

**COMMERCIAL DEMONSTRATION OF THE NOXSO
SO₂/NO_x REMOVAL FLUE GAS CLEANUP SYSTEM**

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DOE Field Office, Chicago Date

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Project Definition Phase

U.S. DOE Patent Clearance Is Not Required Prior to the Publication of this Document

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EXECUTIVE SUMMARY

The NOXSO process is a dry, post-combustion flue gas treatment technology which uses a regenerable sorbent to simultaneously adsorb sulfur dioxide (SO₂) and nitrogen oxides (NO_x) from flue gas. In the process, the SO₂ is converted to a sulfur by-product (elemental sulfur, sulfuric acid, or liquid SO₂) and the NO_x is converted to nitrogen and oxygen.

The objective of the NOXSO Clean Coal Project is to design, construct, and operate a flue gas treatment system utilizing the NOXSO process at Alcoa Generating Corporation's (AGC) Warrick Power Plant. A project agreement between NOXSO and AGC was signed on August 30, 1994 enabling the project to be conducted at the Warrick Power Plant near Evansville, IN. The NOXSO plant is being designed to remove 98% of the SO₂ and 75% of the NO_x from the flue gas from the 150-MW equivalent, unit 2 boiler. The by-product to be generated by the project is liquid SO₂. Sufficient construction cost and operating data will be obtained during the project to confirm the process economics and provide a basis to guarantee performance on a commercial scale.

The project is nearing completion of phase 1A, the project definition and preliminary design phase. The continuation application is being prepared to request DOE approval to proceed to phase 1B, Front End Engineering/Environmental Evaluation, of the project. Data obtained during pilot plant testing at Ohio Edison's Toronto Power Plant, which was completed on July 30, 1993 has been incorporated into the preliminary design of a commercial-size plant. This preliminary design is currently being updated for the conditions at Warrick Power Plant.

A draft EIV has been prepared by combining EIVs from the NOXSO project which was to be conducted at Ohio Edison's Niles Power Plant and the canceled CanSolv Project which was to be conducted at Warrick.

Preliminary engineering activities this quarter involved development of a construction cost estimating spreadsheet program. This spreadsheet has been used to estimate the cost of NOXSO systems at various sites. It will be updated during the plant construction to incorporate actual construction costs. The end product will be a quick, efficient, and accurate method to estimate the construction cost of a NOXSO plant. Additionally, laboratory experiments have been conducted on a module of the centrifugal separator to be used downstream of the NOXSO adsorber to confirm vendor design data. Test results showed that the separator will not meet

compliance for particulate emissions, due to its inability to remove sufficient amounts of PM-10 material. Therefore, a baghouse will replace the separator in the current NOXSO design.

Process study activities include laboratory fluid-bed adsorber studies, regenerator computer model development and studies, fluid-flow modelling in fluid-bed vessels, and evaluations of SO₂ production processes. The laboratory-scale, cold flow, fluid-bed adsorber was successfully tested incorporating three stages. The design of the metallic, hot flow model is now underway, and will be used to improve the accuracy of the removal efficiency predictions and study the impact of adding a third adsorber stage. The regenerator computer model was updated and verified using data obtained from the POC pilot plant. The regenerator computer model is being used to study design options for improving the regenerator performance. Fluid-flow modelling has been conducted to develop a procedure for determining the required vessel height above the top fluidized bed to prevent sorbent carryover. Evaluation of liquid SO₂ production processes has led to the selection of the burn in oxygen process. The liquid SO₂ plant will be built on one of two potential host sites.

1 PROJECT DESCRIPTION

The objective of the NOXSO Demonstration Project (NDP), with cost-shared funding support from DOE, is to design, construct, and operate a commercial-scale flue gas cleanup system utilizing the NOXSO process. The NDP consists of the NOXSO plant and sulfur recovery unit, designed to remove SO₂ and NO_x from flue gas and produce elemental sulfur by-product, and the liquid SO₂ plant and air separation unit, designed to process the elemental sulfur into liquid SO₂. The NOXSO plant and sulfur recovery unit will be constructed at ALCOA Generating Corporation's (AGC) Warrick Power Plant near Evansville, Indiana, and will treat all of the flue gas from the 150-MW Unit 2 boiler. The elemental sulfur produced will be shipped to the Olin Charleston Plant in Charleston, Tennessee, for conversion into liquid SO₂.

The goals of the NDP include the reduction of the Warrick Power Plant Unit 2 SO₂ and NO_x emissions by 98% and 75%, respectively, and the waste minimization through the beneficial use of the sulfur by-product. In addition, construction costs and operating data from the project will be used to confirm the process economics and provide a basis to guarantee performance on a commercial scale. Ultimately, the successful demonstration of this process would assist utilities in attaining the emission limits specified by the 1990 Clean Air Act Amendments.

2 PROCESS DESCRIPTION

The NOXSO process is a dry, post-combustion flue gas treatment technology which will use a regenerable sorbent to simultaneously adsorb sulfur dioxide (SO₂) and nitrogen oxides (NO_x) from the flue gas from Unit 2 of AGC's Warrick Power Plant. In the process, the SO₂ will be converted to liquid SO₂ and the NO_x will be reduced to nitrogen and oxygen. The NOXSO plant is being designed to remove 98% of the SO₂ and 75% of the NO_x. Details of the NOXSO process are described with the aid of Figure 1-1. Flue gas from the power plant is drawn through two flue gas booster fans which force the air through two-stage fluid-bed adsorbers and a baghouse before passing to the power plant stack. For simplicity, only one adsorber train is shown in Figure 1-1. Water is sprayed directly into the adsorber fluid beds as required to lower the temperature to 250-275°F by evaporative cooling. The fluid-bed adsorber contains active NOXSO sorbent, a 1.6 mm average diameter stabilized γ -alumina bead impregnated with sodium. SO₂ and NO_x are adsorbed on the sorbent simultaneously by the following reactions:

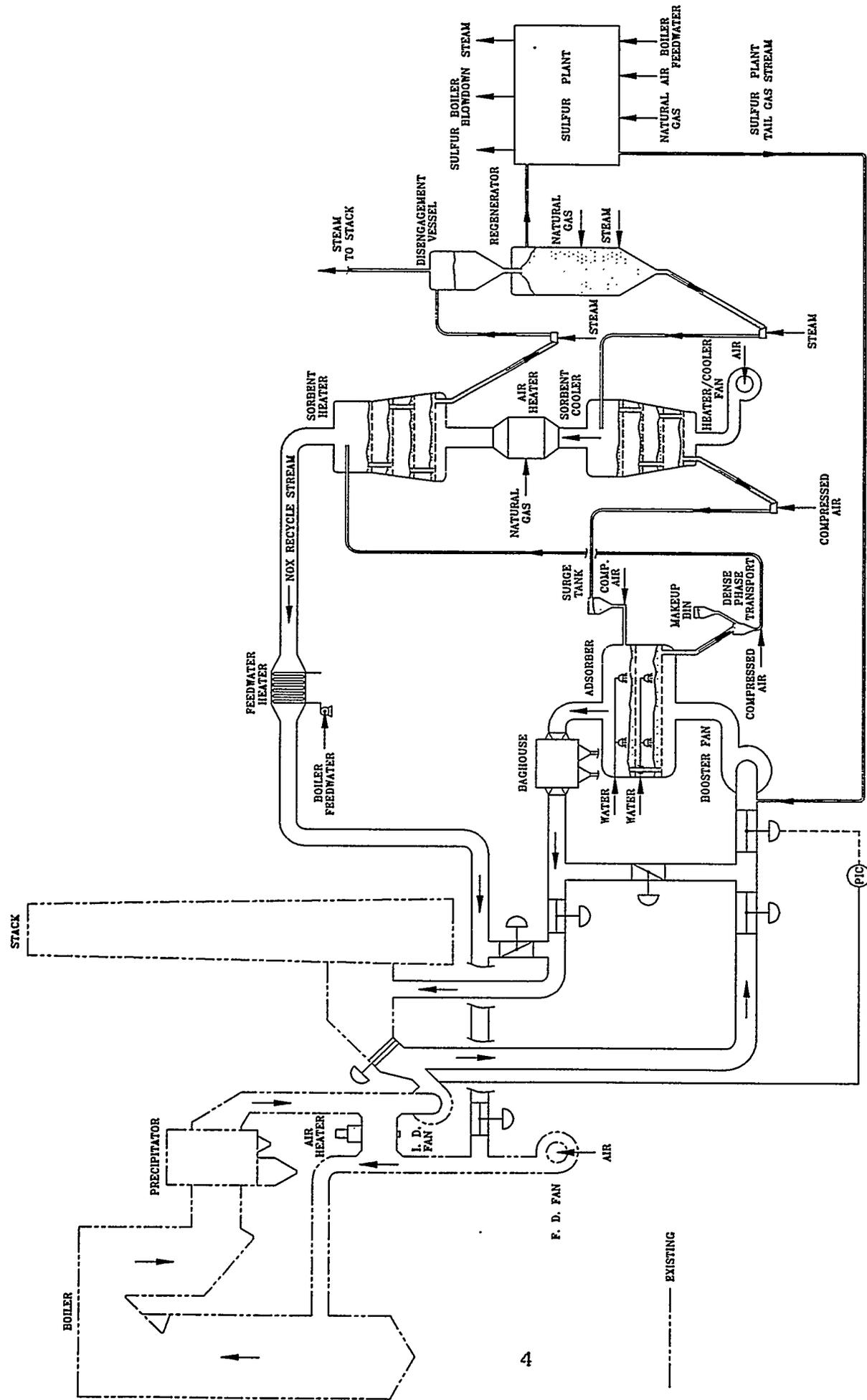
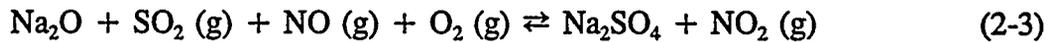
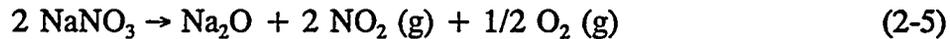


Figure 1-1. NOXSO Process Diagram
 Alcoa Generating Company
 Warrick Plant Unit 2



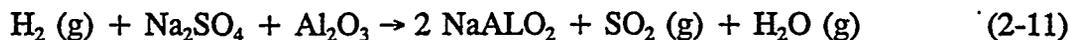
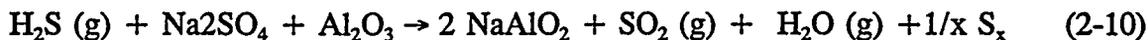
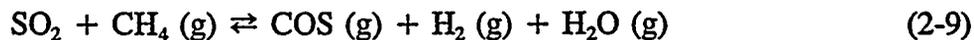
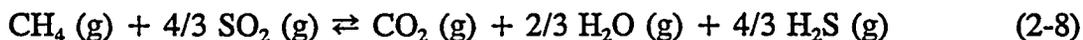
A baghouse separates sorbent which may be entrained in the flue gas and directs it to the fly ash sluicing system. Spent sorbent from the adsorbers flows into a dense-phase conveying system which lifts the sorbent to the top bed of the sorbent heater vessel. The sorbent flows through the four-stage fluidized bed sorbent heater in counterflow to the heating gas which heats the sorbent to the regeneration temperature of approximately 1150°F.

In heating the sorbent, the NO_x is driven off by the following reactions:



The evolved NO_x is then carried to the power plant boiler in the NO_x recycle stream. The NO_x recycle stream is cooled from approximately 360°F to 140°F in the feedwater heater. This heat-exchanger heats a slip stream of the power plant's feedwater, thereby reducing the amount of extraction steam taken from the low pressure turbine. The cooled NO_x recycle stream replaces a portion of the combustion air. The presence of NO_x in the combustion air suppresses the formation of NO_x in the boiler resulting in a net destruction of NO_x .

The heated sorbent is transported through an L-valve to the steam disengaging vessel. Transport steam is separated from the sorbent to reduce the volume of the off-gas stream. Sorbent gravity flows into the regenerator where it is contacted with natural gas. The sulfur on the sorbent combines with the methane and forms SO_2 and H_2S by the following series of chemical reactions.



Additional regeneration occurs in the steam treater section of the regenerator when the sorbent is contacted with steam, converting the remaining sulfur on the sorbent to H₂S. The regenerator off-gas stream is directed to a sulfur recovery plant where the H₂S and SO₂ are converted to elemental sulfur. Tail gas from the sulfur recovery plant will be oxidized and recycled back through the adsorbers to remove any residual sulfur compounds.

The elemental sulfur will be shipped to Olin Corporation where it will be oxidized to SO₂ using a stream of oxygen. The SO₂ vapor is then separated from other gaseous components, compressed, and liquified.

High temperature sorbent exiting the regenerator is conveyed with an L-valve to the four-stage fluidized-bed sorbent cooler. The sorbent flows counter to the ambient air which cools the sorbent. Regenerated sorbent exits the cooler at 320°F. The sorbent is then conveyed through an L-valve to the sorbent surge tank before being returned to the adsorber, completing the sorbent cycle.

Ambient air which is forced through the sorbent cooler by the heater-cooler fans exits the sorbent cooler at approximately 950°F. This preheated air then enters the air heater where it is heated to approximately 1340°F so it is capable of heating the sorbent exiting the sorbent heater to 1150°F.

3 PROJECT STATUS

The project definition and preliminary design phase of the project is complete. AGC's Warrick Power Plant has been selected as the host site for the project and a project agreement between NOXSO and AGC has been executed.

The NOXSO pilot-plant test program was completed on July 30, 1993. Performance at the pilot plant exceeded the initial expectations for pollutant removal efficiency, sorbent attrition, and electrical power and natural gas consumption. Data from the pilot plant has been incorporated into a fully integrated computer simulation which efficiently performs heat and material balances for the combined NOXSO plant, power plant, and sulfur recovery plant. The computer program also calculates sizes and capacities for the major process equipment. This computer simulation is used to evaluate process alternatives to determine their impact on process economics.

A preliminary process flow diagram and associated heat and material balances have been prepared for a commercial-size plant. This flow diagram incorporates lessons learned from the pilot-plant test program as well as results of laboratory process studies, theoretical process studies, and the computer simulation. Preliminary piping and instrumentation diagrams have been prepared for a commercial-size plant based on the pilot plant experience and the preliminary process flow diagram.

A general arrangement has been prepared which incorporates plant design practices developed for the fluidized-catalytic-cracking (FCC) industry. Specifically, this design utilizes self supporting vessels, supported by skirts which extend from the vessel base to the foundation. In contrast, the POC design utilized a tower of structural steel on which the process vessels were mounted.

3.1 Project Management

The continuation application and funding increase request were submitted to the DOE on September 16, 1994. The continuation application reported the accomplishments for phase 1A (Project Definition and Preliminary Design) and the justification for proceeding to phase 1B (Front End Engineering/Environmental Evaluation). The funding increase is required due to the change to a larger host site, cost growths due to the delay while selecting a new host site, escalation as a result of the delay, design changes as a result of the pilot plant test program, and the change to liquid SO₂ as the project by-product.

The continuation application and funding increase requests have been reviewed by the PETC project management team, summarized, and forwarded to headquarters with a recommendation for approval of both. Several project briefings have been prepared by PETC personnel in response to questions asked by DOE headquarters personnel during the evaluation of the requests. Phase 1A was scheduled to end on November 1, 1994. Since headquarters has not completed their evaluation, phase 1A has been extended until December 31, 1994.

A preaward authorization request has been made to allow phase 1B activities to be initiated prior to final approval of the continuation request.

Negotiations are continuing with two potential customers for the purchase of the liquid SO₂ to be produced by the project. The liquid SO₂ plant will be located on the customer's site to minimize transportation cost and concerns associated with transporting the hazardous material.

All project management reports have been prepared and submitted to DOE detailing project status, schedule, costs and labor expended.

3.2 NEPA Compliance

The Alcoa Generating Corporation's Warrick Power Plant will be the host site for the NOXSO Process and the Sulfur Recovery Unit. Two sites are being evaluated for the Liquid SO₂ Unit, however, a final selection has not been made. The potential sites for the Liquid SO₂ Unit are discussed in Section 3.5.4. The Environmental Information Volume will be divided into two main sections, one for each host site.

This quarter a data needs list was developed for the Warrick site and the majority of this data has been collected. The preliminary EIV is currently being updated to include this new information. It is anticipated that the Warrick section of the EIV will be completed by the end of January. Any additional information concerning the Warrick site required for NEPA compliance will not be included in the EIV, but added as addendum reports.

An outline of the second section of the EIV, the portion for the Liquid SO₂ Unit, and a data needs list has been completed. Work on this portion of the EIV has been suspended pending the selection of the host site and the liquid SO₂ production process.

3.3 Preliminary Engineering

3.3.1 Heat and Material Balance

Heat and material balances for the NOXSO Process have been finalized based on existing conditions at the Warrick Power Plant. The balances were generated using the NOXSO Process simulation program and the criteria shown in Table 3-1. The balances have been independently checked for accuracy and are currently being used to design and size process equipment, vessels, and piping and prepare equipment specifications for vendor bid.

Table 3-1. Design Criteria

Coal	
Type	100% Squaw Creek
Feed rate lbs/hr	130,000
Sulfur content wt%	3.4%
Flue Gas	
Flow rate scfm	371,500
Temperature °F	322
Pressure "H ₂ O absolute	401.6
O ₂ content mole%	5.3
NO _x Content ppmw @ 3% O ₂	514

3.3.2 Process Flow Diagram and Piping & Instrumentation Diagrams

The process flow diagram (PFD) is being revised to reflect the new heat and material balances as described in the previous section. The PFD is scheduled to be issued for approval in January 1995. Several process revisions were included in the latest version of the PFD and these are detailed below.

The steam, used to convey sorbent in the sorbent heater to disengaging vessel L-valve and the regenerator to sorbent cooler L-valve, is supplied by the sulfur recovery unit (SRU). The latest revision includes superheating the steam to 1200°F by placing a heat exchanger in the ductwork between the air heater and the sorbent heater. Superheating the steam helps maintain higher regeneration temperatures which in turn increases the rate of regeneration. Ultimately, this should allow higher sulfur loadings to be regenerated from the sorbent. In addition, the steam supply pressure was changed from 15 to 25 psig.

The pressure differential across the standpipe connecting the disengaging vessel and the regenerator is controlled so that a small amount of steam flows from the disengaging vessel to the regenerator. Previously this pressure differential was set at one inch of water. Calculations show that the amount of steam transferred is small, even when this pressure differential is increased to 10 inches of water. The higher pressure differential is used since it is easier to measure and control.

Previously the small amount of NO_x formed in the sulfur-recovery unit's tail-gas incinerator was not included in the material balance. This has now been added.

The sorbent cooler's sorbent exit temperature was increased from 315 to 325°F. This was done to reduce the gas flow through the sorbent heater/sorbent cooler train. There is minimal impact on the adsorber energy balance as this simply requires spraying a small additional amount of water to control the adsorber temperature.

The natural gas heating value was changed from 937 to 1000 Btu/scf to more accurately reflect the local natural gas conditions.

The attrited sorbent and fly ash material balances were modified to reflect the higher collection efficiency of the baghouse that has replaced the mechanical separator downstream of the adsorbers. The attrited sorbent and fly ash collected in the baghouse are routed to the fly ash sluice lines and deposited in the power plant's ash ponds. Previously it was assumed that some sorbent was removed by the existing plant ESP. This assumption has been eliminated. Now it is assumed that no sorbent is removed by the ESP, but the downstream baghouse has an assumed 99% efficiency. Work on the piping and instrumentation diagrams is ongoing. The current work involves updating line sizes based on the newest heat and material balances. In addition, the heat exchanger and related piping has been added for the L-valve steam superheater. The P&ID's are scheduled to be issued for approval at the end of January 1995. The sulfur plant P&ID and the trip matrices are scheduled to be issued for approval in February of 1995.

3.3.3 Mechanical Design of Process Vessels

The preliminary design of the major process vessels and their internal structures has been completed, and more detailed design work has begun. The major process vessels are the fluid-bed vessels: the adsorbers, sorbent heater, and sorbent cooler; and the steam disengaging vessel and regenerator which are moving-bed vessels. Vessel internals include the grids, grid supports, downcomers, and flapper valves in the fluid-bed vessels, and sparger rings in the regenerator. Preliminary design included the selection of vessel design temperatures, pressures, and loads, as well as establishing the preliminary vessel configurations and dimensions. Detailed design will include vessel load and stress calculations to determine the final vessel configurations, materials of construction, and shell thicknesses; the preparation of mechanical drawings for

construction; and the establishment of operating procedures. The results of the preliminary evaluation are presented here.

Adsorbers

The purpose of the adsorbers is to contact flue gas with NOXSO sorbent in a two-stage, fluid-bed reactor. The demonstration plant has two adsorbers to handle the volume of flue gas generated and to provide adequate turndown capabilities. Operating and design conditions for the adsorbers are shown in Table 3-2.

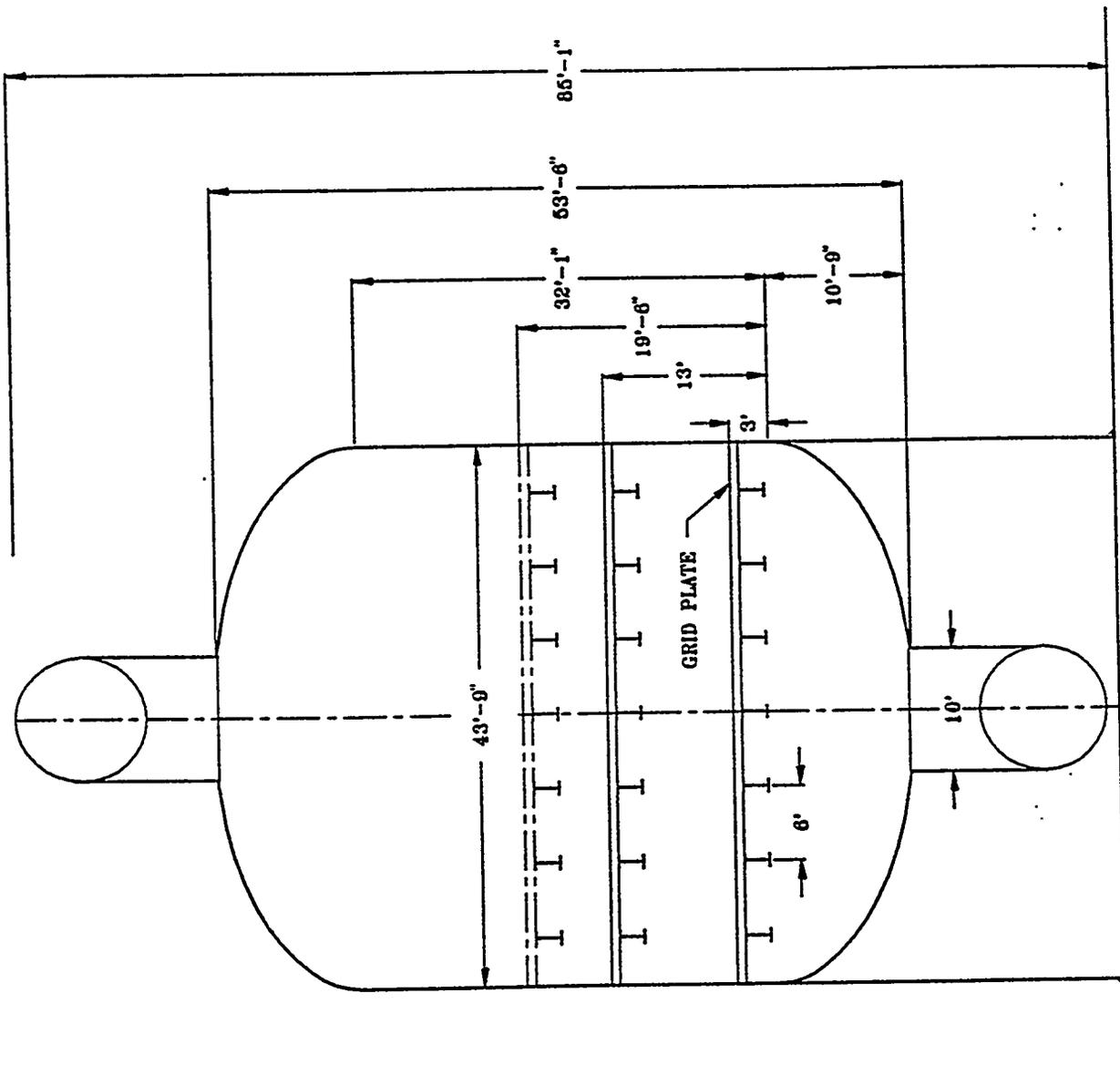
Table 3-2. Adsorber Design and Operating Conditions

	Operating	Design
Temperature, °F	275	650
Internal Pressure, psig	1.2	3.5
Vacuum, "H ₂ O		5.0
Sorbent Static Load, ft/stage	1.5	3.0
Corrosion Allowance, in		0.125

The general configuration and preliminary vessel dimensions are shown in Figure 3-1. The vessel has a cylindrical shell with 2:1 ellipsoidal heads, and is skirt supported. One significant aspect of the adsorber design is that the vessels are being designed for three grids, while only two grids are currently anticipated. Laboratory testing is being conducted (Section 3.5.1) to provide data to make the final decision. It is believed that the third bed may improve pollutant removal and/or decrease operating costs. Designing for the additional stage initially will simplify design changes if a three-stage adsorber is selected.

Due to the relatively low design temperature and pressure, the detailed design of the adsorbers will be the least difficult of the major vessels. Based on these specifications and other process considerations, the design of the adsorbers will avoid having to use refractory linings or exotic materials of constructions.

Figure 3-1. ADSORBER V-101 A & B



Sorbent Heater

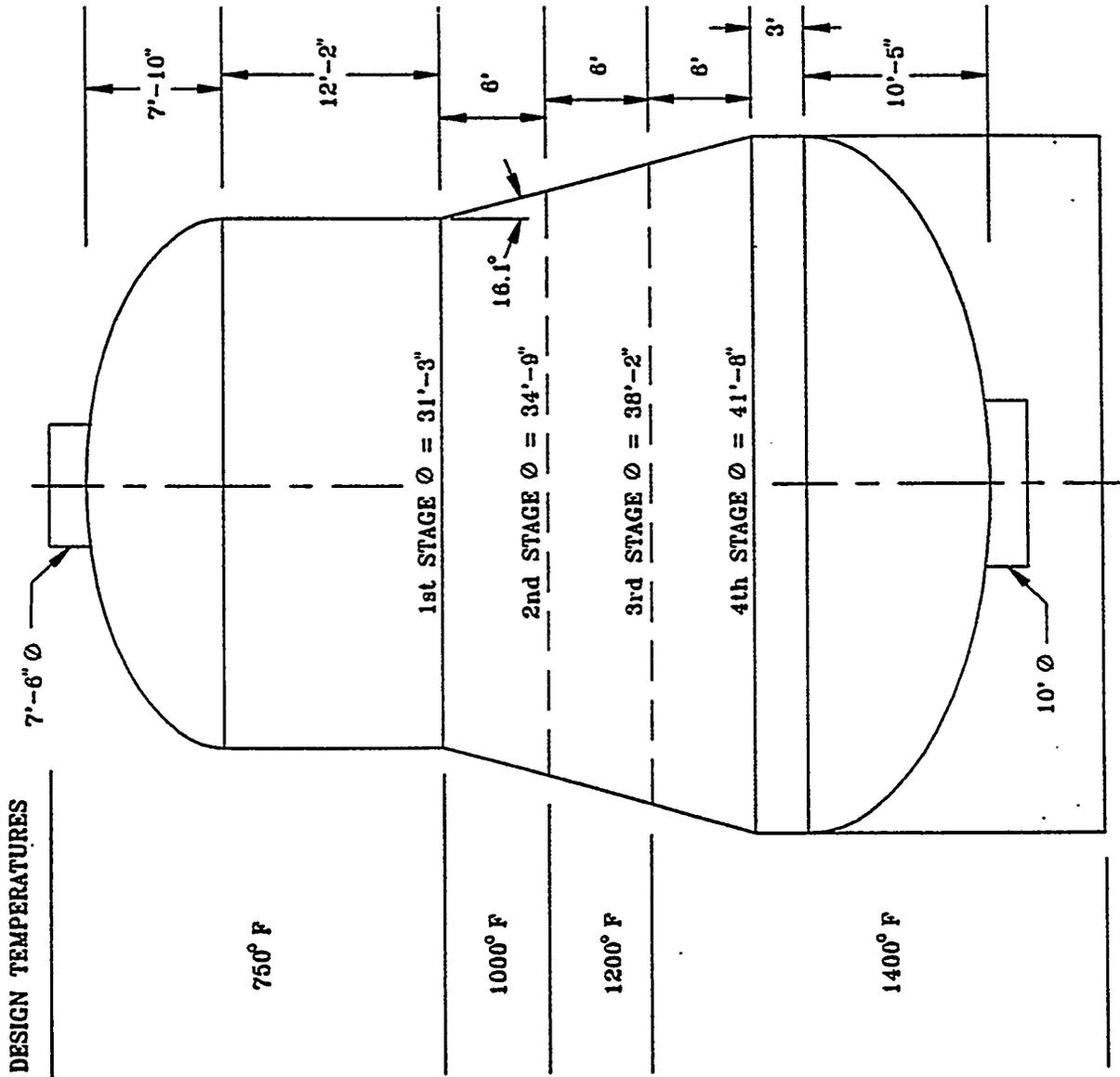
The purpose of the sorbent heater is to raise the sorbent temperature from 275 to 1150°F prior to sorbent regeneration. The general configuration of the sorbent heater has been presented previously (Quarterly Technical Report No. 13), Figure 3-2 shows this configuration with the preliminary vessel dimensions and design temperatures for the various areas of the vessel. The design temperatures are varied along the length of the vessel in order to relax the mechanical requirements of the vessel material in the upper, cooler sections of the vessel. Operating and design conditions for the sorbent heater are shown in Table 3-3.

Table 3-3. Sorbent Heater Operating and Design Conditions

	Operating	Design
1 st Stage (Top) Temperature, °F	370	750
2 nd Stage Temperature, °F	610	1000
3 rd Stage Temperature, °F	865	1200
4 th Stage Temperature, °F	1100	1400
Internal Pressure, psig	1.8	5.0
Internal Vacuum, "H ₂ O		5.0
Sorbent Static Load, ft/stage	3.0	3.0
Corrosion Allowance, in		0.125

The sorbent heater represents the most difficult fluid-bed design challenge in the demonstration plant. The fundamental concern for designing the sorbent heater is the effect of high temperatures in the bottom region of the vessel on material selection and design life. Besides being directly related, material selection and design life are affected by: design temperature, design pressure, structural stability, and process considerations. Two options currently being considered are a cold-wall design (internal refractory lined), and hot-wall design (external insulation on an all metal shell). The problem with allowing the wall to take the full temperature concerns creep stress limitations. The best way to assure that the vessel will meet the design life expectancy is to limit the shell material temperature to a value below the creep range.

Figure 3-2. SORBENT HEATER V-102



A related issue to the high shell temperature of the hot-wall design is thermal expansion. The shell and internals will move together, but supporting the internals at the shell will be a problem because of the low allowable shell stress. The shell will expand about 6 inches in diameter. If the vessel is supported on a skirt welded directly to the bottom head, there will be a severe temperature gradient along the skirt. The stress in the skirt would then be unacceptable, resulting in some kind of support lug arrangement to allow for radial growth. The lugs would have to be massive in order to support the vessel, allow for radial growth, and be within acceptable stress limits.

Since the diameter is about equal to the height, the axial growth will be of similar magnitude. The expansion will cause extreme loading and stress conditions on the connecting piping and expansion joints may be needed to further complicate the design. The result of this analysis is that the cold-wall design may be the best solution, and is currently being further examined. A cold-wall design may also minimize any problems related to vessel supports, piping and other external loads.

Sorbent Cooler

The purpose of the sorbent cooler is to reduce the temperature of the sorbent from 1050 to 300°F prior to being returned to the adsorbers. It is anticipated that much of the knowledge gained during the design of the sorbent heater will be directly applicable to the design of the sorbent cooler, thus the information on this vessel is currently limited to the design conditions and preliminary configuration, and size. Figure 3-3 shows the configuration and dimensions, as well as the design temperatures for the various areas of the vessel. Operating and design conditions for the sorbent cooler are shown in Table 3-4.

Fluid Bed Vessel Internal

In the present design, fluid-bed vessel internals consist of grid plates to distribute the flue gas and downcomers to transport the sorbent. The grid plates are made from 10-12 gauge type 304 SS with 5/32" diameter punched holes. The grid plates are designed to allow for removal and replacement. To accomplish this, the grid plates are made in sections 20" in width, for access through 24" manways. The plates are formed into channel sections and clamped between support angles with bolts for all interior connections. This provides a gas tight seal without gasketing, and allows grid holes to be continued across the joints without loss of fluidization

Figure 3-3. SORBENT COOLER V-105

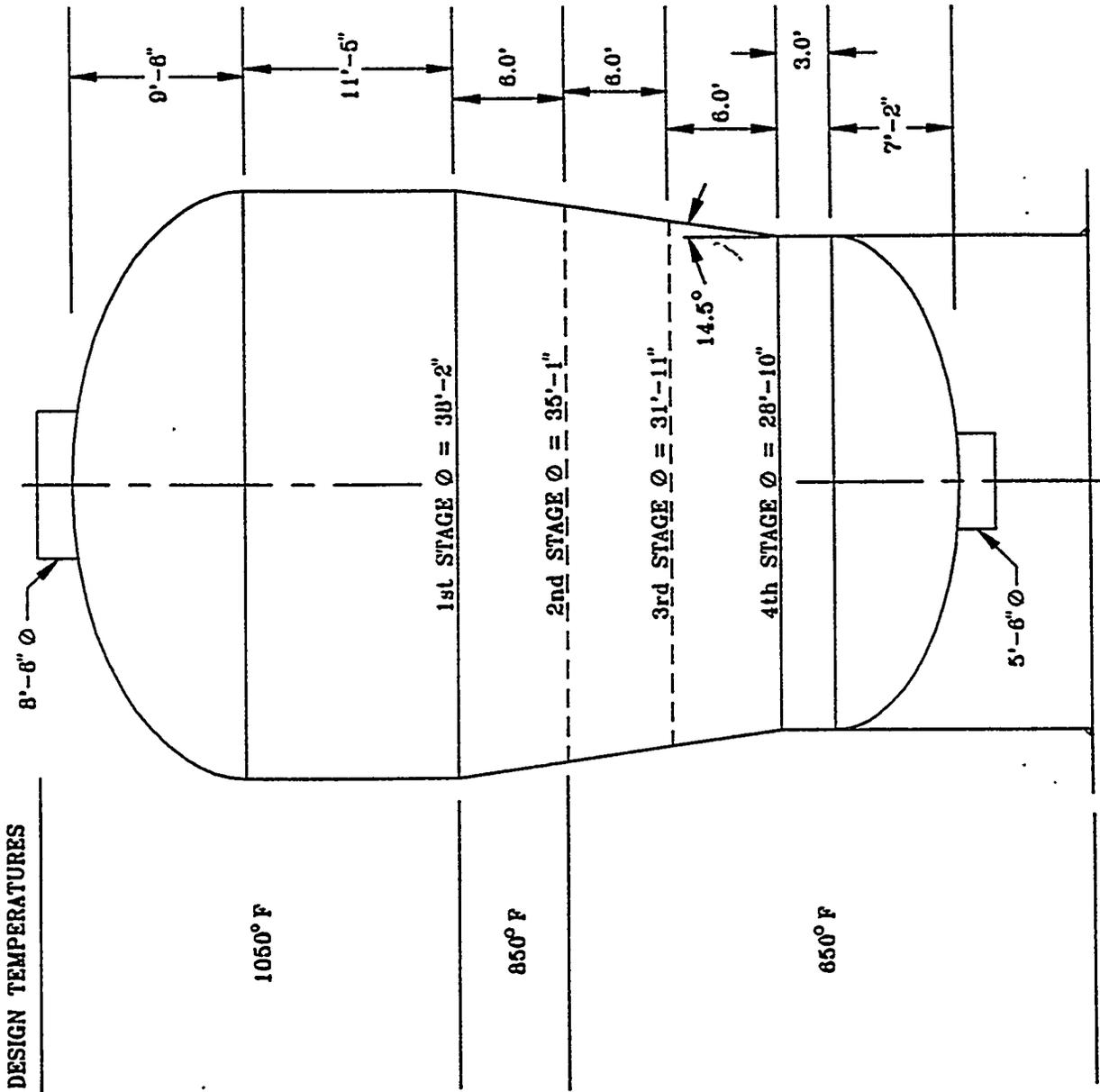


Table 3-4. Sorbent Cooler Operating and Design Conditions

	Operating	Design
1 st Stage (Top) Temperature, °F	900	1050
2 nd Stage Temperature, °F	715	850
3 rd Stage Temperature, °F	530	650
4 th Stage Temperature, °F	350	650
Internal Pressure, psig	2.8	5.0
Vacuum, "H ₂ O		5.0
Design Sorbent Static Load, ft/stage	1.0	3.0
Corrosion Allowance, in		0.125

area. The grid outer edges are clamped between rolled angles which are bolted to rolled angles welded to the vessel wall. Bolting is to allow for differential thermal expansion without buckling of the grid material. The grid hole pattern is determined so that the pressure drop through the bottom grid plate is 40% of the pressure drop through the bottom bed at normal operating conditions, the pressure drop through the remaining grids is 30% of the corresponding bed drop.

The downcomers are rectangular or circular ducts that transport the sorbent from stage to stage within the vessels. There is one downcomer per adsorber, and two downcomers per stage (except the bottom stage) in the sorbent heater and cooler, with a cross sectional area of 1.9 ft². The downcomer also contains an overflow weir and a flapper valve. The height of the overflow weir is 1.2 times the settled bed height, and at least one side of the overflow must be removable so that the beds can be drained. The downcomer outlet is 2 inches above the bottom grid to prevent the possibility of interference with flapper valve operation. A flapper valve is required to prevent gas bypassing through the downcomer, particularly when there is no sorbent in the top bed or downcomer. The flapper valve is simply a metal plate that covers the downcomer sorbent outlet when hanging normally, and can swing freely open to allow sorbent to exit the downcomer when a sufficient sorbent level exists in the top bed.

While it is the present intent to use this design in all of the fluid-bed vessels, other options may need to be examined for the sorbent heater and cooler depending on the final choice of materials of construction.

Steam Disengaging Vessel and Regenerator

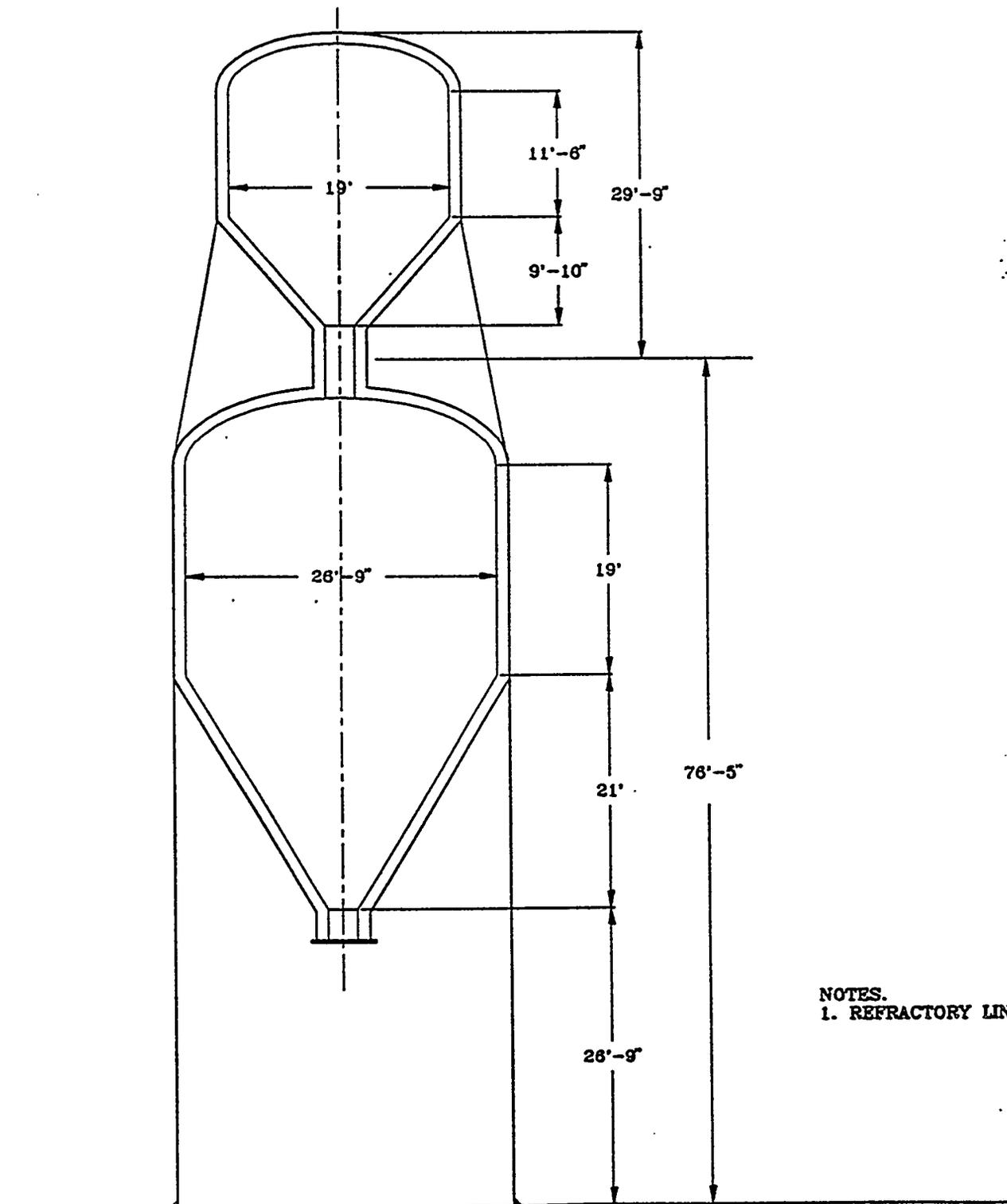
The purpose of the steam disengaging vessel is to separate the top L-valve transport steam from the sorbent prior to its introduction to the regenerator. This reduces the volume of the regenerator off-gas stream, reduces the size of the sulfur recovery unit and increases the sulfur conversion efficiency. The steam disengaging vessel and regenerator are in a stacked arrangement as shown in Figure 3-4. Because of the high operating temperature and corrosive gas environments, these vessels will be internally refractory lined, with carbon steel shells.

The steam disengaging vessel is sized to provide a sorbent residence time of 20 minutes at the base case sorbent circulation rate. During normal operation, the vessel is half full so that operations may continue for ten minutes with the inlet or outlet flow completely stopped. At the maximum sorbent circulation rate, steam disengaging vessel residence time is 18 minutes. A shallow cone angle of 50° is used because no chemistry occurs in this vessel and solid flow patterns are not critical. Any number of height and diameter combinations will provide the necessary volume, thus preliminary calculations use a height to diameter ratio of approximately 1:1, where the height includes the cone section as well as the cylindrical section of the vessel. Demonstration plant design conditions for the regenerator vessel are the same as for the steam disengaging vessel and are discussed below.

The purpose of the regenerator is to contact the sulfur laden sorbent with natural gas followed by contact with steam to remove the sulfur from the sorbent. The regenerator off-gas is then processed in the sulfur recovery unit and the sulfur-free sorbent is recycled back to the adsorbers via the sorbent cooler. The sorbent residence time in the methane treatment section of the regenerator is 50 minutes at the base case sorbent circulation rate, the steam treatment section residence time is 15 minutes. The steam treatment residence time is based on the assumption that 75% of the cone volume is active in the process chemistry. The cone angle at the exit of the regenerator is 60°. A steeper cone angle is required here to maintain, as best as possible, plug flow of solids through the regenerator, due to the process chemistry involved. The vessel height to diameter ratio is approximately 1.5:1 where the diameter is the vessel inside diameter (excluding refractory and shell thickness), and the height includes the cone as well as the cylindrical portion of the vessel.

The normal operating temperature in the regenerator and the steam disengaging vessel ranges from 1150°F at the inlet to 1085°F at the outlet. The internal design temperature is 1200°F and

Figure 3-4. STEAM DISENGAGEMENT VESSEL V - 115
AND REGENERATOR V - 103



NOTES.
1. REFRACTORY LINING 1" THICK.

is based on the maximum sorbent temperature at the outlet of the sorbent heater. Both vessels are refractory lined, as detailed in Quarterly Technical Progress Report No. 8. The external operating temperature is 130°F, while the design temperature is 200°F. The internal design pressure is 13 psig, and the design vacuum is 5" H₂O.

Regenerator Internals

The regenerator internals are much less complicated than the fluid-bed internals. The regenerator vessel requires two sets of sparger rings, one to introduce natural gas and one to introduce steam. The purpose of the spargers is to provide a uniform distribution of gas across the vessel cross section. In order to provide a flow maldistribution of less than 5%, the rule of thumb for the design of perforated pipe distributors in turbulent flow requires that the ratios of kinetic energy of the inlet stream to pressure drop across the outlet hole and of friction loss in the pipe to pressure drop across the outlet hole should be equal to or less than one-tenth. The base case natural gas and steam flow rates are based on the process chemistry at the normal solids flow rate loaded with 1.2 wt% sulfur. The maximum flow rates through the spargers are based on the process chemistry at the maximum solids flow rate with 1.2 wt% sulfur, plus 10%.

3.3.4 Separator Performance Test

The demonstration plant was to employ mechanical separators at the flue gas outlet of the adsorbers to remove attrited sorbent from the cleaned flue gas stream. Particle separation is necessary in order to prevent increasing the power plant's emissions of total suspended particulates (TSP), and more importantly, particulate matter which is less than 10 microns in size (PM-10). The mechanical separator chosen was a straight through flow type centrifugal separator; the manufacturer of this separator claimed a high separation efficiency and a low pressure drop. In order to verify the performance data provided by the manufacturer, a single module of the separator was tested at the NOXSO lab. The test set up and preliminary results have been presented previously (Quarterly Technical Progress Report Nos. 13 and 14). Based on the results of this test program, it has been decided that the mechanical separator will not provide adequate particulate removal and a baghouse will be used in its place.

Required Separator Performance

Once operating data for the demonstration plant host site became available, it was possible to determine the performance required of the particle separators. The host plant is a 144 MW coal-fired power plant with a calculated heat rate of 9770 Btu/KW_{hr} (based on a coal feed rate of 124,500 lb/hr and coal heating value of 11,300 Btu/lb). The plant has a permitted particulate emission rate of .228 lb/MMBtu, although normal operation is between 0.1 and 0.15 lb/MMBtu. By assuming that the post-ESP flyash PM-10 content is 67% of TSP, given as typical in AP-42, TSP and PM-10 emissions from the plant can be calculated.

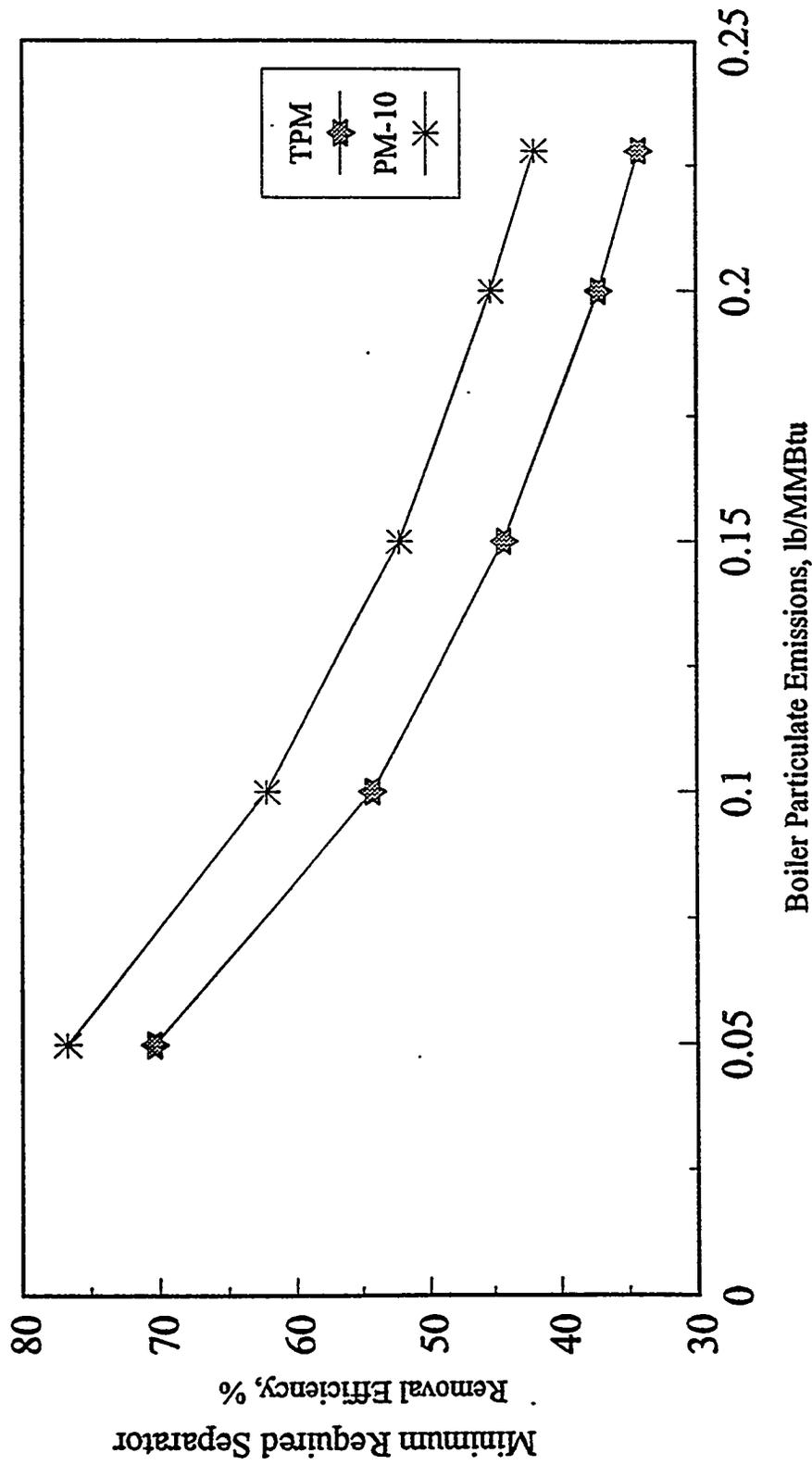
Preliminary process calculations for the NOXSO demonstration plant, as computed by the process simulation program, predict a sorbent attrition rate of 167 lb/hr, with 93% PM-10 based on POC tests. Nearly all of the attrited sorbent will exit the NOXSO system in either the adsorber off-gas/cleaned flue gas stream, or the sorbent heater off-gas/NO_x recycle stream. While it is believed that most of the attrited sorbent which exits the system in the NO_x recycle stream will be collected as bottom ash in the boiler or as flyash in the ESP, the present analysis conservatively assumes that all of the attrited sorbent will eventually find its way through the adsorbers and into the particulate control devices.

By combining the flyash and sorbent emissions, and given that the addition of the NOXSO plant must not increase the host plant's particulate emissions, either as TSP or PM-10, the required performance of the particle separator, independent of separation technology, was calculated as a function of the power plant emission rate, and is shown in Figure 3-5. Under normal operating conditions, i.e., power plant emissions of 0.1 lb/MMBtu, the separation device must capture 54% of the TSP and 62% of the PM-10 in the stream. Based on the results of the first test of the mechanical separator this efficiency can not be achieved, thus the separator with a secondary collector was tested to evaluate any improvement.

Separator Test Results

The secondary collector and test set up have been presented previously (Quarterly Technical Progress Report No. 14). In the earlier tests, large particles in the collected dust had created difficulties in the data analysis of the particle size distributions (PSD). As reported in the results of the first test, there were larger particles in the dust collected in the separator's hopper than there were in the original challenge dust. Thus, prior to the test of the separator with a

Figure 3-5. Required Separator Performance
as a function of particulate emissions



secondary collector, the challenge dust was screened so that all solid particles fed into the separator were known to be smaller than 355 μm (#45 sieve). The results of this test are presented in Table 3-5, along with the previous test results.

Table 3-5. Separator Test Results

	Dust Input, g	Primary Collector, g	Secondary Collector, g	TPM Removal, %	PM-10 Removal, %
Separator	1362	508.5	NA	37.3	1.5
with Secondary System	1362	80.6	480.7	41.2	6.9

In both cases, 1362 g of challenge dust input corresponds to 0.07 gr/acfm, or 0.131 lb/MMBtu in terms of firing rate at the demonstration plant, after correcting for the presence of attrited sorbent.

Based on Figure 3-5, the tested centrifugal separator will not meet the performance requirements of the demonstration plant. While the results were again affected by larger particles appearing in the separator collection hoppers than were originally in the challenge dust, the separator is unable to remove particles at a high enough efficiency to prevent increasing the particulate emission rates of the host plant, particularly PM-10 emissions. Because this test used pre-screened challenge dust, the appearance of larger particles again suggests particle agglomeration, thus use of an agglomerating agent upstream of the centrifugal separators may be an option for the future. However, the choice of separation technology for the demonstration plant can not wait for additional testing, so mechanical separators will no longer be considered, based on their inability to remove sufficient amounts of PM-10 material.

Design Options

With the elimination of mechanical separators, and the impracticality of ESPs, due to the low dust loading, the remaining commercially proven separation device is a baghouse. Preliminary research has begun to estimate the cost, size, and impact of using baghouses downstream of the NOXSO adsorbers. The effect of pressure drop must be carefully considered, one advantage

of the centrifugal separator which made it favorable was a low operating pressure drop. A low pressure drop is required to minimize both capital and operating costs of the demonstration plant. Also, because of the low dust loading and high flow rate of the stream to be treated (approximately 0.1 gr/acf at 560,000 acfm), the baghouse design may employ a high air-to-cloth ratio, which will reduce baghouse size and cost. Finally, because the baghouse is a high efficiency device, generally greater than 99% removal, the installation of a baghouse at the demonstration plant will result in a net reduction of TSP, PM-10, and opacity. Therefore, the baghouse design effort will attempt to optimize performance based on air-to-cloth ratio, pressure drop, and particle removal efficiency.

3.3.5 Site Layout and Undergrounds

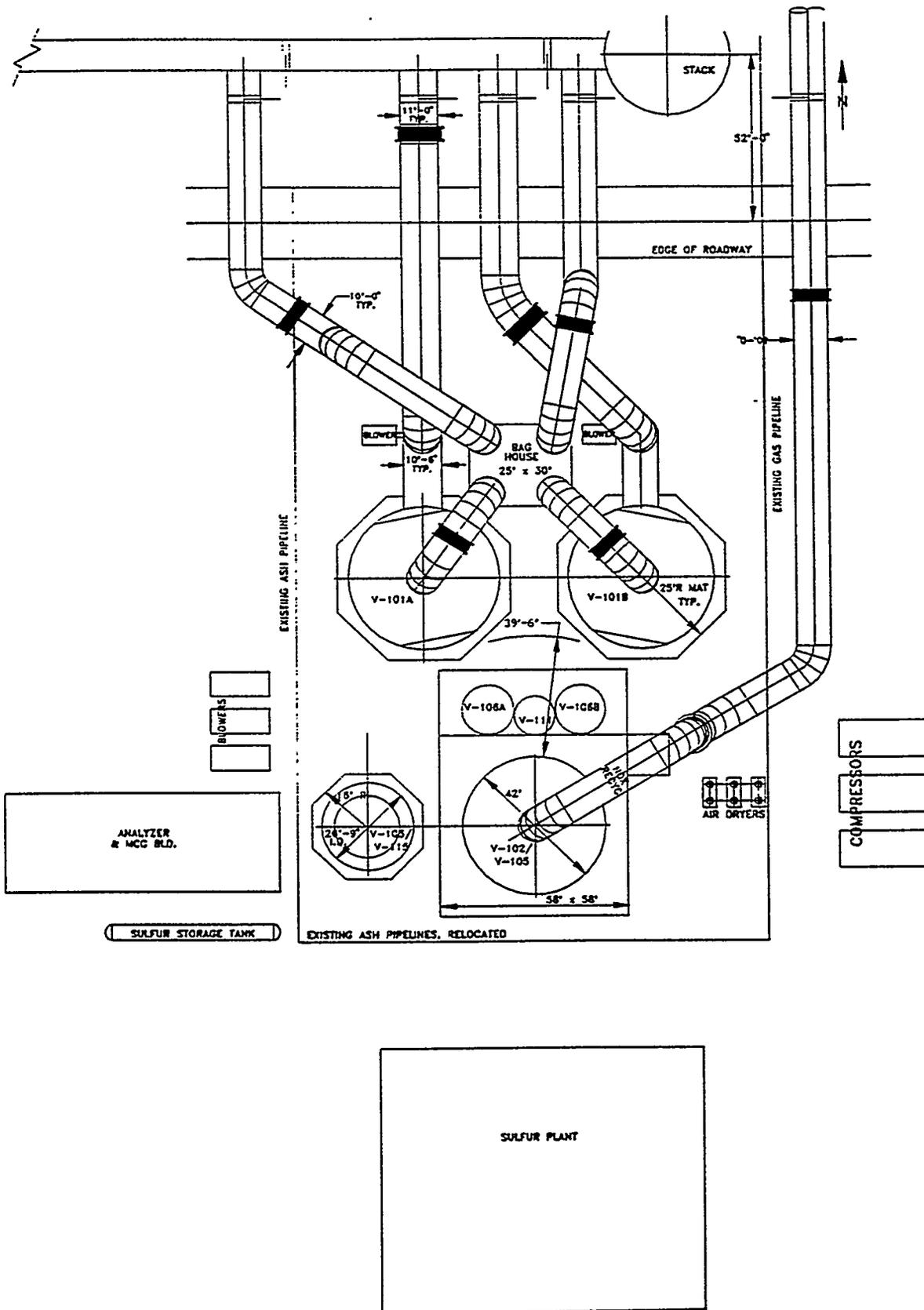
The NOXSO Demonstration Plant will be located just south of Warrick Power Plant's Unit No. 2, on the South side of the power plant. Figure 3-6 is an overhead view of the power plant site with the proposed NOXSO battery limits and the alternatives for the rail siding shown, both of these issues are discussed below.

NOXSO Battery Limits and Site Survey

The NOXSO plant will take up an area approximately 300' x 150' in size, just south of the access road which lies just south of the power plant. The plant will be bounded on the north by several underground water lines (which are located south of the roadway), on the east by the 10" natural gas main line feeding the power plant, on the south by existing ash lines which will be relocated south by about 25' to accommodate the NOXSO plant, and on the west by Unit #2's ash line. This area gives adequate space for the NOXSO plant installation and offers a convenient tie-in point for the flue gas ductwork, the plant flue gas duct is just north of the access road. The preliminary site layout is shown in Figure 3-7.

Another advantage to the selected site is that site preparation activities will be minimal. Figure 3-6 shows a building on the eastern edge of the NOXSO battery limits. This building was originally built as a temporary storage building and will be removed as opposed to relocated. The figure also shows what is a chemical drain system on the western edge of the battery limits; this drain is actually west of the ash lines shown as the battery limit in Figure 3-7, thus it will not interfere with NOXSO plant operations. Besides the ash lines to the south, there are few underground lines in the area of the NOXSO plant which will need to be relocated. The

Figure 3-7. Preliminary Site Layout



remaining underground lines, in the area of the sulfur plant and the transformer have yet to be fully evaluated; however preliminary evaluations suggest that this will not delay the project. All of the site survey and geotechnical work required for this project is expected to be completed during the coming quarter.

Site Layout

The locations of the major process vessels are chosen to minimize the amount of ductwork required to deliver and return the flue gas, and to minimize the lengths of the horizontal runs required at the discharge points for the L-valves. Thus, the adsorption trains, including booster fans, adsorbers, and baghouses, are situated the furthest north within the battery limits. While Figure 3-7 shows only one baghouse, modular design allows the two halves of the baghouse to be isolated and dedicated to the two adsorption trains.

The regeneration train is just south of the adsorption trains. The sorbent cooler and sorbent heater are in a stacked arrangement, and centered behind the two adsorbers, to minimize the horizontal distance requirement of the dense phase conveyors, and the sorbent cooler to adsorber L-valves. The tower height for the sorbent heater is not known precisely as of yet, due to uncertainties in the size of the duct mounted air heater between the sorbent cooler and sorbent heater, but preliminary calculations estimate a distance of 155' to the top of the sorbent heater off-gas duct.

The regenerator and steam disengaging vessel, also in a stacked arrangement, are situated as close as possible to the sorbent cooler, to minimize the horizontal runs required of the L-valves into and out of the regenerator. The regenerator is shown to the west of the sorbent cooler in Figure 3-7 in order to minimize the amount of ductwork required for the NO_x recycle stream. While the locations of the auxiliary equipment, i.e., air compressors, analyzer and MCC building, sulfur plant and sulfur storage tank, may change from their preliminary placement as shown in Figure 3-7, the locations of the major process vessels should change location very little if at all.

Rail Siding Location

While there are rail lines north of the power plant switchyard for coal delivery, an additional rail siding must be built to provide service to the sulfur plant. Norfolk Southern Railway was

consulted to provide alternatives for track layouts in order to serve the sulfur load out requirements. Alternatives A and B of Figure 3-6 were the alternatives presented. Alternative A is not possible since it requires routing through Alcoa's engine maintenance building. Alternative B is not practical because the track does not extend to the sulfur storage tank area. Alternative C, a combination of alternatives A and B, is the layout of choice because it provides direct access to the sulfur plant site, and a direct link to the main rail line. Norfolk Southern noted that the radius of curvature of this alternative may be less than they would recommend for a main line; however, when explained that use would be infrequent, and at very slow speed, agreed that it is a viable alternative. The site of the proposed route has been examined with all obstructions, changes in elevation, and required turns observed and noted. The site survey and geotechnical investigation will be conducted independently from work done for the NOXSO plant, sulfur plant and transformer sites; however, this work should also be completed in the coming quarter.

3.4 Nitrogen Oxide Studies

No nitrogen oxide studies were conducted during this reporting period, and no nitrogen oxide studies will be required for the plant at Warrick.

3.5 Process Studies

3.5.1 Laboratory Fluid-bed Adsorber Model

Laboratory Multi-stage Fluid-bed Reactor (MSFBR)

The design of the plexi-glass MSFBR used to confirm fluidization characteristics, sorbent transport, and downcomer/flapper design is shown in Figure 3-8 and Figure 3-9 (flapper detail not shown). Figure 3-8 shows the reactor arranged with two 18-inch fluid beds similar to what was tested at the POC. Figure 3-9 shows the reactor arranged with three 12-inch beds, similar to the proposed arrangement for improved performance.

Figure 3-8. MSFBR with Two 18-inch Deep Beds

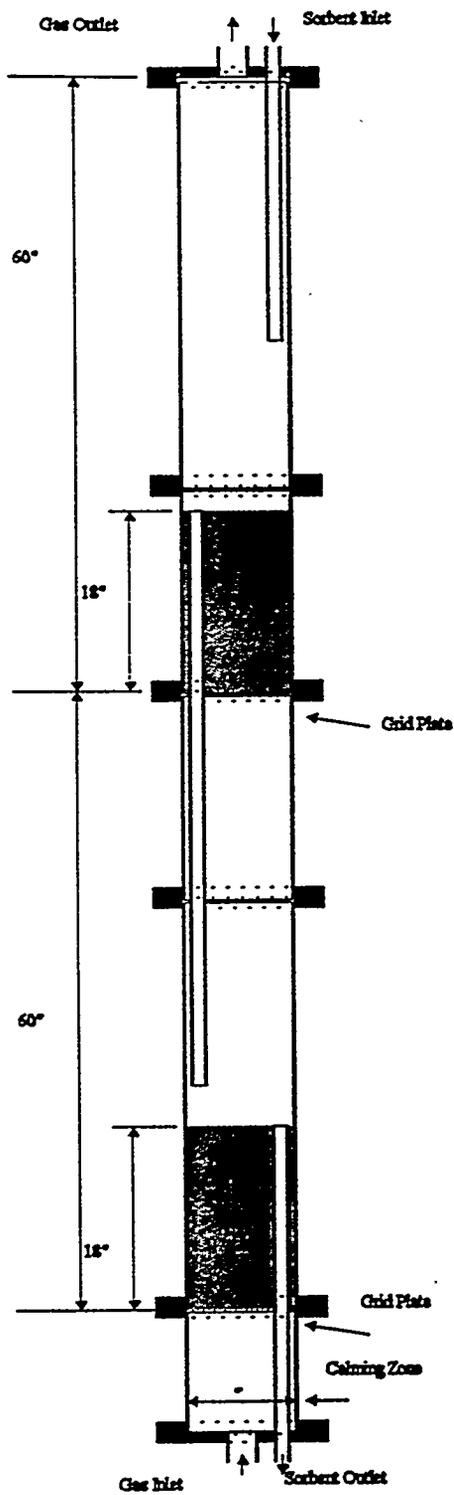
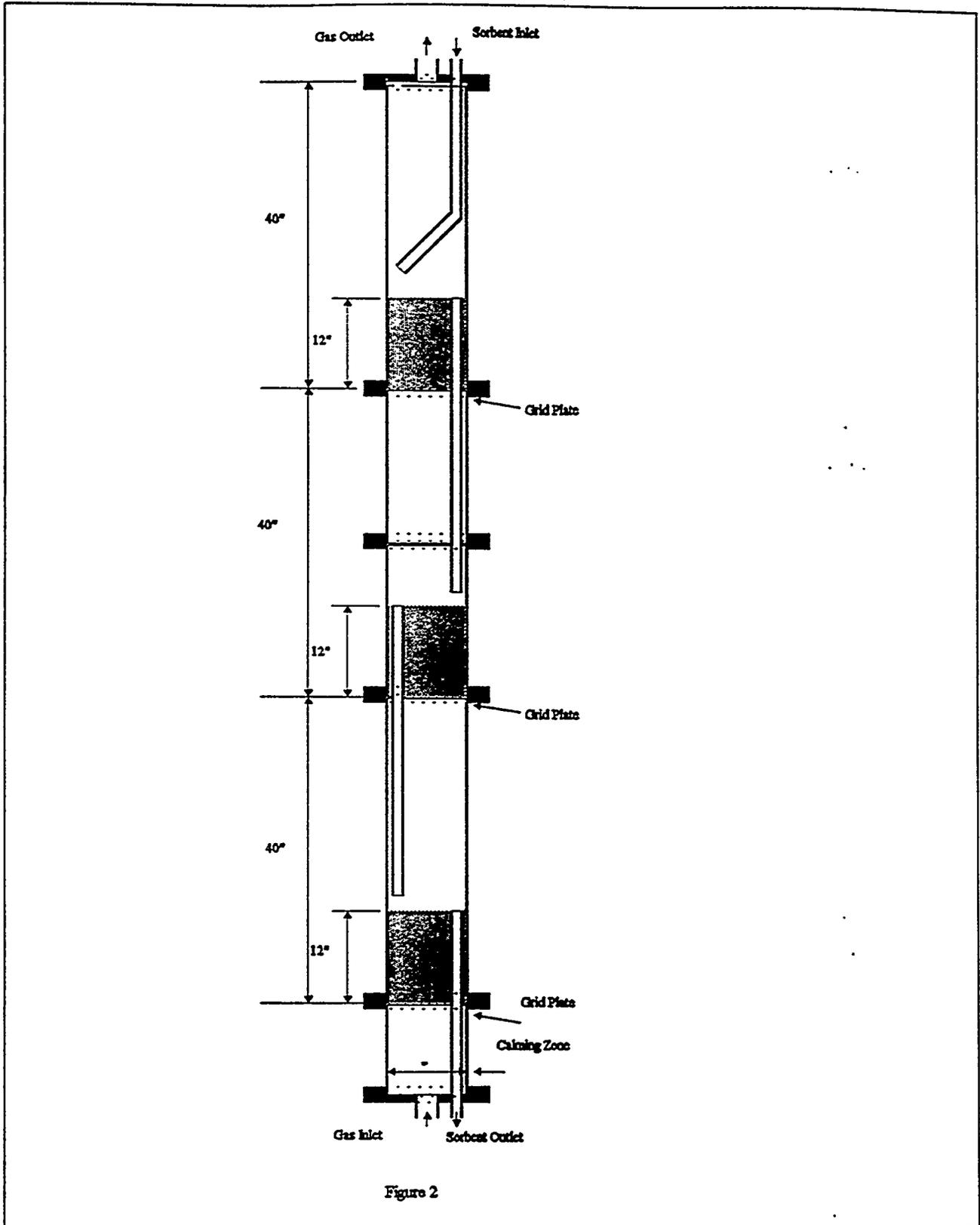


Figure 1

Figure 3-9. MSFBR with Three 12-inch Deep Beds



Testing

The MSFBR downcomers were tested using first a two-stage vessel requiring only one downcomer and flapper. Then a three-stage vessel was used to test the final downcomer and flapper design. The three-stage vessel used two downcomers and two flappers. In addition to the specific design of the flapper, operating parameters which affect the flapper performance include downcomer length, fluid bed depth, and grid pressure drop.

Three flapper designs were tested in the three-stage vessel. The first flapper used in the three-stage vessel was the last flapper used in the two-stage vessel. The downcomer lengths were shorter because of the closer grid-to-grid spacing for the three-stage vessel. For this reason, the downcomer could fill but could not produce adequate pressure on the flapper needed to push it open. Therefore, the same flapper that worked with the two-stage vessel failed to operate with the three-stage vessel. The second flapper was a totally new design. This new design also failed to prime the downcomers automatically during the initial loading of the sorbent. The biggest problem was the gas by-pass through the downcomer, which created a hang or blow-out in the downcomer. A third and final design had a reduced outlet area with a diameter of 7/8", opposed to the 1" oval created by the 45 degree cut on the 1" tube. The vessel was primed and loaded without a problem. A maximum flow rate of 152 lbs/hr was attained with this arrangement. This flow rate is about 50% greater than the maximum required for adsorption tests to be conducted in the metallic model.

3.5.2 Regenerator Computer Model Update & Results

During this quarter the moving-bed regenerator computational model was used to fit the POC regeneration data. The purpose was to verify the proposed regeneration chemistry and reaction mechanism. The POC data obtained from July 26, 1992 day-shift to November 22, 1992 night-shift were selected for the analysis. During this period, the material balance of the POC plant was closed within $\pm 15\%$. This gives an idea of the quality of the experimental data. Since the CH_4 treater off-gas contained steam from the top J-valve, the data of water concentrations in the off-gas are invalid for the data analysis. In the report, the "measured" water concentrations were actually estimated according to the following equation,

$$[\text{H}_2\text{O}] = 2[\text{CO}_2] - [\text{H}_2\text{S}]$$

which assumed the methane's hydrogen atoms producing only H₂O and H₂S. These "measured" water concentrations are not used in the data analysis, but are cited to compare with those calculated from the computational model.

After intensive data correlation, it is concluded that only seven reactions are needed to correlate the POC data. These reactions are shown in the following.

- (1) $\text{H}_2\text{S} + \text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 \rightarrow 2 \text{NaAlO}_2 + \text{SO}_2 + \text{H}_2\text{O} + 1/x \text{S}_x$
- (2) $\text{H}_2 + \text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 \rightarrow 2 \text{NaAlO}_2 + \text{SO}_2 + \text{H}_2\text{O}$
- (3) $3 \text{H}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{S} + 2 \text{H}_2\text{O}$
- (4) $\text{CH}_4 + 4 \text{Na}_2\text{SO}_4 + 4 \text{Al}_2\text{O}_3 \rightarrow 8 \text{NaAlO}_2 + 4 \text{SO}_2 + \text{CO}_2 + 2 \text{H}_2\text{O}$
- (5) $\text{CH}_4 + \text{SO}_2 \rightarrow \text{CO}_2 + \text{H}_2 + \text{H}_2\text{S}$
- (6) $\text{CO}_2 + \text{CS}_2 \rightarrow 2 \text{COS}$
- (7) $\text{CH}_4 + 2/x \text{S}_x \rightarrow \text{CS}_2 + 2 \text{H}_2\text{S}$

Based on those reactions, regeneration is likely to start with methane reactions. Methane first reacts with spent sorbent according to reaction 4 to produce SO₂. Then, methane reacts with sulfur dioxide and forms H₂ and H₂S according to reaction 5. Methane, hydrogen and hydrogen sulfide together regenerate the spent sorbent through reactions 1, 2 and 4, however, most sorbent is regenerated by hydrogen sulfide. Reactions 3, 6, and 7 do not participate in the actual regeneration of the sorbent, however, these reactions impact the final composition of the off-gas stream.

The reaction heats, Gibbs free energies, and equilibrium constants for the seven reactions are listed in Table 3-6. All the proposed Na₂SO₄ (1,2,&4) reactions have positive Gibbs free energies and equilibrium constants which are less than one. A positive Gibbs free energy means that the reaction is thermodynamically unlikely. Since regeneration occurs, the alumina and associated hydrates must play some roles in regeneration. For example, reaction 2 can be rewritten with various hydrate forms to make Gibbs free energy negative. Some of the alternative forms of reaction 2 are listed in Table 3-7, which also contains the reaction heats and Gibbs free energies.

Although the moles of H₂O produced have changed to balance the hydrates, the stoichiometric ratio between H₂ and Na₂SO₄ remains the same. Because the stoichiometric ratio is unchanged, the POC data can be correlated with any alternative form. To avoid guessing the number of

Table 3-6. Reaction Heats, Gibbs Free Energies, and Equilibrium Constants of the Regeneration Reactions

Reaction	Reaction Heat, kcal/mol	Free Energies, kcal/mol	Equilibrium Constant
1	75.917	25.915	3.257e-7
2	54.45	14.657	2.143e-4
3	-53.018	-35.397	7.253e+8
4	262.693	58.056	2.933e-15
5	-8.125	-35.970	1.009e+9
6	-1.753	-3.963	9.818
7	-24.3	-27.902	9.650e+6

Table 3-7. Alternated Hydrogen Regeneration Reaction Equations

Possible Equation Form for Reaction 2	Reaction Heat, kcal/mole	Free Energy, kcal/mole
$H_2 + Na_2SO_4 \rightarrow Na_2O + SO_2 + H_2O$	96.386	58.607
$H_2 + Na_2SO_4 + Al_2O_3 \rightarrow 2NaAlO_2 + SO_2 + H_2O$	54.45	14.657
$H_2 + Na_2SO_4 + Al_2O_3 \cdot H_2O \rightarrow 2NaAlO_2 + SO_2 + 2H_2O$	75.651	0.391
$H_2 + Na_2SO_4 + Al_2O_3 \cdot 3H_2O \rightarrow 2NaAlO_2 + SO_2 + 4H_2O$	87.993	-36.835
$H_2 + Na_2SO_4 \cdot 10H_2O + Al_2O_3 \rightarrow 2NaAlO_2 + SO_2 + 11H_2O$	123.75	-142.357

hydrated water molecules, reaction equations without hydrates are used to correlate the regenerator off-gas concentrations at constant temperature. To correlate the non-isothermal data, the correct reaction equation has to be known in order to calculate the heat of reaction. This barrier is overcome by using the reaction heat as an adjustable parameter to match the sorbent temperature.