductors will be specified in the detailed design An semi-automatic control and data acquisition is recommended

Based on interviews of regeneration equipment,, and the just discussed NTP scaling algorithm, direct costs (not including personnel to monitor GAC hardware and fabricate NTP hardware) is 263 k$ Operating expenses, based on continuous operation are estimated to be 261 k$ More detailed is provided in FIGURES 31 and 32

VI Experimental Plan(s) for Phase II

Specific tasks for phase two will depend upon the priorities set by RFETS waste management and environmental restoration The key technical issue remains the measurement of the required energy density for treatment of the TABLE 1 compounds to RFETS standards Previously we have worked with air like and inert gas mixes with water content from 0 to 15% Operation with the close to 100% water vapor for this project requires additional study The presence of such high water vapor concentrations should increase the production of OH radicals, and result in a more efficient system Unfortunately it is also possible that discharges in steam may be become more tightly filamented, resulting in a less efficient system However, based on our experience with off-gas streams for thermal treatment units, the water should not be a problem as long as the cells are maintained at >100°C to prevent condensation The experimental setup shown in FIGURE 34 will provide this data, and generate the scaling parameter, a, in joules/liter that is required for final specification of the full-scale system We propose two alternate phase two efforts for the remainder of FY95 First, task IIA the originally planned construction of a prototype GAC treatment system includes both a commercial GAC regenerator and the NTP off- gas system This prototype, shown in FIGURE 35 can be used in FY 96 for either extended lab testing at LANL, or upgraded for delivery and implementation at RFETS Secondly, an alternative effort focuses on the experimental setup in FIGURE 34 and will deliver only the offgas system The advantage of the first option is the availability of a complete pilot scale system for either lab or field demonstrations in early FY96 The second option, while costing less in FY95, would require more support in FY 96 to reach the field demonstration stage We hope to participate with RFETS WM/ER personnel to identify the most productive implementation schedule for this technology - for both the remainder of FY95 and outyears The specifics of these two option follow

Task IIA Start procurement of long lead time items carbon regenerator and SDP power supplies Assemble batch GAC regenerator and SDP subsystems and begin tests with steam, air-like and "inert" (non-oxidizing) gas streams Assemble complete system This work will demonstrate 3 main sub-systems

1 - The GAC regeneration equipment will be purchased from an outside vendor and modified to meet our needs This is the most costly piece of equipment (35 k$) and also has a long lead time (4 months)
2 - The SDP sub-system will be different that those built in the past The SDP design for this project will allow treatment very humid gas streams, including steam, without any condensation within the cells Power supplies, heating control, and electrical diagnostics will be designed and built into the system Some materials optimization may be required
3 - The gas handling system will allow for recycling of system exhaust, eliminating gaseous emissions For the full scale system this will reduce the danger of rad lofting when radionuclide contaminated GAC is used Additionally, this system will allow the simultaneous use of several existing chemical diagnostics GC/MS and FTIR for quantification of organic removal and byproduct formation, IR detection of CO/CO2/O2 for process monitoring, and an FID for easy measurement of total hydrocarbons These diagnostics will be optimized for both the specific organics to be treated and the gas matrix that will be carrying them

FULL SCALE SYSTEM CAPITAL COSTS

DIRECT COSTS

Equipment	
Feed Hopper	$2,000
Screw Feeder	$1,500
Rotary Kiln	$60,000
Discharge System	$5,000
SDP Unit	$50,000
Heat Exchanger	$6,500
Chiller	$10,000
Hot Oil Heater	$10,000
TOTAL	$145,000
Installation @ 45%	$65,000
Instrumentation @10%	$15,000
Piping & Electrical @ 25%	$38,000
TOTAL DIRECT COST	$263,000

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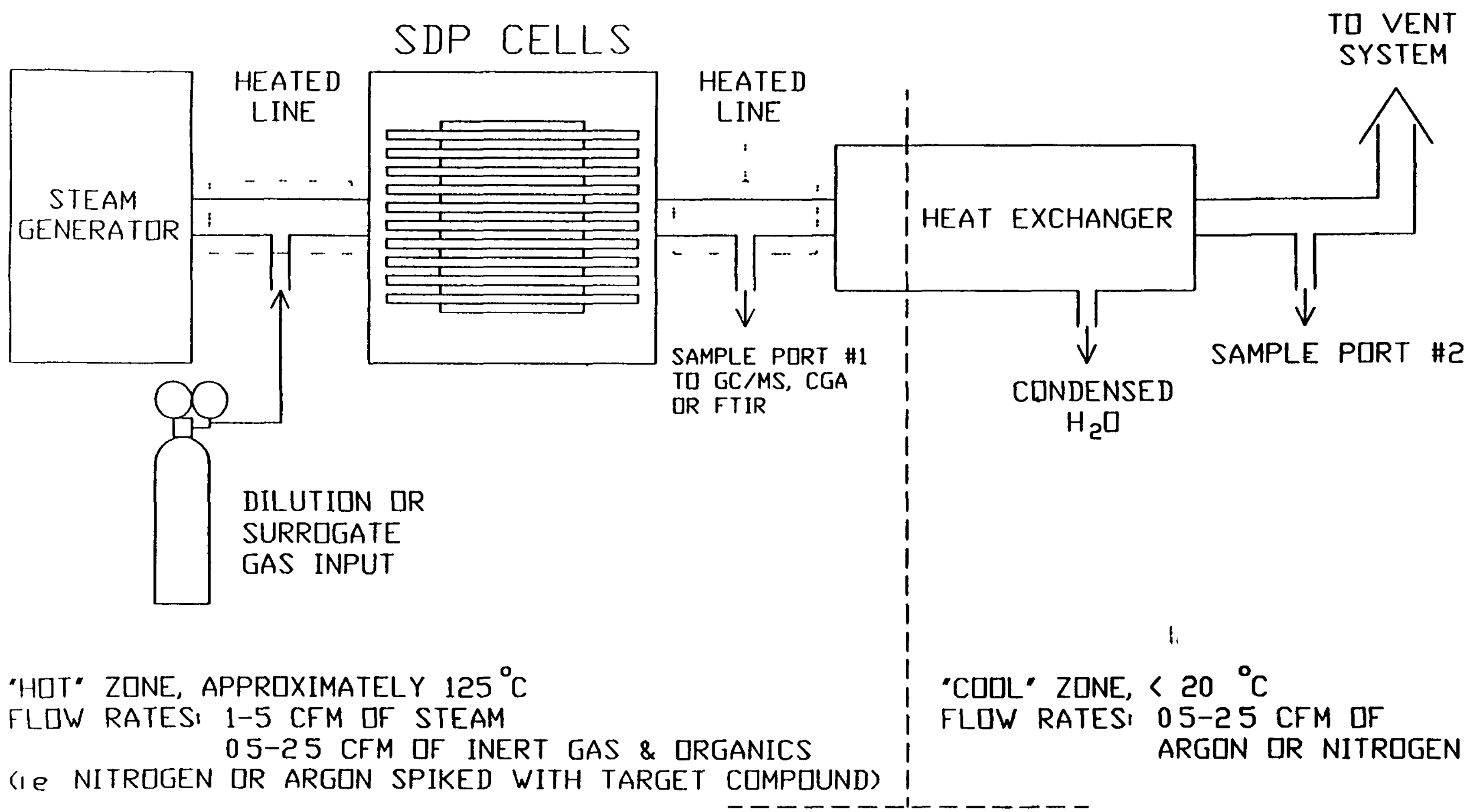
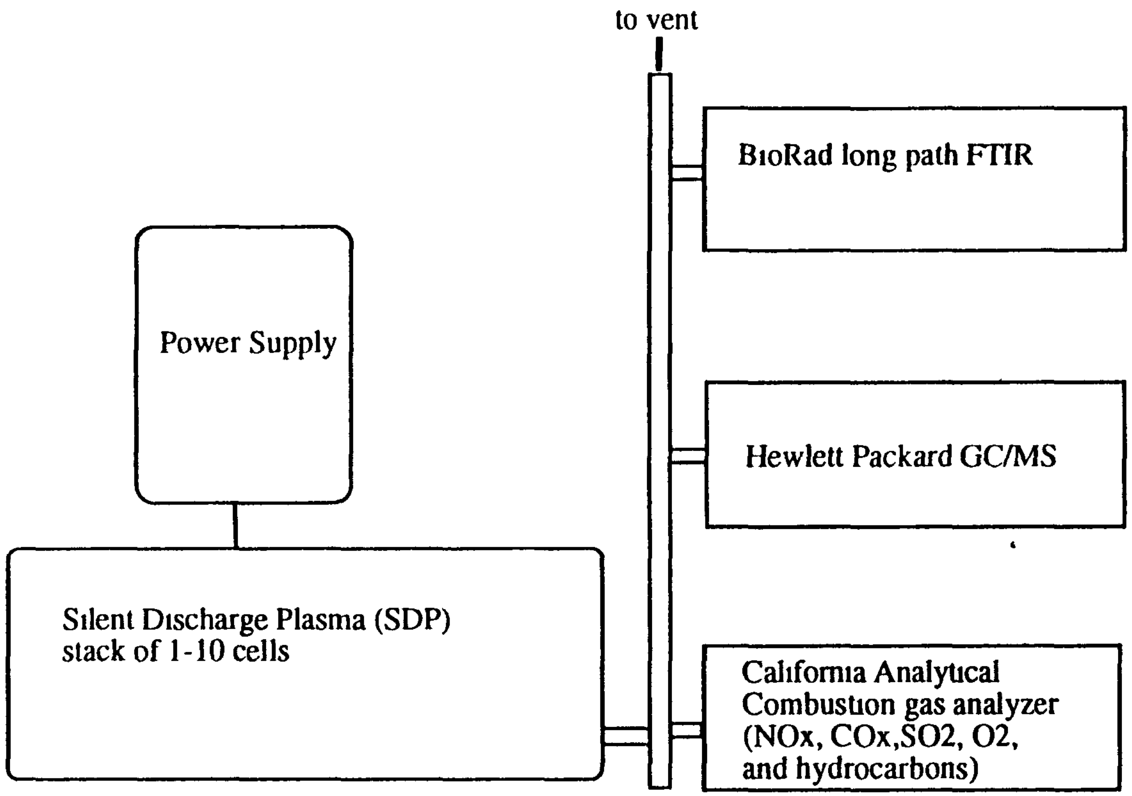
FULL SCALE SYSTEM OPERATING COSTS

LABOR		
2 operators/shift @ $35/hr		$1,680/day
1 engineer/day @ $100/hr		$800/day
UTILITIES		
Electrical		
CONSUMABLES		
Argon	2 bottles/day	$100/day
ANALYTICAL		
TCLP, water, gas		$500/day
TOTAL		$3,480/day
TOTAL COST @ 15 weeks of operation		$261,000

EXPERIMENTAL SETUP #1
SDP TREATMENT OF GAC OFF-GASES
MEASURE DRE & BY-PRODUCTS AS FUNCTION OF P/Q and [H_2O]



Chemical Analysis



Los Alamos
Los Alamos National Laboratory
Chemical Science and Tech Div
MS E525 Los Alamos, NM 87545
ph 505-665-0186 FAX 505-665-8441

Until the delivery of the GAC regenerator, the complete system will be tested using an in-house, semi-batch GAC regenerator and steam generator This system will allow a complete ring out of the other subsystems Laboratory tests will work first with surrogate materials that approximate the contaminants of interest to RF environmental restoration and waste management When possible, actual samples from RF will be tested at Los Alamos When the GAC regenerator arrives (capacity about 20-50 lbs/hr) it will be installed and tested We will prepare for testing of the integrated system with three goals 1- Starting from the present state of the art designs, optimize volatilization from the GAC as a function of temperature, pressure, flow rate, and gas composition A key metric will be the volume and form of the secondary waste stream 2- Quantify off-gas treatment for a range of compounds as a function of gas composition and NTP power for the most promising regeneration schemes 3 - Demonstrate the utility of closed-loop, i e gas recycling, designs These systems will recirculate exhaust gases from the non-thermal plasma reactor back into the regeneration chamber - eliminating exhaust stacks and the potential for releases of toxic or radioactive vapors A fiscal year end report will include a conceptual design, produced with LANL's engineering design team and a more detailed regulatory review by CST-27's RCRA team, of a system suitable for field work at Rocky Flats, a summary of our data, a more detailed design of the future field unit, and an evaluation of the performance of the regenerated carbon This information will be presented for review at RFETS on or around September 10 In the summer of 1995, LANL, NMRT/TT and RFETS personnel will meet to discuss the optimal mix of activities for FY 96 Based upon those discussions and the review of September 10, we will produce a detailed plan for FY96

Task IIA Summary Prototype fabrication and testing 6/1/95 - 9/30/95
- a - Fabricate/Acquire pilot scale GAC regeneration chamber
- b - Design and fabrication-thermal plasma reactor
- c - Design and fabricate gas scrubbers and pumps
- d - Test with surrogates for both ER and WM GAC
- e - Evaluate NTP treatment of off-gases
- f - Data summary and analysis

Milestone Program review at RFETS (9/10/95) and final report (9/30/95)

Cost estimate
CST SM, 1 0 FTEs, 245k$
CST Tec, 0 8 FTEs, 112k$
CST GRA, 0 75 FTEs, 31 k$
NMRT SM, 0 33 FTEs, 88k$
M&S, 211 k$ includes major procurements GAC regenerator (35k$) and power supply (30 k$)
Total 687k$ (program tax may add 3%)

Task IIB We do not acquire the commercial GAC regenerator, but instead evaluate the efficiency of non-thermal plasmas to GAC regeneration through testing with surrogates This is essentially sub-tasks b,d, and e above The lab is equipped to generate any off-gas mixture, with controllable amounts of water vapor or steam We will build a prototype GAC off-gas treatment system and generate data to support the design and cost of ownership of a full scale system Our deliverables are 1- a fully characterized off-gas equipment, and 2- a detailed design, cost estimate, and timetable for full scale implementation at RF The hardware produced in FY95 can be used in FY 96 for extended lab testing at LANL with a carbon regenerator, or combined with a GAC regenerator at RFETS as part of a pilot demonstration The results of this work will be presented for review at RFETS on or around September 10 In the summer of 1995, LANL, NMRT/TT and RFETS personnel will meet to discuss the optimal mix of activities for FY 96 Based upon those discussions and the review of September 10, we will produce a detailed plan for FY96

Task IIB Summary NTP off-gas optimization and testing 6/1/95 - 9/30/95
- a - Design and fabrication-non-thermal plasma reactor
- b - Test with surrogates for both ER and WM GAC
- c - Evaluate NTP treatment of off-gases
- d - Data summary and analysis

Milestone Program review at RFETS (9/10/95) and final report (9/30/95)

Cost estimate
CST SM, 0 5 FTEs, 123k$
CST Tec, 0 5 FTEs, 69k$
CST GRA, 0 66 FTEs, 26 k$
NMRT SM, 0 33 FTEs, 88k$
M&S, 65k$
Total 371k$ (program tax may add 3%)