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Laboratory evaluation of high-temperature sulfur removal sorbents for direct coal-fired turbines: Final report

Newby, R.A.; DeZubay, E.A.; Chamberlin, R.M.

Jun 1987

Westinghouse Electric Corp., Pittsburgh, PA (USA). Research and Development Center

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Laboratory Evaluation of High-Temperature Sulfur Removal Sorbents for Direct Coal-Fired Turbines

Final Report

R.A. Newby E.A. DeZubay R.M. Chamberlin

Work Performed Under Contract No.: DE-AC21-85MC22087

For

U.S. Department of Energy Office of Fossil Energy Morgantown Energy Technology Center P.O. Box 880 Morgantown, West Virginia 26507-0880

By

Westinghouse R&D Center 1310 Beulah Road Pittsburgh, Pennsylvania 15235

June 1987

ABSTRACT

Direct coal-fired turbine concepts currently being developed require substantial levels of sulfur removal from high-temperature gas streams. Calcium-based sorbents, limestones, dolomites, limes and lime hydrates, are capable of sulfur removal in direct coal-fired turbine combustor environments at temperatures up to 1200°C. Two types of desulfurizer processes are considered in this report using calcium-based sorbents: fluidized bed desulfurizers using coarse sorbent particles $(300-1000 \ \mu m)$, and entrained desulfurizers using fine sorbent particles $(1-40 \ \mu m)$. Small-scale laboratory tests were performed on a variety of calcium-based sorbents to determine the kinetics of sulfation and sulfidation over ranges of conditions applicable to both types of desulfurizer processes. Correlations are developed in the report for the effect of pressure, temperature, and particle size. Engineering models are also developed for both desulfurizer types that incorporate the laboratory reaction kinetics and predict potential commercial performance and performance trends. It is concluded that both desulfurizer concepts can be effective in direct coal-fired turbines, with calcium-to-sulfur molar feed ratios ranging from 1.5 to 3.0, if the correct calcium-based sorbent is selected, and if applicable design and operating conditions are identified. Both desulfurizer concepts have limitations and key development requirements, and site and fuel specific engineering assessment is required to select the best concept for a given combustor system. The influence of the desulfurizer concepts on turbine protection, through their influence on particle loading and alkali release must also be assessed.

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The authors acknowledge the outstanding test work and equipment maintenance of W. F. Kittle and C. A. Hughes, who applied much timely imagination to this program. The very reliable analytical chemistry contribution of M. L. Theodore is also noted. Finally, the guidance of Suresh C. Jain, the METC COTR, in the performance of this program and in the preparation of this report is acknowledged.

LIST OF ACRONYMS

AFBC: Atmospheric-pressure Fluidized-Bed Combustion

PFBC: Pressurized Fluidized-Bed Combustion

LIMB: Limestone Injection with Multistage Burners

CAFB: Chemically Active Fluidized Bed Process

KRW: KRW Energy Systems, Inc.

EPA: U.S. Environmental Protection Agency

CURL: Coal Utilization Research Laboratory

IEA: International Energy Agency

EER: Energy and Environmental Research Corporation

STP: Standard Temperature and Pressure

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1. EXECUTIVE SUMMARY

This report projects the performance and identifies the major issues in the use of calcium-based sorbents for sulfur removal in direct coal-fired turbine systems. This is accomplished by laboratory measurements of sulfur removal rates, development of kinetic correlations, and model estimates of desulfurizer behavior.

Two generic types of sulfur capture processes are of potential interest to direct coal-fired turbine systems: the fluidized bed desulfurizer, using relatively coarse sorbent particles on the order of 300 to 1000 microns in diameter, and the entrained desulfurizer, using relatively fine sorbent particles on the order of 1 to 40 microns in diameter. Both of these desulfurizers could be placed in either a rich stage (i.e., with excess fuel) of the turbine combustor to remove primarily H_oS (sulfidation), or in a lean stage (i.e., with excess air) of the combustor to remove SO_2 (sulfidation). The process concepts are illustrated in Figure 1. Primarily "external" desulfurization stages are considered in this study -- that is, stages where significant combustion does not occur and where the temperature and gas composition are relatively well defined and nearly constant throughout, as compared to "in-situ" desulfurization stages (slagging stages with sorbent injection for example) where the temperature and gas composition change radically within the stage. Indirect information, though, is provided by this program that reflects on the in-situ stage behavior.

This report is arranged in two major sections. The first section considers the fundamental kinetics and the commercial performance of coarse calcium-based sulfur sorbents in the fluidized bed desulfurizer environment. The second is devoted to the fine calciumbased sulfur sorbents in the entrained desulfurizer.

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Entrained Desulfurizer Concept



Fluid Bed Desulfurizer Concept



Overall, both desulfurizer concepts can be effective in direct coal-fired turbines if the correct calcium-based sorbent is selected and if applicable design and operating conditions are identified. Both concepts have limitations and key development requirements. Site and fuel specific engineering assessment is required to select the best concept for a given combustor system.

COARSE PARTICLE, FLUIDIZED BED DESULFURIZER

Seven sorbents were selected for the testing in the coarse particle phase of the program: 2 dolomites (Plum Run, and Tymochtee), 3 limestones (Greer, Mississippi, and Vicron), and 2 dolomitic limestones (Highland, Carbon).

Thirty-six tests with the sorbents were conducted in SO₂ to determine the effect of sorbent type, sorbent particle size, and temperature on the sulfation kinetics. The experimental technique was shown to give reproducible and consistent results. The dolomites were found to degrade slightly in performance as the temperature was increased from 1000 to 1200°C; the two dolomitic limestones, Highland and Carbon, were found to improve or nearly maintain the same reactivity as the temperature was increased; and the three limestones were found to degrade extensively as the temperature was increased.

Six tests with precalcined sorbents using a procedure designed to improve sulfur removal performance in atmospheric pressure fluidized bed combustion were completed. No improvement in reactivity, or in some cases reduced reactivity, was found.

Three tests in H_2S were conducted with the coarse particles. These tests indicated the beneficial effect of increased pressure. The sulfidation rate was found to be comparable to the sulfation rate, but the ultimate extent of calcium conversion was considerably higher for sulfidation than in sulfation.

The sulfur removal kinetics were evaluated by first performing a dimensional analysis of the data collected. This analysis implies that the initial reaction period is controlled by the rate of solid phase

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diffusion while the subsequent period is controlled by pore diffusion. Secondly, the reaction kinetics were correlated using standard multiple regression techniques.

An engineering model of the fluidized bed desulfurizer has been developed as a tool for evaluating potential performance based on a laboratory reaction kinetics. The calcium-to-sulfur feed ratio required to achieve a given level of sulfur removal efficiency was determined as a function of the sorbent type, the average particle diameter in the bed, the bed depth, the superficial gas velocity through the bed, and the bed temperature. For SO₂ removal, both dolomites tested are found to give acceptable calcium-to-sulfur ratios (from 1.8 to 3.0 depending on the particle size selected) at a temperature of 1200°C, and gas residence times in the bed of 0.5 seconds. It is expected that almost all dolomites will show this type of general acceptability. The dolomitic limestönes, Highland and Carbon, were found to yield results as good as or better than the dolomites (calcium-to-sulfur molar feed ratio of 1.8 to 3.6 depending on the particle size selected) at a temperature of 1200°C. The other three limestones result in unacceptable performance at temperatures greater than 1000°C.

The commercial sulfur removal performance in H_2S is expected to be comparable to that in SO_2 removal, where at 1100°C both sorbents tested would require very acceptable sorbent feed rates (1.5 for Plum Run dolomite and 2.8 for Highland limestone) using a 0.5 second gas residence time in the fluidized bed.

FINE PARTICLE, ENTRAINED DESULFURIZER

Three sorbents were selected for testing based on their performance variation found in the coarse particle testing -- Plum Bun dolomite, Highland limestone and Vicron limestone. In this experimental technique the sorbent particles are first heated to the test temperature, calcining them completely and essentially sintering their surface to a minimum and stable value. The nature of the sorbents tested, then, are categorized as "sintered" sorbents and are not directly representative of freshly calcined, high surface area sorbents.

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Thirty-two tests were conducted on sulfation at temperatures of 1100 and 1200°C, pressures of 6 and 12 atmospheres, particle sizes of $\langle 400 \text{ mesh} \rangle$ and $\langle 20 \rangle$ micron diameter, and gas-particle contact times of 0.75 and 1.5 seconds. The test results were found to be reproducible and it was confirmed that the sulfation rate is first-order in the SO₂ mole fraction in the gas. The relative reactivity of the sorbents is qualitatively the same as in the coarse particle testing.

A commercial lime hydrate and hydrated Vicron limestone were also tested in sulfation. Because of the sintered nature of the sorbents in these tests, the hydrated sorbents behaved almost identically to the raw limestone sorbent tests.

Eight tests were conducted to measure the sulfidation kinetics of Plum Run dolomite and Highland limestone. The tests were done at 1100°C. The sulfidation rate of Plum Run dolomite was slightly greater than the sulfation rate was under comparable conditions, but the sulfidation rate of Highland limestone was much greater than the sulfidation rate. The sulfation and sulfidation kinetics were correlated with the operating conditions.

An evaluation of the commercial performance of entrained desulfurizers using calcium-based sorbents was made based on a simple entrained contactor model. The model results indicate that the calciumto-sulfur ratio required is dependent on the sulfur removal efficiency, the SO₂ or H_2S mole fraction in the gas at the point of sorbent injection, the particle residence time in the entrained desulfurizer, and the sorbent type.

The performance of sintered sorbents were first evaluated using the kinetic correlations directly. It is concluded that sintered sorbents are probably only acceptable in cases where high sulfur coals are used, and high sulfur removal efficiencies are not required, and relatively long particle residence times are available (on the order of 1 second). Their use in a rich zone with H_2S is greatly favored over their use in a lean zone. The sintered dolomites and limestones perform comparably on a weight feed basis for SO₂ removal, but the sintered limestones perform better than the sintered dolomites on a weight feed basis for H₂S removal.

Active, high surface area sorbents were evaluated by combining the sintered sorbent kinetics with the transient surface area generated during calcination.

Projections of the performance of dolomites, limestones, and high surface area limes and lime hydrates injected into rich and lean combustor sones were developed. In general, it is found that there is no benefit from increasing the gas residence time in the entrained desulfuriser to values greater than 0.5 seconds. Low-sulfur coals require higher calciumto-sulfur ratios than do high-sulfur coals, but the mass feed rate of sorbent is nearly independent of the coal sulfur content, depending only on the temperature, pressure, particle diameter and sulfur removal efficiency. Lower sorbent consumption can result with H_2S removal than with SO_2 removal, and higher operating pressures significantly reduces the sorbent consumption. Increasing the gas temperature from 1000 to 1100°C results in a small increase in sorbent consumption, while increasing the temperature to 1200°C results in a higher consumption.

High surface area limes and lime hydrates result in the smallest sorbent consumption and have the potential for operation with the smallest gas residence times. Limestones and dolomites are comparable for SO_2 removal on a weight feed basis, but limestones are superior to dolomites for II_2S removal. A major tradeoff exists between the sorbent consumption rate, the cost of the sorbent material (high surface area limes and lime hydrates being much more expensive than limestone and dolomites), the gas residence time in the desulfuriser, and the sorbent particle sise. This can only be resolved by evaluating the design and cost of specific direct coal-fired turbine systems, and will be site and fuel sensitive in many respects.

Key questions remain as to the actual occurrence of H_2S in the rich sones (versus COS, CS₂, and SO₂), the ability to feed and disperse fine sorbent particles effectively into a hot, pressurised gas stream so that good gas-particle contacting is achieved over short residence times, and the possibility of ash-sorbent interactions and particle deposition in the

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combustor. The impact of potentially "sticky" particles on particulate collection devices, and the protection of turbine components (erosion, corrosion and deposition) must also be resolved.

1. INTRODUCTION

The Department of Energy (DOE), Office of Fossil Energy, is guiding and sponsoring the development of a variety of advanced power generation technologies based on the utilization of coal. One such technology is the direct coal-fired turbine, using existing gas turbine machines, or "ruggedized" versions of these machines, in series with advanced coal combustors. Applications range from locomotive transportation to electric utility power generation. Much of the development effort in the direct coal-fired turbine program is related to developing advanced coal combustors that have, combined with the characteristics of high combustion efficiency and low NOx generation, the potential for significant simultaneous removal of ash and sulfur contaminants.

The options in this technology that can be considered are many: 1) coals can be cleaned of ash and sulfur to various levels and can be fed as coal-water slurries or in dry form; 2) combustion may be performed in a staged manner going from rich to lean zones, and slagging phenomena may be incorporated to remove ash; 3) stages of particulate control may be inserted into the combustor ranging from cyclones to high-temperature filters; 4) stages of sulfur control may be inserted into the combustor either "in-situ" with the combustion stages (as in a slagging combustor with sorbent injection) or separate from the combustion phenomena (as in an "external" zone following complete combustion). Sulfur control may occur in a stage where conditions are predominantly reducing (i.e., $H_{2}S$ is the major sulfur species) or in a stage that is predominantly oxidizing (i.e., SO₂ is the major sulfur species). Sorbent-gas contacting may be in a fluidized bed, using relatively coarse sorbent particles, or in an entrained bed, using relatively fine sorbent particles. Performance must achieve control

levels for sulfur species and particulate that are sufficient to meet turbine protection limits and environmental regulations.

Because calcium-based sorbents are the cheapest and most highly available sulfur sorbent materials that have the potential for hightemperature, high-pressure sulfur capture, their use in direct coalfired turbine power systems is of prime interest. The term calciumbased sorbent includes raw, untreated limestones and dolomites as well as processed forms such as limes and hydrated limes. It is known that calcium-based sorbents will be thermodynamically capable of capturing sufficient sulfur at temperatures within the range of interest to direct coal-fired turbines. Kinetically, the use of calcium-based sorbents may be limited to lower temperatures than the thermodynamic limits due to phenomena relating to sintering. The gas residence times in the desulfurizer that meet economic criteria for the power system will also define kinetic limits on calcium-based sorbents in direct coal-fired turbines. It was the major purpose of this study to determine the effect of high temperature operation on the sulfur capture potential of calcium-based sorbents.

This report considers "external" desulfurizers rather than "insitu". The in-situ arrangements, such as slagging zones with sorbent injection, have temperatures and gas compositions that change dramatically with position, and ash-sorbent interaction may be great. External arrangements have temperatures and gas compositions that are relatively fixed throughout the desulfurizer, and little interaction between combustion and desulfurization occurs. The information presented in this report relates only indirectly to the more complex environment of in-situ desulfurization.

The report is arranged in two major sections. The first is devoted to the kinetics of "coarse" calcium-based sorbent particles (300 to 1000 microns in diameter) in sulfur dioxide and in hydrogen sulfide gases, and evaluates their performance in fluidized bed desulfurizer contactors. The second major section considers "fine" calcium-based sorbent particles (less than 40 microns in diameter), measuring their

kinetics in sulfur dioxide and hydrogen sulfide gases and evaluating their commercial performance in entrained desulfurizer contactors. The program must be described as preliminary in its consideration of kinetics in that the minimum data required to propose correlations are produced. The consideration of commercial performance must be described as conceptual because the use of ideal contactor models is made to scale the laboratory kinetic data to large-scale performance estimates. Thus, performance potential, performance trends and required test directions are identified in the program.

2. COARSE CALCIUM-BASED SORBENT PARTICLE FOR SULFUR REMOVAL

Section 2 is devoted to the evaluation of coarse, calcium-based sorbents for sulfur removal from the combustion products of direct coalfired turbines. Coarse particles are defined as having a size potentially applicable to fluidized bed desulfurizers, say in the range of 300 to 1000 microns in diameter. Background information on the use of these sorbents is extensive, based mostly on studies from fluidized bed combustion, and is presented to explain the rationale for the test effort. The test sorbent properties, the test plan, and the testing equipment and procedures are described. Test results are presented in three areas: untreated sorbent kinetic performance with sulfur dioxide; pretreated sorbent kinetic performance with sulfur dioxide; and untreated sorbent kinetic performance with hydrogen sulfide. The kinetic data is evaluated and a conceptual evaluation of fluidized bed desulfurization for direct coal-fired turbines is discussed.

2.1 BACKGROUND

Subsection 2.1 summarizes the available background information on the "sulfation" of coarse calcium-based sorbents (the conversion of calcium oxide to calcium sulfate on contact with sulfur dioxide), and on the "sulfidation" of coarse calcium-based sorbents (the conversion of calcium oxide to calcium sulfide on contact with hydrogen sulfide), to identify the existing data gaps for the use of these sorbents in direct coal-fired turbine power systems.

The thermodynamic limits for SO_2 and H_2S capture are shown in Figure 2.1 using standard thermodynamic data available in the literature. This figure plots the quantity (1-E) (1 minus the sulfur removal efficiency) times X_s (the weight fraction sulfur in the coal) as a function of the temperature of the zone of sulfur capture in the

combustor system. For a 3 wt% sulfur coal and 90% sulfur removal this quantity is 0.003. A broad band is shown for H_2S capture to reflect the possible range of performance for both dry coal and coal-water slurries using either water or steam injection for quenching to the rich zone temperature. A similar band is shown for SO₂ capture, where the band width is indicative of the range of oxygen levels that might appear in the combustion products for both dry coal and for coal-water slurries. Again considering a 3 wt% sulfur coal and 90% sulfur removal, the figure indicates that efficient H_oS capture in a rich zone of a direct coalfired turbine will be limited to temperatures less than about 1100°C, and will also be limited to relatively high sulfur coals. S0, removal may be limited to temperatures less than about 1200°C and will be suitable for lower sulfur coals than those for H_oS removal. These thermodynamic limits set the temperature range of concern for kinetic studies.

2.1.1 Sulfation Background

It is well known that calcium oxide (CaO) when contacted with sulfur dioxide (SO_2) at relatively high temperatures (greater than 500°C) is converted to calcium sulfate (CaSO₄), and this conversion is the basis for the use of calcium-based materials as sulfur sorbents in a variety of processes. Natural calcium-containing materials, limestones (primarily CaCO₃) and dolomites (primarily CaCO₃ MgCO₃) exist in the carbonate form, and on heating to their transition temperature will calcine to the oxide form:

$$CaCO_3 \Rightarrow CaO + CO_2$$
 (calcined limestone or lime) (2-1)
 $CaCO_3 MgCO_3 \Rightarrow CaCO_3 MgO + CO_2$ (half-calcined dolomite) (2-2)

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 $CaCO_3$ MgCO_3 => CaCO_3 MgO + CO_2(half-calcined dolomite)



Figure 2.1 — Equilibrium SO₂ and H_2S Removal at 10 Atmospheres Pressure

 $CaCO_3$ MgO => CaO MgO + CO_9 (fully-calcined dolomite)

The overall sulfation reaction is, for uncalcined sorbent

$$C_{a}CO_{3} + SO_{2} + \frac{1}{2} O_{2} => C_{a}SO_{4} + CO_{2}$$

or, for calcined sorbent

 $Ca0 + SO_2 + \frac{1}{2}O_2 \Rightarrow CaSO_4$ (2-5)

(2-3)

(2-4)

While these overall reactions are known, the detailed mechanisms involved in the reaction are still speculative.

Several phenomena play an important part in the sulfation of coarse particles of calcium-based sulfur sorbents. The key ones with respect to the current topic are based on these observation

- -- the temperature and gas composition during calcination impact the sulfation behavior
- -- the sorbent pore and grain structure is transient (sulfate shell formation, crystal growth, sintering, interaction with coal species)
- -- the sulfation rate depends on the pressure, temperature, and gas composition (sulfation rate is defined in this report as the fraction of the sorbent calcium converted to calcium sulfate per unit of time)

Much of the current understanding of these observations results from related development programs that have applied coarse, calciumbased sorbents for sulfur control at high temperatures. These include programs in atmospheric-pressure fluidized-bed combustion (AFBC), programs in pressurized fluidized-bed combustion (PFBC), and, to some extent, early programs (pre-1975) in conventional furnace sorbent injection (the LIMB process -- Limestone Injection with Multistage Burners) where relatively coarse particles were considered. These programs have generated kinetic data, correlations, and understanding of the above observations under conditions that are close to those required by the direct coal-fired turbine.

Characteristic operating conditions required for the direct coal-fired turbine and ranges of experience for the related technologies are shown in Table 2.1. Note from Table 2.1 that the coarse sorbent particle sulfation rate is slow and the particles reside in the desulfurizer for hours. This table indicates not only the complimentary areas between these technologies, but also clearly shows where gaps are found in the existing data base. The data gaps between the needed kinetic information and the existing information is seen to be specifically in the area of higher temperatures, from 1000 to 1200°C, under conditions of elevated pressure.

The major factors relating to the sulfation of coarse calciumbased sorbents for direct coal-fired turbines are the effect of temperature, the effect of pressure, the effect of sorbent type, and the effect of the gas composition. A brief discussion of the background information in each of these areas is presented.

2.1.1.1 Bffect of Temperature

Several observations on coarse particle calcium-based sorbent sulfation guide this program. There are at least three interrelated phenomena that impact the overall sulfation rate and are highly temperature dependent: 1) the effect of temperature on the rate of calcination (calcination rate is defined in this report as the fraction of the sorbent calcium converted to CaO per unit of time) and the pore

	Conditions For Direct Coal- <u>Fired Turbine</u>	Experience Fluidized-Bed Combustion	Early Experience Sorbent Injection (LIMB)
Pressure (atm)	6 to 20	1 to 20	1
Temp (°C)	up to 1200	750 to 1000	up to 1700
Particle Diameter (microns)	300 to 1000	50 to 2000	1 to 1300
Particle Residence time(hr)	5 to 50	5 to 100	up to 2
Sorbent Type	limestones, dolomites, limes	limestones, dolomites, limes	limes, hydrates, dolomites limestones,
Calcining Conditions	high-temperature with low CO ₂ - pressure	medium-temp with low to high CU ₂ -pressure	high-temperature with high CO ₂ - pressure

Table 2.1 — Coarse Sulfation Operating Conditions and Related Experience

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size distribution that results from calcination; 2) the sintering that occurs as a function of time due to both surface diffusion and bulk diffusion in the solid phase; and 3) reversible adsorption on the pore surfaces.

The well-known experience in atmospheric-pressure fluidized-bed combustion (AFBC) indicates that temperature is a critical parameter, and an "optimum" temperature exists, depending on the specific sorbent, at about 840°C, above which and below which the sulfation performance of the sorbent will drop significantly. This behavior has been demonstrated in both fluidized-bed combustion development units and in laboratory equipment (1-5). Several explanations have been given for this optimum temperature behavior ranging from thermodynamic influences to catalytic influences, but it has been clearly shown that the major reason is related to the pore structure that is generated in the particle when it calcines -- an optimum pore structure for sulfation is formed at the temperature where a balance exists between fine pores and large pores (6,7).

Early LIMB studies demonstrated the severe impact of high temperatures on limestone sulfation performance with fairly coarse sorbent particles (8). Sintering due to surface diffusion is sensitive to gas components that are adsorbed on the pore surfaces (CO_2 , H_2O , H_2 , etc). Sintering due to bulk solid-phase diffusion is sensitive to impurities in the solids. Some reversible effects of temperature on sorbent reactivity have also been observed, indicating that lowering the temperature of a saturated sorbent particle could result in further sulfation (9). Thus, irreversible sintering-type effects may not be the sole reason for loss of sorbent activity with increased temperature (10).

An optimum temperature, as observed in AFBC, is not observed in PFBC when the gas pressure is elevated above about five atmospheres, at least at temperatures up to 1000°C (11). The explanation for the difference between atmospheric-pressure and pressurized behavior is that the performance is again controlled by the physical pore structure that is developed when the sorbent is calcined, and the calcination behavior

is controlled by two parameters: the temperature and the CO_2 partialpressure. When the CO_2 partial-pressure is low, as at atmospheric pressure, the higher temperatures result in smaller pores that are less conducive to SO_2 diffusion and more conducive to sulfate layer plugging. When the CO_2 partial-pressure is high, as at elevated pressures, even higher temperatures will not generate the fine pore structure, and large, easily sulfated pores exist. This observed behavior is the basis for the precalcination scheme proposed by Westinghouse to generate higher activity calcium-based sorbents for atmospheric pressure fluidized-bed combustion (6).

These results lead to the exception that the higher temperatures representative of direct, coal-fired turbines may not hinder the use of calcium-based sorbents because of the counteracting effect of the elevated pressure. Surely a detrimental temperature effect will exist at some temperature, due to both particle sintering and because of thermodynamic limitations on the sulfation reaction leading to increased thermal decomposition. It has not been previously shown, though, if temperatures of up to 1200°C, that are thermodynamically acceptable, will be acceptable for sulfation from a kinetic standpoint.

2.1.1.2 Effect of Pressure

Another important conclusion from previous pressurized thermogravimetric balance studies is that pressures above about 6 atmospheres do not exert much influence on sulfation behavior for coarse sized particles (12). Pressurized fluidized-bed combustion testing has also demonstrated a limited pressure impact (13). The explanation for this observed behavior is based on the predominant pore diffusion rate controlling step with coarse sorbent particles.

2.1.1.3 Bffect of Sorbent Type

It is observed in all of the related technologies using natural, calcium-based sorbents for high temperature sulfur control that the specific type of sorbent exerts a strong influence on the sulfation performance (14-16, 6), and selection of a specific quarry to supply a

sorbent for commercial plant becomes an important issue. The chemical composition (calcium content, magnesium content, inert content, and the nature of the inert species), and the physical structure of the sorbent (grain size, pore size distribution, internal surface area, etc.) may all contribute to this diversity of behavior. The relation between these sorbent parameters and the sulfation performance is not currently understood, although the trends are generally predictable. The least understood factor is the relationship between the sorbent properties and its sensitivity to temperature.

2.1.1.4 Effect of Gas Composition

The rate of the sulfation reaction is known to be first-order in the sulfur dioxide concentration over a wide range of concentrations, so long as these are far above the equilibrium sulfur dioxide concentration at the prevailing temperature and pressure.

The effect of carbon dioxide concentration on the sorbent effectiveness is known to be through its impact on the calcination behavior and the resulting pore structure. The carbon dioxide concentration exerts less impact as the total pressure increases. Also, an important thermodynamic transition exists between the calcined and the uncalcined states of the sorbent that is influenced by the carbon dioxide concentration (reactions 1 - 3). At carbon dioxide concentrations above the equilibrium for calcium carbonate decomposition most limestones have such a low porosity that they are quite ineffective for sulfur removal. Dolomites, on the other hand, will have a significant voidage even if the calcium carbonate is not decomposed because the magnesium carbonate fraction of the dolomite calcines at a significantly lower temperature (reaction 2). Thus, half-calcined dolomites are very reactive. At the conditions of the direct coal-fired turbine full calcination is generally thermodynamically favored, so this transition will be of little concern.
The oxygen partial-pressure in the gas phase has been found to be unimportant, the reaction rate being zero-order in oxygen (11). There are some reports that the oxygen concentration is important through its interaction with SO₃ formation (18, 19), although this effect has not been demonstrated. Other major gas phase species, such as H_2O and N_2 are not expected to have any impact on the sulfation reaction at the concentrations typical to the direct coal-fired turbine, although H_2O may induce increased rates of sintering.

Trace species released from coal have been conjectured to have impacts on the sorbent behavior. While it is known that alkali salts can interact with calcium-based sorbents, when at relatively large concentrations, to increase the pore sizes (20), the sulfation results in fluidized-bed combustion tests where the sorbent particles are intimately in contact with coal ash closely correspond to the sulfation performance of sorbents in laboratory tests that have not been exposed to coal species (21, 22). Thus, at temperatures up to 1000°C, coal species interaction is an effect of limited importance.

2.1.2 Sulfidation Background

The sulfidation reaction (the conversion of calcium oxide to calcium sulfide on contact with hydrogen sulfide) for coarse particles has been studied somewhat less extensively than the sulfation reaction. The overall reaction for sorbent sulfidation is

$$C_{a}CO_{3} + H_{2}S \Rightarrow C_{a}S + H_{2}O + CO_{2}$$
 (2-6)

for uncalcined sorbent particles, and

$$Ca0 + H_0S \Rightarrow CaS + H_0O$$
 (2-7)

for calcined sorbent particles. As with the sulfation reaction, the mechanisms involved in the sulfidation reaction are not completely understood. The MgO component of dolomites does not sulfide to a significant extent at the conditions of interest.

Experience with the sulfidation reaction comes mainly from applications related to the gasification of fossil fuels (heavy oils and coal) and conditions have ranged from atmospheric pressure to pressures of 30 atmospheres at temperatures up to 1100°C. An application example at atmospheric pressure is the CAFB process (Chemically Active Fluidized Bed) for gasifying heavy oils and low-rank coals at atmospheric pressure to retrofit existing boilers. Limestone was used as the sulfur sorbent directly in the fluidized bed gasifier (23, 24). An application at elevated pressures is the KRW coal gasifier, used to generate low- and medium-Btu fuel for industrial uses or for combined cycle applications. Dolomites and limestones are used either directly in the gasifier or in an external fluidized bed desulfurization stage (25, 26). The major factor differentiating the existing process experience from the conditions needed in the direct coal-fired turbine application is the higher temperature level needed and the much less intimate contact between coal and sorbent particles in the direct coal-fired turbine.

A number of laboratory kinetic studies have been reported and these provide a detailed background for the effects of the major parameters (27-33). Conclusion drawn from these studies are summarized here.

2.1.2.1 Effect of Temperature

The effect of temperature on the initial reaction rate in the range of 700 to 1000° C is very limited, especially at elevated pressures, although the extent of conversion of calcium oxide to calcium sulfide tends to drop as the temperature is increased in this range. This reflects the fact that structural changes in the sorbent particle during reaction are not as important in the sulfidation reaction as they are in the sulfation reaction, and the reaction is not chemical reaction rate controlled. It is felt that the sulfidation reaction is less sensitive to sorbent pore structure and to temperature than is the sulfation reaction because of the smaller molecular volume of CaS compared to CaSO₄, also resulting in the extent of sorbent particle

utilization being larger with the sulfidation reaction than with the sulfation reaction.

2.1.2.2 Bifect of Pressure

Increasing the pressure from atmospheric to elevated levels has a dramatic impact on the rate of sulfidation, the rate being proportional to the total pressure to the 0.3 to 0.5 power depending on (\cdot) the specific sorbent.

2.1.2.3 Bffect of Sorbent Type

Dolomites and limestones as groups are found to behave significantly different in sulfidation, although not as much differently as they do in sulfation. Likewise, the differences between specific limestone types is not as great in sulfidation as it is in sulfation. Limestones having poorer reactivity with SO, tend to also have poorer reactivity with H_2S . As in SO_2 , uncalcined limestones are not reactive, while half-calcined dolomites are very reactive. Specific dolomite types tend to behave very similarly during sulfidation.

2.1.2.4 Effect of Gas Composition

Hydrogen, water vapor, and carbon dioxide are all found to have small influences on the rate of sulfidation in the temperature range of 700 to 1000°C, probably due to their influence on pore structure and on the rate of sintering. The sulfidation rate is found to be first order with respect to the hydrogen sulfide concentration. Other sulfur species also exist in reducing gases to a lesser extent, COS and CS, for example, and the rate of reaction with these species has to be studied only to a minor degree.

2.1.2.5 Other Factors

The generation of magnesium sulfide when sulfiding dolomites, especially at higher pressures, has been confirmed, but the rate of magnesium sulfide generation is much lower than calcium sulfide generation and is hindered by water vapor. The rate of calcium sulfide

generation in dolomites has generally been found to be first-order with respect to the fraction of unsulfided oxide remaining (that is, the sulfidation rate is proportional to the quantity [1 - the fraction ofthe calcium sulfided] to the first power). The initial sulfidation rate is lower than the initial sulfation rate, all conditions being identical, but the extent of sulfidation ultimately achieved is greater than the extent of sulfation achieved. It is found that the initial reaction rate is proportional to the sorbent particle diameter to the -0.5 to -1.0 power depending on the sorbent type.

2.1.3 Modeling Background

A multitude of particle reaction models have been proposed for the sulfation and sulfidation of calcium-based sorbents, consisting of various forms of pore, grain and homogeneous models (for example, see recent reviews of particle reaction models (34, 35)) but all have an inability to predict several key factors: 1) the calcined pore/grain structure in the sorbent as a function of the calcination conditions and the raw sorbent properties; 2) the transient pore/grain structure due to crystallite growth, sintering, sulfate layer growth, crack development, impurity interactions, etc; and 3) reversible effects due to adsorption versus nonreversible effects. While modeling activities can provide conceptual pictures of the behavior of hypothesized phenomena, they are not predictive, and they cannot be extrapolated outside of their region of data fitting. For this reason, a laboratory simulation of the reaction environment to yield direct estimates of the reaction kinetics is applied in this program rather than depend on the extreme uncertainties of particle reaction model extrapolations.

2.2 SORBENT PROPERTIES

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Carbonate rocks, the source of calcium-based sulfur sorbents, are composed of the mineral forms calcite (CaCO₃, rhombohedral), dolomite (CaMg(CO₃)₂) and aragonite (CaCO₃, orthorhombic arrangement). Various constituents may act as binding agents for the particle grains,

or crystals and impurities may be mixed with the mineral grains.

Carbonate rocks have been classified into several different groups, sometimes with conflicting definitions by different authors. Calcites are very high calcium content rocks; limestones are moderately high calcium rocks; dolomites contain a high proportion of the mineral form dolomite; and dolomitic limestones contain a significant mixture of both the calcite and the dolomite mineral forms. These are the carbonate rocks most available and suitable for high temperature sulfur removal. Detailed classifications of carbonate rocks based on geological origin have been proposed in the literature (36). The definitions used in this report are: limestones contain $<5 \text{ wt% MgCO}_3$; dolomitic limestones contain 5-20 wt% MgCO₃; and dolomites contain >20 wt% MgCO₃.

Other terms have also been added to modify the carbonate rock classification with respect to the nature of the impurities in the material. For example, the terms arenaceous (high in quartz), argillaceous (high in clay), carbonaceous (high in carbon), ferriferous (containing iron), or bituminous (containing organic hydrocarbons) have been used. Because of the great range of calcium-based sorbent properties existing it is important for any exploratory program to consider as large a range of sorbent types as is practical.

The type of calcium-based sorbents that are applicable for use in a fluidized bed desulfurizer are raw limestones and raw dolomites as obtained directly from quarry sources, or specially prepared calcines of limestone, or limes, (not commercially available) having pore size distributions favorable for fluidized bed sulfur capture. Commercially produced limes have no performance advantage over the use of raw limestones, and would carry with them a large cost penalty. Commercially available hydrated forms of limestone (Ca(OH)₂) and dolomite (Ca(OH)₂.MgO) are not applicable to use in fluidized bed desulfurizers because their characteristic particle size is much too small to be used in a fluidized bed.

Westinghouse has previously investigated the sulfation and sulfidation behavior of calcium-based sorbents having the following range of characteristics:

 calcium content (wt % CaCO ₃): 40 to 99
 <pre>magnesium content (wt % MgCO₃): 0.5 to 50</pre>
 inert content (wt %): 0 to 40
 Al ₂ 0 ₃ (wt %): up to 10
 Fe ₂ 0 ₃ (wt %): up to 4
 SiO ₂ (wt %): up to 15
 Na_2^0 (wt %): up to 1
 K ₂ 0 (wt %): up to 3

-- hydrocarbon (wt %): up to 12

No general correlation of sulfation performance versus the properties has been developed, and not enough detailed information is available to attempt a comprehensive correlation.

For the test program conducted and reported on in this program a broad range of sorbent types have been selected using previous tests as the basis for selection. The sorbents selected are listed in Table 2.2. With the definitions used in this report two of the sorbents are dolomites (Plum Run and Tymochtee), two are dolomitic limestones (Highland and Carbon) and the remaining three are limestones.

Chemical analyses for calcium and magnesium were performed by EDTA titrations. Grain size has been determined by standard thin

	Composition (wt %)			Grain size	Porosity	Surface
Sorbent	Ca	<u>_</u> ₩g	Inert	(microns)	(%)	<u>(m²/gm)</u>
Tymochtee dolomite	20.2	12.9	4.6	30-45	10.2	0.80
Plum Run dolomite	20.1	13.0	4.5	75-90	11.0	0.43
Highland limestone	34.1	3.8	1.5	200-250 75-90	6.5	0.70
Carbon limeston e	35.1	2.6	3.2	9-27	6.2	0.43
Mississippi limestone	38.3	1.4	0.6	200-250	11.8	0.55
Greer limestone	37.8	1.0	2.0	25-40	8.6	0.47
Vicron limestone	37.8	1.5	0.3	360-730	3.2	0.03

Table 2.2 - Coarse Test Sorbent Properties

section optical methods (ASTM E112-80 intercept procedure). Porosity and surface area has been measured using standard mercury porosimetry on a Micromeretics Autopore 9200 porosimeter. The surface areas shown in the table differ from those that would be obtained by BET methods, and they apply only to the coarse particles sizes considered. Detailed measurement results are presented in Appendix A.

All of the sorbents selected have been previously tested by Westinghouse on thermogravimetric balance equipment for use in fluidized-bed combustion applications. A standard test used for ranking the sorbents has been conducted previously on all of them except for Vicron limestone. The standard test consists of heating a 20 mg sample of the sorbent sized at 1000 to 1190 microns suspended in the thermogravimetric balance. The sample is heated to 840°C in 15% carbon dioxide/85% nitrogen at a rate of 10°C/min at atmospheric pressure. After complete calcination, about 20 minutes, a sulfation atmosphere of 0.5% SO₂, 4% O₂, and N₂ is switched on and the sample weight is recorded as a function of time. The sorbents are ranked according to their performance in this test. The ranking results are: Tymochtee, highly reactive; Plum Run, average reactivity; Highland, medium-low reactivity; Carbon, average reactivity; Mississippi, medium-high; Greer, medium-low; and Vicron, not tested, but expected to be of low reactivity. Thus, a diversity of standard sorbent rankings is also represented by the selected sorbents.

Several of the selected sorbents have also been tested in development facilities for the related technologies. Carbon limestone (or Lowellville limestone) has been extensively tested on the Babcock & Wilcox 6 ft by 6 ft atmospheric-pressure fluidized-bed combustor under EPRI sponsorship. It has also been used in some circulating fluidizedbed combustion test work. Tymochtee dolomite has been extensively tested by Exxon on a pressurized fluidized-bed combustion Miniplant under EPA sponsorship. Plum Run dolomite has been extensively tested on the CURL pressurized fluidized-bed combustion test facility and in the Grimethorpe IEA PFBC facility. Greer limestone has been a test material

in many AFBC programs, including the Rivesville plant. Vicron limestone has been used in several conventional furnace injection programs.

A listing of the sorbent suppliers for these materials are shown in Appendix A.

2.3 OBJECTIVES AND TEST PLAN

The objectives of the program were to assess the potential of coarse calcium-based sorbents for use in a fluidized-bed desulfurizer for direct coal-fired turbines. The specific program objectives were to:

- -- test the reactivity of a variety of coarse calcium-based sorbents at temperatures up to 1200°C and pressures up to 10 atmospheres
- -- generate kinetic correlations as a function of temperature, particle size, sorbent type and pretreatment conditions
- -- develop commercial design equations for the sizing and performance of fluidized bed desulfurizers
- -- perform a preliminary assessment of the performance potential of calcium-based sorbents in fluidized-bed desulfurizers for direct coal-fired turbines

The following specific questions were addressed:

- -- Can satisfactory sulfur reactivity be obtained in the temperature range of 1000 to 1200°C, both for SO₂ and H₂S capture? If so, for what sorbent types?
- -- Does precalcination of the sorbent by previously determined methods improve the tolerance of the sorbents to high temperature?

The sets of test series were: one for SO_2 capture with raw, untreated sorbents, a second for SO_2 capture with precalcined sorbents, and a third for H_2S capture with raw sorbents. The test matrices were:

1) SO_2 capture with raw, untreated sorbents

Sorbent Types

- -- Tymochtee dolomite
- -- Plum Run dolomite
- -- Highland limestone
- -- Carbon limestone
- -- Mississippi limestone
- -- Greer limestone
- -- Vicron limestone

Simulation Gas Composition

- -- Carbon dioxide 8 mole %
- -- Oxygen 10 mole %
- -- $SO_2 0.5$ mole %
- -- Nitrogen 81.5 mole %
- -- Total pressure 10 atmospheres

Test Conditions

Temperature (°C)	<u>Particle Diameter (mesh)</u>
1000	-40 +45
	-16 +18
1200	-40 +45
	-16 +18
1100	-20 +25

2) Precalcined Sorbent Tests

Sorbent Types

Precalcination is most effective for limestones, but not for dolomites. Three limestones were selected:

-- Vicron limestone

-- Greer limestone

-- Carbon limestone

Precalcination conditions

The sorbents were precalcined on a thermal gravimetric balance at conditions of 60 mole % CO₂, 950°C, and atmospheric pressure, conditions found to give nearly optimum sulfation performance in atmospheric pressure fluidized-bed combustion.

Simulation gas composition

The same composition as in the raw sorbent test sequence was used.

Test Conditions

 Temperature (°C)
 Particle size (mesh)

 1100
 -20 +25

 1200
 -40 +45

3) Hydrogen Sulfide Tests

These tests provided an estimate of the potential performance of the sorbents with H_0S in a rich stage of the combustor.

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Sorbent Types

-- Plum Run dolomite

-- Highland limestone

Simulation gas composition

-- CO₂ 8 mole %

-- H₂S 0.3 to 0.46 mole %

-- balance nitrogen

-- total pressure 1 to 5 atmospheres

Test conditions

Temperature (*C)Particle Size (mesh)1100-16 +18

2.4 TEST EQUIPMENT AND PROCEDURES

Sulfation rates were determined as a function of the sorbent utilization (fraction of the calcium oxide sulfated) from data collected on a DuPont 951 thermogravimetric balance. The thermogravimetric balance provides a direct determination of reaction rate by measuring sample weight continuously during reaction. The rates are reported in this study as the fraction of the total sample calcium being sulfated per minute.

This system has been described previously by Westinghouse (12). The balance has been adapted for operation with corrosive gases by a simple modification to gas flow paths. A baffle separates the reactant gas flow, entering through a preheater region before passing over the balance mechanism. Both reactant and purge gases exit the reaction tube on the balance side of the baffle. The reaction tube has been extended to twice the standard quartz tube length in order to accommodate two furnaces wired for parallel control. The two-furnace system has doubled the heated reactant gas zone. Several modifications have been made to the furnace materials to accommodate the higher temperature range. The balance, reaction tube, and furnaces are mounted in a stainless steel pressure shell (Figure 2.2) capable of operation to 30 atm. Gas flow rates were controlled by linear mass flow controllers (Figure 2.3).



KEY

B1 Stainless Steel Pressure Vessel B2 External Cooling Coil ₿3 Internal Cooling Coil **B**4 TG Balance Housing **B**5 Reaction Zone Furnace **B6** Reaction Zone Thermocouple **B**7 Preheat Zone Furnace **B**8 Preheat Zone Thermocouple B9 Quartz Reaction Tube

B10 Sample Basket

- Bll Sample Thermocouple
- B12 Baffle Assembly
- B13 Reaction Tube Retaining Ring
- B14 TG Bell Jar
- B15 Flexible Metal Exhaust Hose
- B16 Atmospheric-Pressure Vent
- B17 TG Balance Electrical Feedthrough

1 A

- B18 Inert Purge Gas Inlet
- B19 Exhaust Gas Outlet
- B20 Reaction Gas Inlet :

Figure 2.2 — The Pressurized Thermogravimetric Balance ; Apparatus



Figure 2.3 — System Diagram for the Pressurized Thermogravimetric Balance Facility

Extensive testing at pressures up to 20 atmospheres was performed on this unit as a function of several key parameters.

Experiments were run according to the following procedure:

- Sized limestone by sieving.
- Suspended a 20 mg sample in a platinum mesh basket from the balance arm; placed the thermocouple into the basket, ~1 mm from the sample.
- Pressurized the system.
- Heated the sample at a rate of 10° C/min to reaction temperature in the reactant gas, minus SO₂, flowing at a rate of 2 1/min (STP).
- After complete calcination or half-calcination as indicated by a stable sample weight, introduced SO₂ into the reactant gas mixture.
- Monitored the sample weight gain as a function of reaction time.

A reactant gas flow rate of 2 l/min (STP) was found to be necessary to exclude external mass transfer effects on the initial reaction rate. Using the initial rate data, a mass balance on the system predicted the SO₂ concentrations around the sample during the initial reaction period.

These results showed little dilution of the SO_2 concentration during initial reaction. The initial rates, however, increase with flow rate from 1 to 2 l/min. Further increasing the flow to 4 l/min have no effect on the initial reaction rate. Reactant gas flow rates of 2 l/min (STP) were used for the experimental program since the data indicate that this flow rate was sufficient to exclude mass transfer effects.

Nominal sorbent temperature was measured by a Platinum/Platinum-10% Rhodium thermocouple positioned ~ 1 mm from the sample during loading. Temperature calibrations were done using the magnetic transition point (Curie point) of iron. The magnetic transition temperature was determined on the balance by placing a magnet over the sample. The sample was heated at 2°C/min. Upon reaching the transition temperature, the substance changes from ferromagnetic to paramagnetic (non-magnetic). An abrupt weight gain was observed due to the loss of upward magnetic force on the balance arm.

Iron's transition from ferromagnetic to paramagnetic should occur within a 5°C temperature range, reported at 770°C, with little influence from impurities. The results were fairly insensitive to flow rate and pressure. The initial detected transition occurred at 737 + $2^{\circ}C$. The transition was complete at $752 \pm 4^{\circ}C$. These results indicated that the thermocouple was reading a temperature 15 to 33°C lower than the sample temperature. Limestone experiments verified that calcination of the carbonate fraction occurred at temperatures 30°C lower than reported equilibrium decomposition temperatures. Calculations indicated that conduction of heat down the thermocouple leads did not cause much measurement error: When samples were wrapped in a platinum sheath to eliminate radiant heating, the temperature measurement remained constant. A baffle was designed to mount two thermocouples in the system, one being mounted directly in the sample to determine if this gas/solid temperature differential can be measured at reaction conditions.

2.5 UNTREATED SORBENT TEST RESULTS IN SO,

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Sulfation tests were completed with the raw sorbents to explore the effects of sorbent type, sorbent particle size, and temperature. The reproducibility of the test data was also checked. A total of 36 tests were conducted with the seven sorbent types. A listing of the run conditions, and the corresponding run numbers, are listed in Table 2.3. The complete run data summaries are presented in Appendix B. This subsection illustrates and discusses the qualitative characteristics of the data collected. The quantitative assessment of the results is made in a later section.

Table 2.3 - Run Numbers and Conditions in Untreated Sorbent Tests

Temperature: Size:	1000°C 40-45 Mesh	1000°C 16-18 Mesh	1200°C 40-45 Mesh	1200°C 16-18 Mesh	1100°C 20-25 Mesh
Sol benc:					2.
Tymochtee Dolomite	P437	P444	P460	P459	P452
Mississippi Lst.	P441	P448	P472	P471	P456
Greer Limestone	P440	P451/P447	P470	P469	P455
Highland Limestone	P439	P446	P468	P467	P454
Plum Run Dolomite	P438	P445	P462	P461	P453
Carbon Limestone	P442	P449	P466	P465	P458
Vicron Limestone	P443	P450	P464	P463	P457

Calcination in 10% 0_2 , 8% $C0_2$, N₂ at 2.0 L/min, 10 atm. Sulfation in 10% 0_2 , 8% $C0_2$, 0.5% $S0_2$, N₂ at 2.0 L/min, 10 atm.

During the tests significant difficulty with heater burnout was experienced at the higher temperature levels of operation. Considerable modification was made to the heaters to minimize replacement frequency and near the end of the testing campaign the thermogravimetric balance operation had reached a state of only limited occurrences of burnout.

2.5.1 Data Reproducibility

It has been found in more than 2,000 previous tests on the thermogravimetric balance that reproducibility was quite good if a homogeneous sorbent sample were prepared. A replicate run using Greer limestone, a generally nonuniform sorbent, was conducted to check reproducibility in these higher than usual temperature ranges. Results, shown in Figure 2.4, are good, with the erratic shape of the rate versus fraction sulfated curve being reproduced when comparing runs P447 and P451. In this figure, and several figures to follow, the reaction rate is defined as the fraction of the total calcium in the sorbent being converted to calcium sulfate per minute of time. This rate is plotted after multiplication by 100 in the figures against the fraction of calcium converted to calcium sulfate. The rate curve shapes in most of the runs at the high temperatures of interest tend to be more erratic than those at lower temperatures (less than 1000°C) with the high temperature runs showing discontinuities where the rate may suddenly increase rather than continue the normal drop in reaction rate. This is probably due to physical structure changes such as particle expansion and crack formation that are thermally induced, but this erratic nature is reproducible and consistent. See, for example, in Figure 2.5 how the nature of the rate curve for Mississippi limestone is parallel for the two particle sizes shown in the figure, with a sudden increase in reaction rate occurring at about 20% conversion for the 16-18 mesh particles and at a larger conversion (about 25%) for the 40-45 mesh particles. It is concluded that the results are reproducible and consistent.





2.5.2 Effect of Sorbent Type

The rate curves illustrating the effect of sorbent type on performance are shown in Figures 2.6 through 2.9. Comparisons are similar at temperatures of both 1000 and 1200°C. While the two dolomites have very similar behavior at 1000°C with their rate curve almost coincident (Figure 2.6), their behavior differs significantly at 1200°C with the Plum Run rate falling below the Tymochtee rate at intermediate conversions. This means that even though the dolomites behave very similarly at 1000°C, there are thermally induced differences that only appear at the higher temperature, and these differences appear mainly during the intermediate conversion of the sorbents with their rates being similar for greater than 50% conversion to calcium sulfate.

Note that both dolomites achieve calcium utilizations greater than 100% at 1000°C. This is consistent with previous testing at elevated pressure and indicates that either one or all of the following are occurring: 1) impurities in the sorbent are reacting with sulfur (iron, sodium, potassium, etc have the potential to form stable sulfates); 2) the magnesium component is entering into the sulfation reaction (magnesium oxide is known to sulfate at these conditions although the magnesium content of dolomites has only been found in past investigations to form traces of sulfate species); or 3) complex Mg-Ca-S-O components are being generated (39).

The five limestones show a large variation in sulfation performance at both 1000 and 1200°C. Ranking of the sorbent reactivity at 1000°C based on the extent of conversion of the sorbents when the rate is 2% per minute is Carbon > Highland > Mississippi > Greer > Vicron. The ranking of the limestones change in going from 1000 to 1200°C, becoming Highland > Carbon > Mississippi = Greer > Vicron. As has been found in all previous testing on coarse calcium particle sulfation, the impact of the sorbent type is critical to the performance. Note that the two dolomitic limestones (Highland and Carbon) rank higher than the other three limestones.



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Figure 2.9 — Comparison of 40-45 Mesh Limestones at 1200°C

2.5.3 Effect of Particle Size

The effect of particle size is illustrated in Figures 2.10 through 2.16 for a temperature of 1000°C. There is a clear and consistent rate reduction in the sulfation rate as the particle size is increased, and this trend holds also at 1200°C. For example, the two dolomites shown in Figures 2.10 and 2.11 have relatively smooth rate curves showing complete calcium sulfation for both particle sizes. The larger 16-18 mesh particles have a considerably smaller rate (at 20% calcium sulfation the rate is about 20% per minute) than the 40-45 mesh particles (at 20% calcium sulfation the rate is about 40% per minute). This trend agrees with previous testing and modeling expectations. Note that the initial reaction rate is difficult to obtain from the rate curves because the reactor induction period covers up the initial reaction results.

The limestone rate results in Figures 2.12 through 2.16 show the same trend of reduced rate with increased particle diameter and indicate much less than 100% final calcium conversion is obtained. Again, each limestone behaves differently. In addition, the limestones, other than Highland, all show discontinuous behavior where the reaction rate increases suddenly at an intermediate level of conversion. While the mechanism for this feature of increasing reaction rate has not been determined, it is a reproducible occurrence.

2.5.4 Bffect of Temperature

The effect of temperature is illustrated in Figures 2.17 through 2.23. Comparisons in the rate curves at 1000 and 1200°C are made for each sorbent at particle sizes of 40-45 mesh. The behavior with respect to temperature is mixed, with some sorbents being reduced in performance, some being only slightly impacted, and some being improved. These trends are fairly consistent between the two particle sizes tested. The two dolomites (Figures 2.17 and 2.18) behave similarly, with the Plum Run being slightly more sensitive to temperature (at 20% calcium sulfation the rate is about 8% per minute) than the Tymochtee dolomite (at 20% calcium sulfation the rate is about 14% per minute).



Figure 2.11 — Effect of Particle Size for Plum Run Dolomite at 1000°C







Figure 2.13 — Effect of Particle Size for Carbon Limestone at 1000°C



















Figure 2.19 — Effect of Temperature for 40-45 Wesh Highland Limestone







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Highland limestone (Figure 2.19), a dolomitic limestone, shows a slight reduction in conversion rate at calcium sulfation levels less than 20%, but the final extent of conversion is increased slightly as the temperature is increased. The coarser 16-18 mesh Highland limestone shows a little less sensitivity to increased temperature than do the 40-45 mesh particles. Carbon limestone of the 40-45 mesh size (Figure 2.20), the other dolomitic limestone, shows a significant decrease in sulfation rate when the temperature is increased. On the other hand, the coarser 16-18 mesh Carbon limestone shows a significant increase in sulfation rate as the temperature is increased from 1000 to 1200°C. The other three limestones all show a significant reduction in sulfation rate with increased temperature not only for the 40-45 mesh sizes considered in Figure 2.21 through 2.23, but also for the 16-18 mesh sizes not shown.

Another factor found with respect to the effect of temperature is that a reversible effect exists. Once a sample has approached a saturated condition at a high temperature it will be further sulfated if its temperature is reduced. This behavior is illustrated in Figure 2.24 and 2.25 for Vicron limestone and for Plum Run dolomite. In Figure 2.24 the Vicron limestone sample was heated at 1100°C and had reached a low sulfation rate after about 30 minutes. The temperature was then reduced to about 1000°C and the sulfation level then increased. Similarly, in Figure 2.25, Plum Run dolomite was sulfated at 1100°C for about 130 minutes to a conversion level of about 90% where the reaction rate became very small. When the temperature was reduced to about 1000°C the sulfation rate increased and the conversion jumped to about 110%. This behavior is of great interest in understanding the nature of high temperatures on calcium-based sorbent sulfation because it has previously been assumed that all of the high temperature behavior was due to irreversible sintering effects such that once a sorbent was exposed to high temperatures its reactivity would be permanently reduced.

2.5.5 Overall Qualitative Behavior

Many characteristics may be selected to depict the sorbent sulfation performance. One characteristic is the extent of calcium sulfation when the sulfation rate has dropped to some low value, such as 0.1% calcium sulfation per minute and is a quantity that might be considered the final or saturation sulfation level of the sorbent. This characteristic is listed in Table 2.4 for all of the coarse particle tests. The numbers in Table 2.4 are characteristic of the effects of sorbent type, particle size and temperature. The table indicates that Carbon limestone, a dolomitic limestone, performance nominally improves with increased temperature, as does Highland limestone, the other dolomitic limestone, while the other sorbents performance decrease with increasing temperature. While the characteristic is an indicator of the relative performance of the sorbent, it is not quantitative and should not be used to project the fluidised bed desulfuriser performance. As will be seen the integrated, quantitative performance, taking into account the total shape of the sulfation rate curve, may be significantly different from the values in Table 2.4. On the other hand, the relative ranking of the sorbents will not change.

Other qualitative observations made were 1) Highland limestone, Carbon limestone and Mississippi limestone all showed a tendency to "pop", or spontaneously explode into smaller particles when heated to about 400°C; and 2) some agglomeration of the sorbent particles and sticking to the platinum pan was found at 1200°C, especially for the smallest particle size of 40-45 mesh, and most strongly with Highland limestone. The popping phenomena is quite common with limestones and is likely to result from the breaking of hydrate bonds that occur at this temperature or the transition from the aragonite crystal to the calcite crystal. Calcination does not occur until a much higher temperature is reached and so does not contribute to popping. The agglomeration is likely to be due to sintering and low melting impurity interactions.

Sorbent	Particle Size	Fraction Sulfated Temperature (°C)			
	(mesh)	1000	1100	1200	
Tymochtee	-40+45	1.03		0.65	
dolomite	-20+25		0.90		
	-16+18	<1.0		0.52	
Plum Run	-40+45	1.07		0.63	
dolomite	-20+25		0.95	•	
	-16=18	1.04		0.41	
Mississippi	-40+45	0.41	0.15	0.11	
limestone	-20+25				
	-16+18	0.24		0.10	
Carbon	-40+45	0.51		0.51	
limestone	-20+25		0.18		
	-16+18	0.19		0.33	
Greer	-40+45	0.28		0.08	
limestone	-20+25		0.08		
	-16+18	0.09		0.07	
Righland	-40+45	0.52		0.65	
limestone	-20+25		0.66		
	-16+18	0.37		0.36	
Vicron	-40+45	0.15		0.05	
limestone	-20+25		0.05		
	-16+18	<0.09		0.03	

Table 2.4 — Characteristic Sorbent Performance

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2.6 PRETREATED SORBENT TEST RESULTS IN SO.

Coarse sorbent particles were pretreated by precalcination using a technique that has been shown to improve the reactivity of calciumbased sorbents used for atmospheric-pressure fluidized-bed combustion. The precalcination technique also showed a tendency to reduce the extent of sulfation performance lost as the sulfation temperature was increased at atmospheric pressure.

The test sorbents, Vicron limestone, Greer limestone, and Carbon limestone were precalcined at 950°C, in 60% carbon dioxide, and at atmospheric pressure. Two sizes were tested, 20-25 mesh, with sulfation at 1100°C, and 40-45 mesh, with sulfation at 1200°C. The sulfation rate curve for the untreated and pretreated sorbents are compared in Figures 2.26 through 2.31. There is no improvement in performance upon precalcination with any of the sorbents tested. In fact, Carbon limestone shows lower sulfation rate after precalcination than it does when it is used in the raw condition (Figures 2.28 and 2.31). The normal sorbent calcination that occurs when operating at high pressure and high temperature apparently yields the same type (or even better) of sorbent pore structure as does the precalcination procedure, so little change in sulfation performance is found.

2.7 TESTS RESULTS WITH HYDROGEN SULFIDE

Tests with hydrogen sulfide in the pressurized thermogravimetric balance were found to result in a severe operating problem: elemental sulfur would form within the back-pressure controller, making the pressure and gas flow very erratic such that data could not be collected. During the test program several attempts to correct this problem were made. Finally, an after-burner was placed downstream of the balance, but upstream of the back-pressure controller to convert the hydrogen sulfide to sulfur dioxide. This conversion permitted successful test operation.










Figure 2.28 - Precalcination Performance With Carbon Limestone: 20-25 Mesh, 1100°C



Figure 2.29 — Precalcination Performance With Vicron Limestone: 40-45 Mesh, 1200°C



Figure 2.30 — Precalcination Performance With Greer Limestone: 40-45 Mesh, 1200°C



Figure 2.31 — Precalcination Performance With Carbon Limestone: 40-45 Mesh, 1200°C

Limited testing of coarse sorbent particles was conducted to supplement the existing data base. The effect of temperature was the major parameter of interest, and runs only at 1100°C were completed to determine the reaction kinetics at this high temperature. Two tests were performed at atmospheric pressure, 1100°C, and with 0.3 mole % hydrogen sulfide, using Plum Run dolomite and Highland limestone. Then, a single test was completed with Plum Run dolomite at 5 atmospheres pressure and 1100°C with 0.46 mole % hydrogen sulfide. A comparison of the test results in H_2S and in SO_2 under similar conditions is made in Table 2.5, all for a particle size of 16-18 mesh. The detailed test results for the H_2S tests and for the sulfation tests made for comparison are compiled in Appendix B4.

Sorbent	H ₂ S mole%	SO ₂ mole%	Pressure (atm)	Maximum Calcium conversion(%)	Initial Rate % / minute		
Plum Run	0.3		1	0.95	3.1		
Plum Run	0.46		5	1.20	11.1		
Plum Run		0.1	5	0.60	3.9		
Highland	0.3		1	0.50	1.5		
Highland		0.1	5	0.50	1.6		

Table 2.5 — H_0S Test Results and Comparison With Sulfation

The values in the table indicate first that sulfidation of the Plum Run dolomite at 1100° C will proceed to higher calcium conversion than does sulfation of Plum Run dolomite. The dolomite test indicates that significant MgS is generated, although this occurs at a very slow rate. Water vapor in the gas would essentially eliminate MgS formation at these conditions. Also, sulfidation of Highland limestone leads to calcium conversion comparable to that obtained on sulfation. A comparison of the values in the table and the sulfidation rate curves

for Plum Run dolomite at 1 atmosphere and 5 atmospheres pressure (compiled in Appendix B4) shows that the sulfidation rate at 5 atmospheres pressure is much greater than it is at 1 atmosphere pressure, increasing at a power of the pressure of about 0.53. Also, the initial sulfidation rate is lower than the initial sulfation rate by a factor of about 0.6 to 0.7 for both the limestone and dolomite tested under comparable conditions of pressure and H_2S and SO_2 concentration.

These limited results show that hydrogen sulfide removal is comparable in effectiveness to sulfur dioxide removal at 1100°C. Further testing and use of the existing data base on coarse sorbent particle sulfidation is needed to make significant quantitative conclusions.

2.8 EVALUATION OF SULFUR REMOVAL KINETICS

In this section the test results described are evaluated to generate quantitative correlations of reaction kinetics behavior. First, the controlling reaction resistances are evaluated using dimensional analysis. Secondly, empirical rate correlations are developed for the sulfation and sulfidation reactions.

2.8.1 Dimensional Analysis of Controlling Resistances

A valuable technique to gain perspective on the controlling resistances in the reaction kinetics studied is to apply dimensional analysis. Such an analysis has been conducted and the details of the development are reported in Appendix C. A summary of the results of the dimensional modeling are shown in Table 2.6, showing the impact of particle size, pressure, temperature, and internal particle structure on the reaction rate for two key cases: reaction rate control by gas diffusion into the pores of the sorbent particle, and reaction rate control by solid diffusion in the sorbent particle grains. The case of chemical reaction control is not considered since it is unlikely to control for the coarse particle sizes studied. The dimensional analysis leads to the conclusion that the reaction rate should be first order in

the SO_2 (or H_2S) concentration, as has been observed consistently for coarse particle sulfation (or sulfidation) in many previous investigations.

The thermogravimetric data collected has been analyzed with respect to the dimensional analysis performed. For example, according to Table 2.6 (the column for solid diffusion control and the item "particle size") the sulfation rate, da/dt, should be independent of particle size if it is controlled by the rate of solid diffusion and should be only a function of time, so a plot of the rate versus time data for the 400 and 1000 micron particle runs at 1000°C should indicate the possibility of solid diffusion control if no particle size dependency is shown. Such plots are shown for each of the seven sorbent tested in Figures 2.32 through 2.38, suggesting that solid diffusion may control in the early stages of the reaction where the rate curves are close together and particle size has little impact. Note that in these plots, the logarithm to the base 10 of the sulfation rate multiplied by 100 is shown.

Similarly, from Table 2.6 a plot of (the reaction rate times the particle diameter squared) versus (the time over the particle diameter squared) will indicate the existence of pore diffusion control. From Appendix C it is equivalent to plotting (the reaction rate times the particle diameter squared) versus (the fraction sulfated). This type of plot in Figures 2.39 through 2.45 for the 400 and 1000 micron sizes of all seven sorbent tested suggests that pore diffusion may control in the latter stages of the reaction for most of the sorbents. Pore diffusion control appears to be initiated after about 60 to 70% calcium sulfation for the dolomites in Figures 2.39 and 2.40. Pore diffusion control begins in the limestones at conversions ranging from about 5% up to about 30% depending on the specific limestone.

	Pore Diffusion Control	Solid Diffusion Control
Particle	1) ^a d $\alpha_1/dt \Phi R_o^2 = f \{t/R_o^2\}$	$d a_1/dt = f \{t\}$
Size	2) ^b = f {t/R _o ² , R _p /R _o }	
Pressure	1) $d a_1/dt = f \{t/P\}$	$d a_1/dt = P f \{t\}$
	2) = $P f \{t\}$	
Temperature	1) $d \alpha_1/dt = T^{.8} f \{t T^{1.8}\}$	$d a_1/dt = \exp[-(E_a+E_s)/T]/T$
		x f {t $exp(-E_x/T)$, k_s }
	2) d $a_1/dt = T^{5} f \{t T^{.5}, k_s\}$	
Internal Structure	1) $da_1/dt = 1/(m_r(1-\epsilon_o-\epsilon_i))$	$d a_1/dt = 1/(\Phi_g R_{go}^2)$
	$x f \{t. , r'p\}$	x f $\{t/R_{go}^2, m_r/m_p\}$
	2) d $a_1/dt = 1/(m_r(1-\epsilon_o-\epsilon_i))$	
	x f {t, $R_{po}/R_o, m_r/m_p$ }	

Table 2.6 — Dimensional Analysis Results

- a Case 1 under pore diffusion control is for molecular diffusion in the pores.
- b Case 2 under pore diffusion control is for Knudsen diffusion in the pores.

Table 2-6 (Continued)

Nomenclature is as follows:

<i>a</i> ₁	=	the	fraction of the sorbent calcium reacted
t	=	the	time
Ф.	=	the	particle sphericity
Ф ₂	=	the	grain average sphericity
R	=	the	equivalent radius of the particle
R	=	the	equivalent radius of the grain
R	=	the	average pore radius
P	=	the	gas pressure
Т	=	the	absolute temperature
Es	=	the	activation energy for the solid diffusion
E	=	the	activation energy for the adsorption of ${ m SO}_2$
k_s	=	the	particle sintering rate constant
□	=	the	molar density of the solid reactant species
ш Б	=	the	molar density of the solid product species
έ	=	the	initial calcine porosity
ϵ_{io}	=	the	initial volume fraction of inerts in the particle



Figure 2.32 — Solid Diffusion Control for Tymochtee Dolomite at 1000°C







Figure 2.34 — Solid Diffusion Control for Highland Limestone at 1000°C







Figure 2.36 — Solid Diffusion Control for Mississippi Limestone at 1000°C



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Figure 2.38 — Solid Diffusion Control for Vicron Limestone at 1000°C



Figure 2.39 — Pore Diffusion Control for Tymochtee Dolomite at 1000°C



Figure 2.40 — Pore Diffusion Control for Plum Run Dolomite at 1000°C



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Figure 2.41 — Pore Diffusion Control for Highland Limestone for 1000°C



Figure 2.42 - Pore Diffusion Control for Greer Limestone for 1000°C



Figure 2.43 — Pore Diffusion Control for Mississippi Limestone for 1000°C



Figure 2.44 — Pore Diffusion Control for Carbon Limestone for 1000°C



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Figure 2.45 — Pore Diffusion Control for Vicron . Limestone fcr 1000°C

This behavior trend seems to be confirmed by earlier testing of the effect of pressure on the sulfation rate for Plum Run dolomite (12), again following the dimensional analysis presented in Table 2.6, and it is concluded that solid phase diffusion control in the early stage of conversion and pore diffusion control in the late stages of conversion are probable mechanisms.

While this type of analysis provides insights into the reaction mechanisms, it has certainly not been fully developed to consider phenomena such as adsorption. Further evaluation of sulfation rate data using this type of analysis is needed.

2.8.2 Empirical Rate Correlation for Untreated Sorbent Sulfation

The rate data was subjected to statistical analysis using the empirical model suggested by the shape of the rate curves:

$$d a/dt = k (1 - a)^{m}$$
 (2-8)

where a is the fraction of the calcium sulfated, t is the time, k is an empirical reaction constant, and m is an empirical reaction order constant. Plotting the sulfation rate data in the form of

$$Ln(da/dt)$$
 versus $Ln(1-a)$ (2-9)

should yield a straight line having slope m. The sulfation rate data is found to actually plot as three straight lines segments for all of the runs performed rather than the ideal single line, and it is believed that this is because the reaction controlling resistance changes as the level of sulfation increases, as was shown in the previous section using dimensional analysis. Note that a higher value of the reaction order m means that the sorbent has a lower reaction rate for the same fractional conversion to calcium sulfate.

A typical rate curve in this form is shown in Figure 2.46. This curve for Carbon limestone of 20-25 mesh size shows line segment 1 Ő

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Figure 2.46 — Empirical Fit of Rate Expression to Rate Data: Three Straight Line Segments

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extending from Ln(1-a) = 0 to about -0.15 (equivalent to the fraction of calcium sulfated extending from a = 0 to 0.14). The line segment 2 extends from Ln(1-a) = -0.15 to about -0.22 (equivalent to calcium sulfation extending from 0.14 to 0.20) and line segment 3 extends beyond 0.22 calcium sulfation. A tabulation of the value of a at each of the two intersection points of the three line segments; the initial sulfation rate (equal to the rate constant k for the first line segment); the rate constant, k, for the second and third line segments; and the reaction order, m, for each of the three line segments are shown in Table 2.7 for all of the untreated sorbent tests conducted.

Examination of the data in Table 2.7 and of the rate curves compiled in Appendix B.1 shows several things:

1) The behavior is similar for five of the seven sorbents, a loss of reactivity is seen as the temperature is increased, while the two that increase in reactivity, Highland and Carbon limestones, show behavior trends that strongly contrast. This can be seen in Table 2.7 by noting that the values of m in all of the line segments increase as the temperature is increased (for equal values of the particle size) for the sorbents Tymochtee, Plum Run, Greer, Mississippi, and Vicron, while the value of m drops as the temperature is increased for Highland and Carbon limestones. This behavior is seen qualitatively in Figures 2.22 through 2.28 as has been described earlier.

2) All seven of the sorbents have initial sulfation rates that display the same behavior trends, with the initial sulfation rate decreasing as the temperature is increased from 1000 to 1200°C. This is clearly seen in Table 2.7 by comparing the initial reaction rate for each sorbent for equal particle sizes. This is more difficult to discern from the actual rate graphs.

3) The data suggests that, at least for the five sorbents with decreasing reactivity as the temperature is increased, there is a similarity in behavior such that:

-- the reaction rate at each of the two intersection points is constant relative to the initial reaction rate, or R_0/R_1 is a constant and R_0/R_2 is a constant, where R_0 is the initial reaction rate, R_1 is the reaction rate at the first intersection point in the curve, and R_2 is the rate at the second intersection point in the rate curve.

-- the points of intersection are related by the ratio $(1 - a_1)/(1 - a_2)$ being constant, where a_1 is the fractional calcium conversion at the first intersection point and a_2 is the fractional calcium conversion at the second intersection point in the rate curve.

Thus, the only factors that need to be correlated are the ratios R_o/R_1 , R_o/R_2 , and $(1-a_1)/(1-a_2)$, the initial reaction rate R_o , and the quantity a_1 .

The parameters involved are the sorbent characteristics:

the mass fraction calcium carbonate, X_{CaCO_3} the mass fraction magnesium carbonate, X_{MgCO_3} the inert mass fraction, X_{inert} the pore surface area, A (m²/gm) the average pore diameter, d_p (microns) the average porosity, ϵ_p and the average grain size, d_g (microns)

and the operating parameters:

the particle diameter, D (microns)

and the temperature, T (°C)

Table 2.7 — Correlation of Coarse Particle Reaction Kinetics

Sorbent	Run . Number	Particle Diameter, Microns	Temperature, °C	Calcium Fraction Sulfated at First Intersection	Calcium Fraction Suttatat at Second Intersection	Initial Reaction Rate, min ⁻¹	Second Segment k	Third Segmen k	First t Segment m	Second Segment m	Third Segment m
Tymochtee	P437	327	1000	á TI	0. 935	0.511	0.836	LZZ	1.00	1.40	19
Dolumite	P444	1095	1000	Û. 55	0. 89	L 333	0, 206	0.027	240	1.63	0.713
	P452	774	1100	0, 18	0.49	0, 162	0, 264	0.009	2,96	543	0.48
	P460	387	1200	0, 35	0.59	0, 261	2,58	0.005	2 65	7.97	103
	P459	1095	1200	0. 217	0,45	0.182	0,688	0, 609	12	8.69	<u>8.49</u>
Plum Pun	P439	217	1000	6.62	Q. 66	0. SGP	0.040	0.400	1_18	1.00	1.34
Dolomite	P445	1095	1000	0, 33	0,83	0.383	0, 278	0. 031	2.77	1.98	0,746
	P453	T 74	1100	0,15	£ 23	0, 147	1.08	0.013	4.92	17. 2	0.572
	P462	387	1200	0.25	0, 429	0, 237	1.41	0.003	12	10.8	0.257
	P461	1099	1200	û. 185	0.523	0, 251	L 79	0.082	62	15.9	8.1D
Highland	P439	387	1000	0, 233	0.35	0.285	3.44	0.030	<u> </u>	14.9	394
Limestone	P446 .	1095	1000	0.19	0, 31	Q. 178	0.407	0, 367	9,12	13.0	12.7
	P454	774	1100	Q 18	0.34	0, 133	0.242	0.007	7.17	10.1	1.80
	P468	387	1200	0, 238	0, 48	0, 162	0, 597	0.011	3.19	7.99	1,99
	P467	1095	1200	0.138	ù, 27	UL 14/	0,452	0.029	9,11	16.3	1. 89
Greer	P440	387	1000	0.0875	0.138	0.261	5Å. 0	Q. 010	16.4	68.7	ш.)
Limestena	P451/447	1075	1000	0.045	0.003	0, 300	4.07	0.043	43.4	102.1	<u>12</u> 4
	P455	T 74	1100	0.068	0.081	0, 18	Z76.0	0.003	41.0	145.2	12.5
	P470	387	1200	0.056	1.084	0. 214	37.2	0.002	32.9	122.5	12.1
	P469	1095	1200	0.043	0.073	0.22	18.4	0.001	43.8	144.5	15.3
Mississippi	P441	387	1000	0.154	0.28	0.383	17	.011	9.14	ZL 9	4.80
Limestone	P448	1095	1000	0, 095	0. 222	0.261	0.479	123	14.3	20.4	28.0
	P456	774	1100	0,060	0.125	2 16	0. 271	1.05	Z1. Z	29.7	39.9
	P472	387	1200	0.051	0.115	0.178	L 29	2 005	23.8	61. 8	16. B
	P471	1095	1200	ù, 058	0,0%	0,18	6.81	0.002	叉3	93.2	16.2
Cárbón	P442	387	1000	0. 718	0.34	0.422	14.6	0.074	1.85	20.2	165
Limestone	P449	1095	1000	0.09	0.19	0.261	1.25	0.047	14.4	31.0	15.5
	P458	774	1100	0,14	0.20	0.18	171	0.003	11.4	33.1	1.01
	P466	387	1200	0.145	0.34	0.237	0.549	0.009	1.51	12.8	3 20
	P465	1095	1200	6,15	0.31	0.147	0.798	0.004	7. 28	17.3	1.0
Vision	P443	392	1600	0.069	0.11	0.516	24	û. ÎDS	<u>12</u> 0	6Ú.4	12
Limestone	P450	1095	1000	0.024	0.05	0.20	0.539	0.029	Ä 1	85.2	214
	P457	774	1100	0.0185	0.037	0.26	0.025	0.026	140.1	80.5	49.6
	P464	387	1200	0.0375	0.054	0.162	11.5	0.005	66.0	181.8	42.3
	P463	1095	1200	0.015	0.034	0.152	0.788	0.014	116.8	225.7	110.8

The mass fraction of $CaCO_3$, $MgCO_3$ and inerts sum to unity, so the mass fraction of $CaCO_3$ can be eliminated as a parameter. The average pore diameter is directly related to the porosity and the surface area through the mercury porosimeter measurements and calculations, so it may also be eliminated. Also, for the seven sorbents studied, it is found that the porosity correlates very well with the sorbent composition, grain size and surface area by

$$\epsilon_{\rm p} = 1.977 \ ({\rm A})^{0.43} \ ({\rm d_g})^{0.46} \ ({\rm X_{inert}})^{0.46} \ ({\rm X_{MgCO_3}})^{-0.19}$$
 (2-10)

with the standard error of this correlation being about 20%. Then, the porosity of the sorbent may also be eliminated as a parameter in the evaluation.

Six parameters remain: X_{MgCO_3} , X_{inert} , A, d_g, D, and T.

The quantities proposed to be constant, R_0/R_1 , R_0/R_2 , and $(1-a_1)/(1-a_2)$ have been calculated from the test data as reported in Table 2.7, and statistically evaluated for all of the tests completed using standard statistical methods to see if they are indeed approximately constant. The results are as follows:

 R_0/R_1 :

sample average -- 5.34
standard deviation -- 3.51
median -- 4.21
95% confidence limits -- 4.14 to 6.55

 R_0/R_2 :

sample average -- 129 standard deviation -- 140 median -- 75 95% confidence limits -- 81 to 177

$$(1 - a_1)/(1 - a_2):$$

sample average -- 0.80
standard deviation -- 0.22
median -- 0.85
95% confidence limits -- 0.72 to 0.88

While these ratios show a significant variation, they draw the test results very close together considering the extremely wide variation in sorbent behavior observed. Errors arise from several major sources: sorbent sample not representative or homogeneous, thermogravimetric balance measurement errors, rate data evaluation errors, and model errors. Considering the potential magnitude of the errors, the proposed similarity of the rate curves is a good method to bring the data together in a more uniform description.

The initial reaction rate (expressed as the fraction of calcium sulfated per minute in a gas containing 0.5% SU₂ by volume) may be correlated against the parameters for all of the seven sorbents tested since all seven displayed the same trends. In the correlation below, generated by standard multiple regression techniques, each parameter is shown divided by its mean value for the 36 runs.

$$R_{o}/0.2506 = 0.0385 (X_{MgC0_{3}})/17.8)^{-.0075} (X_{inert}/2.55)^{0.215}$$

$$(A/0.486)^{-0.0338} (d_{g}/145)^{0.107} (D/748)^{-0.277}$$

$$exp[4799/(T + 273)]$$
(2-11)

The standard error for this correlation is about 31%. Obviously, the parameters X_{MgCO3} , A, and d are of little significance. The initial rate increases as the inert fraction in the sorbent increases, as the particle diameter decreases, and as the temperature decreases, in the range of conditions tested. The small influence of particle diameter is consistent with a predominant solid phase diffusion control in the initial reaction rate.

In a similar manner the calcium conversion at the point of the first intersect in the rate curve, a_1 , may be correlated with the parameters for the five sorbents that displayed a reduced reactivity with increasing temperature (Tymochtee, Plum Run, Mississippi, Greer and Vicron), all of these showing a reduced value of a_1 as the temperature was increased.

$$a_{1} = 0.00196 (X_{MgCO_{3}})/20.5)^{0.639} (X_{inert}/2.5)^{-0.079}$$

$$(A/.45)^{0.376} (d_{g}/184)^{-0.062} (D/748)^{-0.517}$$

$$exp[5990/(T + 273)] (2-12)$$

The standard error in this correlation is about 36%. The parameters X_{inert} , and d are not significant. The value of a_1 increases as X_{MgCO3} increases, as the term A increases, as D decreases, and as the temperature decreases. The larger the value of a_1 is, the larger is the overall reactivity of the sorbent.

The value of a_1 for the two sorbents tested that display increased reactivity with increased temperature, Highland and Carbon limestones, increases as the temperature increases, although it follows the same trends in X_{inert} , A, and D as for the other five sorbents. The explanation for the behavior of these two sorbents is not found in the values of the chemical and physical properties of the sorbents measured and reported in Table 2.2 and the fact that they are both dolomitic limestones may or may not be significant. Some other chemical/physical

properties as yet not known may explain these results. At this point the only clues are found in the fact that Carbon limestone shows a tendency to "pop", or spontaneously explode when reaching the temperature of about 400°C, probably due to the breakage of hydrate bonds or the transition from aragonite to calcite crystals since this is the temperature of $Ca(OH)_2$ decomposition and aragonite transition. Thus, the crystal structure of Carbon limestone is probably altered when this occurs, giving more favorable performance. Also, previous tests at atmospheric pressure with Carbon limestone show that it is more reactive when it is shock calcined than when it is slowly calcined, contrary to most sorbents that show little or no difference. These two factors, popping and shock activation, may be empirical indicators of sorbents that will perform well at high temperatures.

Highland limestone also shows a tendency to pop, consistent with its improved performance at higher temperatures. Its shock calcination behavior has not been tested. One other sorbent, Mississippi limestone, also shows the popping behavior, but is not increased in activity as the temperature is increased, so this factor alone is not sufficient to indicate the activation at increased temperatures.

It must also be pointed out that the reversible temperature effect found with all of the sorbents, was also found with Carbon and Highland limestones -- that is, when Carbon and Highland limestones approached saturation, a drop in the temperature would increase the reaction rate and the extent of sulfation, although the increase was not as significant as with the other five sorbents.

Other explanations for the behavior of Carbon limestone and Highland limestone may be hypothesized based on thermal sintering influences on the pore size distributions, impurity interactions with the possible formation of liquid phases, improvements in the solid phase diffusion coefficient, etc. All of these are speculative phenomena and would require detailed testing.

2.8.3 Analysis of Rate Data for Sorbent Sulfidation

The rate data for the sulfidation tests with hydrogen sulfide, though not as extensive as the tests with sulfur dioxide, also reveal some important factors. First, it is assumed that the reaction rate is first-order in the H_2S partial pressure from previous studies. Then, from the two runs with Plum Run dolomite in H_2S at pressures of 1 and 5 atmospheres (runs P484 and P481 shown in Appendix B4) it can be determined that the reaction rate is proportional to the 0.5 power of

$$da/dt = k (1 - a) Y P^{0.5}$$
 (2-13)

the total pressure. The reaction is also found to be about first-order in the calcium fraction reacted over at least the first 70% of conversion, so the rate expression becomes for dolomites where Y is the volume fraction of H_2S in the gas and P is the total gas pressure. For Highland limestone (run P485 in Appendix B4, page B-184) the rate expression is roughly

$$da/dt = k (1 - a)^5 Y P^{0.5}$$
 (2-14)

The initial reaction rates with H_2S are slightly lower than with SO_2 . For identical conditions of pressure, temperature and concentration the initial rate of reaction with H_2S is about 70% of the initial rate with SO_2 with both Plum Run dolomite and with Highland limestone. On the other hand, the extent of calcium conversion tends to be considerably greater with H_2S than with SO_2 because, as is expected, the rate of reaction falls off less rapidly as conversion is increased.

2.9 EVALUATION OF THE FLUIDIZED-BED DESULFURIZER

An engineering model of the fluidized-bed desulfurizer has been developed based on previous Westinghouse sulfur removal modeling for fluidized bed combustion systems (21, 37, 38). The model, described in detail in Appendix D, is based mainly on the following set of assumptions:

-- The reaction kinetics in the fluidized-bed desulfurizer may be scaled using the laboratory measured kinetics for the specific temperature, particle size, and sorbent.

-- Significant sorbent particle attrition or agglomeration does not occur in the fluidized-bed desulfurizer.

-- The fluidized bed behaves either in a large particle mode having high rates of gas flow through the slow bubbles in the bed, or it behaves as a turbulent fluidized bed having high particle streaming and good gas-particle contacting.

-- The temperature is uniform in the fluidized bed and the sorbent particles are perfectly mixed within the bed.

These assumptions apply best to the situations of very coarse particles, where bubble are predominantly of the slow type, or for turbulent fluidization, where gas-solids mixing is very uniform.

The model developed uses the thermogravimetric kinetic data reported and evaluated earlier (the kinetic characteristics in Table 2.7) to generate performance estimates for the commercial desulfurizer. The integrated kinetic information will describe the behavior of the specific sorbents tested as a function of the major desulfurizer operating and design parameters: the temperature, the superficial velocity, the bed depth, and the bed particle size. Note that for fluidized bed desulfurizers the sulfur removal performance is independent of the sulfur content of the coal (so long as the equilibrium SO₂ or H₂S concentration in the gas is always far exceeded). This is due to the well mixed nature of particles in the fluidized bed. The performance factors of interest are

-- the calcium-to-sulfur ratio required to achieve a specified sulfur removal efficiency; 90% sulfur removal is assumed as the

requirement in this evaluation since it corresponds to the New Source Performance Standard for large utility boilers.

-- the mass of sorbent fed per mass of sulfur fed in the combustion products to achieve the specified sulfur removal efficiency; since the sorbent mass per unit of calcium may differ significantly between the sorbents considered this factor relates more closely to the economic impact of the purchased sorbent.

-- the gas residence time required in the desulfurizer, or the ratio of the bed depth (H) to the gas superficial velocity (U); this factor relates to the size of the desulfurizer and the pressure drop across the desulfurizer.

-- the energy consumption resulting from the sensible heat loss in the waste sorbent and in calcining and sulfating the sorbent; this factor is small if calcium-to-sulfur ratios as low as about 2 can be used (the exothermic sulfation reaction almost balances the endothermic calcination reaction) and if heat recovery from the solid waste is incorporated into the plant design.

The following Figures (Figure 2.47 through 2.53) show the calculated calcium-to-sulfur ratio (moles of calcium fed per mole of sulfur fed) for SO, removal as a function of the temperature, particle size and the quantity [gas residence time in the bed (H/U) multiplied by the quantity (1 minus the bed bubble volume fraction) times (1 minus the emulsion phase voidage fraction)] for each of the seven sorbents tested. The points shown on the curves are calculated points. Typically the quantity $(1-\delta)(1-\epsilon)$ will be about 0.35 depending on the fluidization velocity and sorbent particle size. The performance variation is very large between the sorbents and the implications on the desulfurizer design and operating conditions are related directly to the figures. Obviously it is economically desirable to operate with a shallow bed so that the desulfurizer is compact and so pressure drops are small, to operate with high gas velocities to minimize the desulfurizer diameter, and to use small calcium-to-sulfur ratios to minimize operating cost and waste disposal.













Figure 2.53 — Fluid Bed Desulfurizer Performance Using Vicron Limestone

For a specific gas residence time, H/U, of one-half second in the bed, the following tabulation, Table 2.8, of calcium-to-sulfur ratios and sorbent mass to sulfur mass ratios result. Note that a typical value of the gas residence time, H/U, in pressurized fluidized bed combustion would be about 2 to 3 seconds or even greater in some designs. The obvious detrimental effect of temperature on some of the sorbents, and the limited temperature effect on other sorbent is apparent from the figures and Table 2.8: dolomites will be suitable sorbent even at temperatures as high as 1200°C, although not as good as at 1000°C; limestones having the characteristics of Highland and Carbon will be very good sorbents at temperatures as high as 1200°C, even better than the dolomites on a weight basis; limestones having the characteristics of Greer, Mississippi, and Vicron will be unacceptable for use at temperatures even as great as 1000°C. The kinetic data for sorbent sulfidation for Plum Run dolomite and Highland limestone has been used to estimate the performance of a fluidized bed desulfurizer for H_2S removal. At the bed temperature of 1100°C and with a particle diameter of 1095 microns, Plum Run dolomite would require a calcium-tosulfur ratio of about 1.5 to remove 90% of the H_2S for the same conditions as those in Table 2.8. Highland limestone would require a calcium-to-sulfur ratio of about 2.6 at these same conditions. Both of the sorbents would perform in HoS removal about the same as they do in SO_2 (with the exception of the differing equilibrium constraints).

Statistical evaluation of the calcium-to-sulfur results for SO_2 removal for the five sorbents that were found to decrease in performance as the temperature was increased (Plum Run, Tymochtee, Greer, Mississippi, and Vicron) results in the following correlation of the calcium-to-sulfur ratio for a gas residence time of one second, a sulfur removal efficiency of 90%, all at a pressure of 10 atmospheres:

$$Ca/S = 1613 (X_{MgC0_3})^{-0.666} (X_{inert})^{-0.073} (A)^{-0.443} (d_g)^{-0.20}$$

$$(D)^{0.342} \exp[-8331/(T + 273)]$$
(2-15)

	Basis:	$H/U (1-\epsilon)(1-\delta) = 0.175 \text{ sec}; H/U = 0.5 \text{ sec}$							
-	•	Calcium/Sulfur Molar Ratio				Sorbent Mass/Coal Mass (3 wt % sulfur in coal)			
	Dp(µm) T (*C)	387 100	1095 0	387 120	1095)0	387 100	1095 00	387 120	1095
Tymochtee Dolomite		1.0	1. 2	1.8	2.4	0.19	0.22	0.34	0.45
Plum Run Dolomite		1.0	1.2	2.3	3.0	0.19	0.22	0.42	0.55
Highland		2.1	3.2	1.8	3.6	0.24	0.37	0.21	0.41
Greer		7.0	13.5	13.0	16.0	0.70	1.35	1.30	1.60
Mississippi		3.2	4.6	10.5	12.4	0.32	0.46	1.05	1.24
Carbon		2.3	5.5	2.7	3.5	0.24	0.58	0.28	0.37
Vicron .	•	10.0	16.0	21.0	38.0	1.0	1.6	2.1	3.8

Table 2.8 - Sorbent Consumption for 90% Sulfur Removal

The standard error of this correlation is about 18%. Increased magnesium content, increased surface area, and, surprisingly, increased grain size, all contribute to a reduction in the sorbent consumption. As is expected, decreased particle diameter and decreased temperature contribute to reduced sorbent consumption. Thus, sorbents for high temperature application having high magnesium content, high surface area, and large grain size should be selected. Designs using small particles sizes (as small as 300 microns) should be used; for example, a circulating fluidized bed rather than a bubbling fluidized bed may provide improved performance.

The two dolomitic limestone sorbents that yield improved performance with increased temperature (Highland and Carbon) show the following statistical behavior for SO, removal:

Highland limestone fits a particle diameter to the 0.56 power, while showing very little temperature effect. With a standard error of about 11%, the calcium-to-sulfur ratio for a one second gas residence time in the bed is given by

$$Ca/8 = 0.0589 (D)^{0.56} cxp[30/(T + 273)]$$
 (2-10)

Carbon limestone shows a particle diameter power very nearly the same, 0.55, with a higher temperature sensitivity:

$$Ca/S = 0.0245 (D)^{0.55} \exp[1699/(T + 273)]$$
 (2-17)

Major factors in the economic balance for the power plant are: 1) the sulfur content of the coal and the required sulfur removal efficiency, 2) the delivered cost of sorbent to the plant, and 3) the cost of solid waste disposal. Comprehensive cost models of direct coal-

fired power plants are not available, but based on fluidized-bed combustion studies it is likely that calcium-to-sulfur ratios of less than 2.0 would be acceptable for dolomites and less than 3.5 for limestones. This also assumes delivered sorbent costs of less than about \$20/ton. On this basis, Tymochtee dolomite and Plum Run dolomite could be economically used at temperatures up to 1200°C if particle sizes of less than 400 microns and H/U $(1-\epsilon)(1-\epsilon_b)$ greater than 0.2 were used. Highland limestone could be economically used at temperatures up to 1200°C with shallower beds or beds having higher velocities than those suitable for the dolomites. Carbon limestone would also be acceptable at temperatures up to 1200°C for a wide range of operating conditions. None of the other sorbents would be expected to be economically suitable for operation in a fluidized bed desulfurizer at temperatures greater than 1000°C. The disposal cost of residue from SO, removal will be lower than the residue from H₂S removal because the sulfided form of calcium is environmently unacceptable for direct disposal and required further processing.

The pressure drop through the fluidized bed desulfurizer will be on the order of about 10 kPa per meter of bed depth. At ten atmospheres pressure an acceptable pressure drop through the desulfurizer system would be about 0.3 atmospheres. Assuming a distributor pressure drop of about 20% of the bed pressure drop, the bed depth could then be up to about 3 meters. Obviously, the gas residence time in the bed is the critical parameter with respect to sulfur removal. Shallow beds could be used if operated at low velocity. For example, with a gas residence time of 0.3 seconds and a velocity of 0.7 m/s, the bed depth would be about 0.2 meters, but the vessel would be very large in cross-section. The deep bed design, with a gas residence time of 1 second, could operate at velocities up to 3 m/s resulting in compact vessel crosssection.

Optimization of the plant economics with respect to the desulfurizer vessel is needed, but many degrees of freedom exist to achieve minimum cost. Contrary to the difficulties of feeding coal in

fluidized-bed combustion systems, the sorbent need not be fed in a well distributed manner, but may be fed at only a few points in the vessel. Factors such as sorbent agglomeration, attrition, and elutriation, as well as the distribution of hot gas to the base of the fluidized bed desulfurizer will also influence the choice of operating conditions.

3. FINE CALCIUM-BASED SORBENT PARTICLE FOR SULFUR REMOVAL

Section 3 is devoted to the evaluation of fine, calcium-based sorbents for sulfur removal from the combustion products of direct coalfired turbines. Fine particles are defined here as having diameters less than about 40 microns, suitable for injection into and entrainment by the hot combustion gases. Background information is reviewed and the key data needs are identified. The test plan, test equipment and procedures are described, using a dispersed particle reactor to simulate the entrained particle environment. Tests that measure the kinetics of sulfation and sulfidation of "sintered", low surface area sorbent particles were conducted -- these are representative of the behavior of sorbents that have been exposed to very high flame temperatures when injected into the combustor or to the behavior of commercial limes. The kinetics of sulfidation and sulfation are evaluated and correlated for the sintered, low surface area sorbents. A conceptual commercial evaluation of sulfur removal performance in entrained desulfurizers using the sintered sorbents is performed based on these measured kinetics. Finally, the kinetics of sulfidation and sulfation of the sintered sorbents is scaled to that expected for active, freshly calcined sorbénts having high, but transient surface areas. The commercial performance of these active sorbents is projected.

3.1 BACKGROUND

The data base for the kinetics of the sulfation and sulfidation of fine calcium-based sorbent particles is very limited, especially in the area of elevated pressures, when compared to the coarse particle data base. The following discussion summarizes what has previously been
reported in the literature, most of which comes from research directed toward sorbent injection into conventional furnaces at atmospheric pressure.

3.1.1 Bffect of Calcined Sorbent Surface Area

The reaction rate of sulfation or sulfidation is observed to be sensitive to the initial surface area of the calcined sorbent. Increased calcined surface area increases the reaction rate and the extent of conversion that can be obtained. Borgwardt, et al, have reported on laboratory studies for both sulfation and sulfidation and have concluded that the reaction rate is proportional to the initial calcined surface area squared (40, 41). Examination of their data shows that they have considered rates for exposure times greater than about 3 seconds that do not apply to the exposure times characteristic of entrained desulfurizers -- the rate has dropped significantly for these long residence times, and exposure times less than 1 second are actually of interest. If the initial reaction rates are estimated from the Borgardt data, it is seen that the reaction rate is roughly proportional to the calcined surface area to the first-power, consistent with the observations of several other investigators (42-47).

These investigators present data on the rate of calcination and surface area development for limestones, dolomites, and lime hydrates.

3.1.2 Effect of Temperature

In the temperature range of interest to direct coal-fired turbines it is known that the surface area of sorbent particles is a strong function of time, changing very quickly during exposure. This transient surface area behavior has been measured by several investigators (42, 46-49). The surface area passes through three stages of development: 1) A sudden surface area increase as the sorbent calcines, 2) a simultaneous surface reduction catalyzed by the presence of H_0O or CO_0 during the calcination process, and 3) a slower thermal

sintering of the particle following complete calcination. Higher temperatures increase the rate of calcination while also increasing the rate of thermal and catalytic sintering.

Hydrated limes calcine much more quickly than do limestones or dolomites. The effect of temperature on the sulfation reaction itself seems to be overshadowed by the impact of the temperature on the initial calcined surface area.

3.1.3 Effect of Pressure

The effect of pressure on the calcination rate of fine sorbent particles has not been previously measured. It is expected based on coarse particle testing that higher pressures will reduce the rate of sorbent calcination and will increase the rate of sorbent sintering, resulting in lower surface areas of calcined particles. Simons, et al (50) measured the rate of sulfation of fine sorbent particles over a range of pressures and concluded that the "intrinsic" reaction rate is directly proportional to the total pressure, but the intrinsic reaction rate has little to do with overall sorbent reaction performance. Their testing was conducted in a packed bed requiring relatively long particle exposure to high temperature before sulfation.

3.1.4 Effect of Sorbent Type

Several classes of calcium-based sorbents may be applicable for use in entrained desulfurizers: raw limestones and raw dolomites having fine grinds; calcitic hydrates $(Ca(OH)_2)$ having characteristic sizes of about 2 to 5 microns; dolomitic hydrates $(Ca(OH)_2.Mg0)$ or dihydrates $(Ca(OH)_2.Mg(OH)_2)$ having characteristic particle sizes of about 2 to 5 microns; commercial limes (CaO) or specially produced high surface area limes (not commercially available) as fine grinds. Significant differences between the sulfation performance of limestones, dolomites, hydrated limes, hydrated dolomites and limes have been noted. Within each class the differences are quite minor compared to the differences found for coarse particles, and this is a result of the small particle

size and the relatively small pore diffusion resistances. The major factors for differences in sorbent types seems to relate simply to the surface area and particle size while impurities may also have an influence on the variations observed. The order of reactivity found is usually hydrated dolomite > hydrated lime > dolomite > lime > limestone with characteristic surface areas of these materials being: limestones and dolomites about 1 to 5 m²/gm; calcitic and dolomitic hydrates about 10 to 30 m²/gm; commercial limes about 1 to 5 m²/gm; and specially prepared limes about 20 to 50 m²/gm.

Borgwardt, et al (49) concludes that the rate of sorbent calcination is directly proportional to the initial surface area of the raw sorbent, which may lead to a variation in the resulting calcine surface area for different sorbent types. The treatment of sorbents with additives of various types has indicated some improvement in reactivity, though this is a secondary effect that may well not be applicable for use in direct coal-fired turbines.

3.1.5 Effect of Gas Composition

The sulfation and sulfidation reactions have been found to be first-order in the SO₂ or the H₂S mole fraction by most investigators. Borgwardt (51), for example, found the rate of sulfation of uncalcined limestone particles to be first-order in the H₂S mole fraction. No impact of the oxygen level in the gas has been reported for the sulfation reaction and it is assumed that the sulfation reaction is zero-order in O₂, just as has been found for coarse particles. H₂O and CO₂ catalyze the loss of surface area, and H₂O has a strong effect on the equilibrium H₂S level in sulfidation. The reported technique for producing lime sorbents having very high surface areas is to calcine them at a moderate temperature under conditions that will minimize the CO₂ content in the surrounding gas (49).

Borgwardt (40) has reported that the sulfation reaction rate is proportional to the 0.67 power of the SO_2 mole fraction in the gas, but again, these are for sulfation rates that occur after longer exposure

times than is characteristic of entrained desulfurizer, and it is concluded that the measurement do not represent the behavior of the initial high sulfation rate period.

3.2 OBJECTIVES AND TEST PLAN

The objectives of the fine particle testing and evaluation were to assess the potential of fine calcium-based sorbents for use in an entrained gas-particle contactor for direct coal-fired turbines. The specific objectives were to:

- -- test the reactivity of a range of calcium-based sorbents at temperatures up to 1200°C and pressures up to 12 atmospheres
- -- generate kinetic correlations as a function of temperature, particle size and sorbent type
- -- develop commercial design equations for the sizing and performance of entrained desulfurization
- -- perform a preliminary assessment of the performance potential of calcium-based sorbents in entrained desulfurizers for direct coal-fired turbines

The effect of pressure on the reaction kinetics was the major consideration. Two major test series were conducted for the sulfur dioxide reaction and for the hydrogen sulfide reaction. The test matrices were:

1) SO₂ capture Sorbent types

- . -- Plum Run dolomite
 - -- Highland limestone
 - -- Vicron limestone

-- hydrated Vicron limestone

-- a commercial lime hydrate

Simulation Gas Composition

-- Carbon dioxide 8 mole %

-- Oxygen 10 mole %

-- SO₂ 0.5 mole %

-- Nitrogen 81.5 mole %

Test Conditions

Seven tests were conducted for each of the raw sorbents and two for each of the hydrated sorbents. For the raw sorbents:

Temperature(*C)	Pressure(atm)	Particle size	Contact	Time(sec)
1100	6	<400 mesh	0.75	and 1.5
1100	12	<20 microns	0.75	and 1.5
1100	6	<400 mesh	0.75	
1200	6	<20 microns	0.75	and 1.5

The particle sizes tested were in the range of 5 to 25 microns (mass mean diameters), and these are typical of the grinds that can be commercially achieved, as well as being representative of sizes previously tested in conventional furnace injection programs.

Some additional tests were also conducted to test the reproducibility of the results and to test the order of reaction with SO_2 . A total of 33 tests were completed. The raw sorbent types were selected, based on their coarse particle test behavior, because of their wide variation in performance. The hydrated sorbents tests were conducted at 1100°C and at pressures of 6 and 12 atmospheres with a contact time of 0.75 seconds.

These test matrices provided the minimum information required to develop preliminary reaction kinetics correlations.

2) H₂S Capture Sorbent types

> -- Plum Run dolomite -- Highland limestone

Gas composition

-- Hydrogen sulfide 0.5 mole %

-- Nitrogen 99.5 mole %

Test conditions

Four tests were conducted with each sorbent:

Temperature(°C)	Pressure(atm)	Particle Size	Contact Time(sec)
1100	6	<400 mesh	0.75
1100	6	<20 microns	0.75
1100	12	<400 mesh	0.75
1100	12	<20 microns	0.75

Again, these tests provided the minimum information needed to produce preliminary kinetic expressions. The two raw sorbents were selected to represent the general classes of dolomites and limestones. Under sulfidation conditions using fine particles, little variation between different limestones or between different dolomites is expected based on the background data review.

3.3 DISPERSED PARTICLE REACTOR TEST EQUIPMENT AND PROCEDURES

All of the fine particle tests were conducted on a "dispersed particle" reactor. In this reactor the particles are first dispersed within a quartz wool matrix, stirring the 20 mg sample of sorbent particles continuously into the wool mechanically for 20 minutes to ensure uniform dispersion of the particles onto the quartz filaments. The wool is placed within a quartz tube that is necked down from a 20 mm inner diameter to a 3 mm inner diameter to provide sufficient gas velocity to minimize mass transfer resistance at the particle surface. The quartz tube containing the wool plug sits horizontally within a pressure shell as shown in Figure 3.1. The quartz tube is surrounded by electric heaters that bring the sample and reaction gases up to the desired temperature. The pressure shell is the shell used to house the thermogravimetric balance for the coarse particle testing.

The system flow diagram is shown in Figure 3.2 and differs for the system diagram for the thermogravimetric balance in only one



KEY TO DISPERSED REACTOR FIGURE

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Figure 3.1 — Dispersed Particle Reactor Apparatus



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Figure 3.2 - System Diagram for the Dispersed Particle Reactor Facility

respect. The reaction gas (premixed SO_2 or H_2S) is contained within a small reservoir having a carefully measured volume that will provide a specified contact time between the reaction gas and the sorbent particles when the control valves are switched. In operation the sample is dispersed within the wool matrix, the wool plug is placed into the quartz tube constriction, the quartz tube is placed within the pressure vessel, the system is pressurized and the flow of inert nitrogen, CO_2 and oxygen is started through the sorbent sample. The sample and inert gas are slowly heated up to the reaction temperature desired. Once at temperature, the reaction gas reservoir valves are switched sending the flow of reaction gas through the quartz tube to contact the sorbent particles for the prescribed time. Following the test the system is cooled down, the wool plug is removed and the reacted sorbent particles are analyzed for calcium and sulfur content. This analysis then provides the conversion of CaO to CaSO₄ or CaS.

This technique is analogous to a method developed and used by Borgwardt at EPA (40, 51) for atmospheric pressure testing of fine sorbent particles. The analytical procedures for $CaSO_4$ and CaS used by Borgwardt were also used in this program.

The potential concerns with this technique are:

1) The sample must be preheated to the reaction temperature before sulfation or sulfidation is initiated. Thus, the important calcination rate is not included as part of the kinetic measurement. Fortunately, at the temperatures of interest to coal-fired turbines the time required for calcination is very small.

2) Because the sample is preheated and held at high temperature for a relatively long time (on the order of 0.5 hours) the sorbent samples will have surface areas very close to their minimum value. Thus, the test results really represent the behavior of minimal surface area sorbents, or "sintered" sorbent. The sintered sorbent kinetics must be scaled to higher surface areas to determine the performance of active, freshly injected and calcined particle.

3) Significant dispersion of the reactant gas in the feed system occurs before the reaction gas reaches the sorbent particles, so the concentration of the SO_2 or H_2S is lower than the specified test value. Fortunately, because the reaction rate is first-order in the sulfur species concentration, the product of the SO_2 (or H_2S) concentration and the contact time determines the conversion. When the reaction gas is diluted the contact time increases in inverse proportion to the drop in concentration so that the product of concentration and contact time is always fixed. Dispersion only influences the test results if the concentration is reduced to values near or below the equilibrium SO_2 or H_2S level. This will be discussed in the evaluation of the test results to demonstrate this behavior.

4) Some of the sorbent particles are entrained out of the quartz wool and are lost from the product chemical analysis. This is not really a concern because the evaluation procedure measures the calcium and sulfur in the product sample collected and does not depend on a material balance on the sample initially placed in the wool matrix. On the other hand, if the entrainment loss represents particles of a predominantly small or large size then the test results would be confused because the size distribution of the particles analyzed would not correspond to the size distribution dispersed in the initial wool plug.

3.4 TEST RESULTS IN SULFUR DIOXIDE

The test results for the 32 tests conducted in SO_2 are listed in Table 3.1. The average particle diameter listed is the mass-mean.

Several tests were done in duplicate to test reproducibility: Runs 1 and 2 showed reproducibility for Plum Run dolomite of about 96% while Runs 15 and 18 showed reproducibility of only 85%. Runs 3 and 7 showed reproducibility for Vicron limestone of about 90%. It is concluded that the experimental technique yields reproducible results. The analytical step for Run 14 indicated a loss of sample may have occurred during analysis, and indeed the result in Run 14 is

Run No.	Sorbent	Average diameter (microns)	Temperature (°C)	Pressure (atm)	Contact time (sec)	% Sulfated
1	Plum Run	25 8	1100	· A	15	55 04
ຸ ້		20.0	1100	6	1.0	60.85
2	Vienen	10 7	1100	6	1.5	00.80
3		12.7	1100	6	1.5	20.00
4	nightand	13.5	1000	Б	1.5	30.12
5	Plum Kun	<u>75.8</u>	1200	b	1.5	40.47
6	Highland	13.5	1200	6	1.5	21.94
7	Vicron	12.7	1100	6	1.5	23.88
8	Plum Run	25.8	1100	6	0.75	26.90
9	Vicron	12.7	1100	6	0.75	16.91
10	Highland	13.5	1200	6	0.75	2.86 a
11	Vicron	12.7	1200	6	0.75	2.92 a
12	Plum Run	25.8	1200	6	0.75	2.08 a
13	Highland	13.5	1100	6	0.75	14.19
14	Vicron	12.7	1200	6	1.5	42.04 b
15	Plum Run	25.8	1100	12	0.75	33.60
16	Highland	13.5	1100	12	0.75	16.83
17	Vicron	12.7	1100	12	0.75	20.45
18	Plum Run	25.8	1100	12	0.75	45.07
19	Highland	13.5	1100	12	1.5	37.71
20	Vicron	12.7	1100	12	1.5	34.72
21	Plum Run	25.8	1100	12	1.5	74.22
22	Highland	6.8	1100	6	0.75	18.73
23	Plum Run	9.8	1100	6	0.75	42.05
24	Vicron	8.5	1100	6	Q.75	22.28
25	Commercial hydrate	. .	1100	6	0.75	13.05
26	Vicron hydrate		1100	6	0.75	12.45

Table 3.1 — Fine Particle Sulfation Test Results

27	Commercial hydrate		1100	12	0.75	18.69
28	Vicron hydrate		1100	12	0.75	14.24
29	Highland	13.5	1100	12	0.75	39.83 c
30	Plum Run	25.8	1100	12	1.5	89.79 c
31	Vicron	12.7	1100	6	1.5	29.88
32	Vicron	12.7	1200	6	1.5	13.18

a -- tests where the SO₂ level dropped below equilibrium c -- tests conducted with 1 mole % SO₂ rather than 0.5 mole %

b -- test result rejected and repeated

inconsistent with the other runs, so this run was repeated in Run 32. Run 14 was thus rejected.

Run 29 was performed to test the first-order behavior of the reaction rate with respect to the SO_2 concentration. The test conditions are identical with those of Run 19, except Run 19 has a contact time of 1.5 seconds in 0.5 mole % SO_2 while Run 29 has a contact time of 0.75 seconds in 1 mole % SO_2 . If the reaction rate is first-order in the SO_2 concentration then the sulfation level resulting from these two tests should have been the same. The sulfation levels were only 5% different and it is concluded that the rate is first-order in $3O_2$.

Run 30 was performed specifically to determine the curvature in the sulfation versus time plot, and this is seen in the data plots that follow. A clear indication of the extent of dispersion of the reaction gas when it was injected into the reactor tube is seen in the three runs at 1200°C and 0.75 second contact time, Runs 10, 11, and 12. In these runs the dispersion must have dropped the SO₂ concentration in the gas contacting the sorbent to a level near or below the equilibrium SO₂ level. These tests used the smallest reactant gas reservoir of the test series, resulting in the greatest reactant gas dispersion in the inert carrier gas, while being at the temperature having the highest SO₂ equilibrium level (about 350 ppm) -- thus, very little sulfation could proceed. These three runs provide no kinetic information, but they do provide information about the operating limits of operation of the dispersed reactor due to gas dispersion.

The sulfation data for Plum Run dolomite is shown graphically in Figure 3.3. The figure shows linear behavior in the degree of sulfation with time (curves 1 and 2), and indicates improved sulfation as the pressure is increased and as the particle diameter is reduced. Increased temperature from 1100 to 1200° C results in reduced sulfation. Note the point run with 1 mole % SO₂ with a 1.5 second contact time is shown in the figure as being equivalent to a 0.5 mole % SO₂ test with a 3.0 second contact time, and this shows that a large degree of curvature occurs when the sulfation level exceeds about 80% conversion.



Figure 3.3 — Fine Particle Sulfation Results for Plum Run Dolomite

A similar plot of sulfation level versus time is shown in Figure 3.4 for Highland limestone. The results have the same trends as for Plum Run dolomite, although the conversion levels are much lower. Linear behavior with time is shown, improved sulfation with increased pressure and reduced particle size, and reduced sulfation with increased temperature is shown. Figure 3.5 illustrates the test results for Vicron limestone. The results are very similar to those for Highland limestone, except that 1) the Vicron limestone appears more sensitive to temperature, with the sulfation level decreasing more as the temperature is increased, and 2) there is a definite, though small degree of curvature in the sulfation data (curves 1 and 2 as shown by the dashed lines).

It is interesting to note that there is a parallel here between the results obtained in the coarse particle testing. The Plum Run dolomite showed the highest level of sulfation of the three sorbents and the Vicron limestone was the most sensitive to temperature (see Table 2.8). Comparing the initial reaction rates in Table 2.7 for the coarse particles also shows a strong parallel between the coarse and fine particle results. The similarity between Highland and Vicron limestones also is consistent with previous fine particle test results reported at atmospheric pressure that indicate limestones on the whole do not behave much differently from one another at these small particle sizes.

Figure 3.6 presents the graphic results for the Vicron hydrate and the commercial hydrate. The two hydrates behave very similarly to each other as well as being close to the results for the Highland limestone and the Vicron limestone. The lack of improvement in the sulfation performance relative to the limestones results from the test procedure that exposes the sorbent to high temperatures for long times prior to sulfation, thus sintering the sorbents severely. It is concluded that hydrates exposed to high temperature will loose surface area to a level of the raw limestone and will behave no better than limestones or limes exposed to high temperatures. The behavior shown in Figure 3.6 does not correspond to that of a fresh hydrate injected into



Figure 3.4 — Fine Particle Sulfation Results for Highland Limestone

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Figure 3.6 — Fine Particle Sulfation Results for Calcium Hydrates

a high temperature SO_2 gas. The behavior shown in the figure is probably similar to that of a commercial lime produced in a rotary kiln and having characteristically low surface areas.

3.5 TEST RESULTS IN HYDROGEN SULFIDE

The test results for the eight runs performed with H_2S are shown in Table 3.2.

Kun No.	Sorbent	Particle Size (microns)	Temperature (°C)	Pressure (atm)	Contact time (sec)	% Sulfidation
33	Plum Run	25.8	1100	6	0.75	39.96
34	Plum Run	9.8	1100	6	0.75	43.26
35	Highland	13.5	1100	. 6	0.75	25.26
36	Bighland	6.8	1100	6	0.75	29. 72
37	Plum Run	25.8	1100	12	0.75	46.56
38	Plum Run	9 .8	1100	12	0.75	49.72
39	Highland	13.5	1100	12	0.75	37.11
40	Highland	6.8	1100	12	0.75	43.47

Table 3.2 - Fine Particle Test Results in H₂S

Trends shown in the data are 1) increased sulfidation occurs with increased pressure; 2) increased sulfidation occurs with decreased particle size; and 3) higher sulfidation levels occur for the dolomite than for the limestone. Comparing the results for sulfidation with those for sulfation in Table 3.1 indicates that slightly higher sulfidation levels occur in the same contact time for Plum Run dolomite than are obtained for sulfation. Greatly higher sulfidation levels occur at the same conditions for Highland limestone than occur with sulfation. This is consistent with expectations, and based on the observed low sensitivity of sulfidation to sorbent type it is expected that the behavior shown here is characteristic of all dolomites and all limestones. Again, these results represent the behavior of low surface area, sintered sorbents.

3.6 EVALUATION OF SULFUR REMOVAL KINETICS

The test data accumulated in Tables 3.1 and 3.2 may be correlated using standard multiple regression analysis. This leads to quantitative descriptions of the qualitative trends demonstrated by the data.

3.6.1 Sulfation Data Correlation

The general form assumed for the correlation is

$$a = k_{o} (d_{p})^{a} (P)^{b} (t)^{c} Y$$
(3-1)

where a is the fraction of the calcium sulfated, k_o is the reaction rate constant, d_p is the mass-mean particle diameter in microns, P is the total pressure in atmospheres, t is the time in seconds, and Y is the mole fraction SO₂ in the gas. The terms a, b, and c are empirical constants. The correlation results are as follows:

Plum Run Dolomite

Range of correlation: dp = 9.8 to 25.8 microns; P = 6 to 12 atmospheres; maximum sulfation level about 85 %.; temperature 1100°C

$$a = 133 (d_p)^{-.42} (P)^{.44} (t)^{1.03} Y$$
 (3-2)

The limited curvature with time implies that the rate of reaction, R = da/dt, is given by

$$R = 133 (d_p)^{-.42} (P)^{.44} Y = k Y$$
 (3-3)

where R is the sulfation rate expressed as the fraction of the sorbent calcium sulfated per second. The limited temperature data collected, while not sufficient for statistical analysis, indicates that the rate constant is related roughly to the temperature by

$$k_{a} = 0.6 \exp \{7417/(T+273)\}$$
 (3.4)

where T is the temperature in $^{\circ}$ C. This is quite close to the activation-term of about 6300 found for 387 micron Plum Run dolomite in the coarse particle testing, giving some confidence in the constants in Equation 3-4.

Highland Limestone

Range of correlation; dp = 6.8 to 13.5 microns; P = 6 to 12 atmospheres; maximum sulfation level about 50 %.; temperature 1100°C

$$a = 70 \left(\frac{d_p}{p} \right)^{-.43} \left(P \right)^{.29} \left(t \right)^{1.13} Y$$
 (35)

The limited curvature with time implies that the rate of reaction is given by

$$R = 70 (d_p)^{-.43} (P)^{.29} Y = k Y$$
(3-6)

where R is the sulfation rate expressed as the fraction of the sorbent calcium sulfated per second. Again, temperature data collected is too limited for statistical analysis, but indicates that the rate constant is given roughly by

$$k_{0} = 0.66 \exp \{6411/(T+273)\}$$

where T is the temperature in *C. This is close to the activation energy-term found for the Highland limestone initial reaction rate of 387 micron particles in the coarse particle testing.

Vicron Limestone

Range of correlation: dp = 8.5 to 12.7 microns; P = 6 to 12 atmospheres; maximum sulfation level about 40%.; temperature 1100°C

$$a = 145 (d_p)^{-.72} (P)^{.31} (t)^{.72} Y$$
 (3-8)

(3-7)

While there is a slight curvature with time, this may be linearized and the implied rate of reaction is given by

$$R = 113 (d_p)^{-.72} (P)^{.31} Y = k Y$$
 (3-9)

where R is the sulfation rate expressed as the fraction of the sorbent calcium sulfated per second. The limited temperature data collected indicates that the rate constant is given roughly by

$$k_o = 0.0041 \exp \{14018/(T+273)\}$$
 (3-10)

where T is the temperature in °C. The 14018 is a much higher activation energy-term than that found for the initial reaction rate in coarse particle Vicron limestone testing, and the observed fine particle behavior is suspected of inaccuracy in this case. Overall, it is concluded that the Highland and Vicron limestones behave almost identically in their sulfation kinetics at these fine particle sizes.

3.6.2 Sulfidation Data Correlation

Here it is assumed that the sulfidation extent increases linearly with time for Plum Run dolomite and Highland limestone, since this behavior was found for sulfation. The same general form for the rate equation is assumed:

$$R = k_{o} (d_{p})^{a} (P)^{b} Y = k Y$$
 (3-11)

where R is now the sulfidation rate, in fraction of the calcium sulfided per second, and Y is the mole fraction of H_0S in the gas.

Plum Run Dolomite

Limits of the correlation: dp = 9.8 to 25.8 microns; pressure = 6 to 12 atmospheres; temperature 1100°C; maximum level of sulfidation about 90%.

$$R = 93.5 (d_p)^{-.08} (P)^{.21} Y$$
 (3-12)

No data was collected on the effect of temperature in this program, but based on coarse particle testing it is likely that the rate will decrease slightly in the temperature range of 1000 to 1200°C, much as for sulfation. Note the very small effect of particle diameter on the sulfidation rate, indicating small diffusion resistance, and the small effect of pressure relative to the pressure influence in sulfation.

Highland Limestone

Limits of the correlation: dp = 6.8 to 13.5 microns; pressure = 6 to 12 atmospheres; temperature 1100°C; maximum level of sulfidation about 70%.

$$R = 46.1 \ (d_p)^{-.23} \ (P)^{.55} \ Y$$
 (3-13)

Again, no data was collected on the effect of temperature in this program, but based on coarse particle testing it is likely that the rate will decrease slightly in the temperature range of 1000 to 1200°C, much as for sulfation. A smaller effect of particle diameter and a larger effect of pressure is seen for sulfidation that was seen for sulfation in Equation 3.6.

3.7 EVALUATION OF ENTRAINED DESULFURIZERS FOR DIRECT COAL-FIRED TURBINES

In this section the commercial performance of entrained desulfurization for direct coal-fired turbines is estimated based on the kinetic correlations developed in the previous section. In contrast to the fluidized bed desulfurizer evaluation in section 2.9 for coarse calcium-based sorbents, the sulfur removal performance of the entrained desulfurizer is sensitive to the sulfur content of the coal and the combustion excess air (or the resulting SO_2 or H_2S concentration in the gas). Thus, specific scenarios for the coal sulfur content and the combustion excess air must be proposed to see what the sensitivity is. Also, the correlations developed are for the low surface area, sintered sorbent particles, and these must be scaled to the performance of freshly calcined sorbents.

3.7.1 Combustor Operation and Coal Scenarios

The entrained desulfurizer is characterized by the equation for the sulfur removal performance developed in Appendix D:

$$Ca/S = [-ln(1-E)] / \{ H/(U - U_s) k Y_o \}$$
 (3-14)

The gas phase SO_2 or H_2S mole fraction at the point of sorbent introduction, Y_0 , appears explicitly in the equation, showing that the calcium-to-sulfur feed ratio required for a given sulfur removal efficiency is inversely proportional to Y_0 . The value of Y_0 in a turbine combustor depends upon the sulfur content of the coal, whether the coal is fed dry or in slurry form, and on the combustion conditions at the point of sorbent injection -- that is, on the degree of excess or substoichiometric air at the point of injection and on the degree of quenching by water or steam injection at that point. For example, a high-sulfur bituminous coal (4 wt % sulfur) if fed as dry coal will produce a combustion product containing about 1600 to 1700 ppm SO₂ at a temperature of 1100 to 1200°C, respectively. The SO₂ content of the gas will be roughly proportional to the sulfur content of the coal, so that a 1 wt % sulfur bituminous coal will yield an SO₂ content of 400 to 425 ppm. Corresponding oxygen and carbon dioxide contents would be about 10 mole % and 8 mole %, respectively.

Un the other hand, if a 4 wt % sulfur bituminous coal is partially combusted in an initial stage of the combustor and quenched to a temperature of 1100°C it will produce a gas having a predominantly H_2S content of about 6200 ppm, with a water content on the order of 32 mole %. Again, the H_2S content will be roughly proportional to the sulfur content of the bituminous coal. This increase in the H_2S content of the gas relative to the previous SO_2 case provides a large potential for improved sulfur removal.

This behavior results from the assumption that the gas and sorbent flow cocurrently through the entrained desulfurizer effectively in plug flow. Any degree of backmixing of gas and particles will tend to reduce the dependency of the sulfur removal on the inlet sulfur content of the gas. Certain combustor designs, such as generally in slaggers where significant backmixing will occur, will result in lower dependence on coal sulfur content and combustion conditions, but this dependence will not be removed entirely.

The next factor influencing the sulfur removal performance is the required sulfur removal efficiency, E. The sulfur removal requirements for direct coal-fired turbines are not yet defined and will depend on the size of the facility (electric utility large scale applications will have standards differing from smaller industrial cogeneration applications, which will also differ from even smaller transportation applications). Even if the New Source Performance Standard for large utility applications is applied there is uncertainty.

If a high-sulfur bituminous coal is fired the required sulfur removal would be 90% with this standard, while a low-sulfur coal would only require about 70% removal. A partially cleaned coal, say with 50% sulfur removed during slurry preparation, would only require about 80% sulfur removal with the utility standard. Standards of sulfur removal may also vary significantly with the specific location of the plant. The impact on the sorbent consumption is large. For a given coal sulfur content, if the sulfur removal efficiency is reduced from 90% to 60% then the required Ca/S ratio, according to equation 3.14, is reduced by a factor of 2.5 if the combustion conditions are the same in both cases. Thus, these two factors, Y_0 and E, have a large impact on the sorbent consumption rate even without considering the kinetics of specific calcium-based sorbents or the specific combustor conditions.

For the combustion conditions at the point of sorbent injection fixed (fixed temperature, excess or substoichiometric air level, and quench gas level); fixed calcium-based sorbent type and size; and fixed combustor design (fixed value of H/U, etc), the calcium-to-sulfur ratio required to achieve a given sulfur removal efficiency is proportional to the quantity $[-Ln(1-E)/X_s]$ according to Equation 3-14, but the sorbent mass feed rate is independent of the coal sulfur content, being directly proportional to the quantity [-Ln(1-E)]. Contrast this to the fluidized bed desulfurizer where the calcium-tosulfur ratio for a given sulfur removal efficiency is independent of the coal sulfur content, and the sorbent mass feed rate is directly proportional to the coal sulfur content.

The quantity U_s is the gas-particle slip velocity, so $H/(U-U_s)$ is the particle residence time in the desulfurizer.

3.7.2 Sintered Sorbent Performance in SO_2 and H_2S

The sorbent testing performed and the kinetics developed are for low-surface area sorbents that have been highly sintered prior to sulfur exposure. The surface areas of these sorbents are at a low and stable level that does not change during the coarse of the test. According to equation 3.14 the Ca/S ratio for these sorbent depends on the factors:

- the sulfur removal efficiency required
- the particle residence time in the desulfurizer stage, $H/(U-U_{1})$
- the particle kinetic constant k, itself a function of temperature, pressure, sorbent type, and particle diameter
- the content of SO_2 or H_2S in the gas at the point of injection of the sorbent into the gas stream, Y

The performance of the sorbents tested can be expressed in the form

 $Ca/S = H/(U-U_s) Y_o(ppm)$ versus (mass-mean sorbent particle diameter)

to simplify the consideration of specific conditions. This is done in Figures 3.7 and 3.8 for sintered Plum Run dolomite and sintered Highland and Vicron limestones. Highland and Vicron limestones behave very similarly as seen from the previous rate comparisons. Each figure shows the effect of pressure at 10 and 20 atmospheres and the effect of SO_{2} and H_2S gases all at a temperature of 1100°C and with a sulfur removal efficiency of 80%. Note that the figures extrapolate beyond the pressure range and particle size range of the testing. The figures are applied by selecting a representative gas SO_{2} or $H_{2}S$ content for the specific coal sulfur content and combustion conditions of interest, a particle residence time, and a particle mass-mean diameter, from which the required Ca/S ratio can then be taken directly. In the figure for Plum Run dolomite, for example, with a 10 atmosphere pressure and a 4 micron diameter sorbent size, the quantity Ca/S H/(U-U_s) Y is equal to about 8000 in an SO_2 gas. If the SO_2 content of the gas were 1600 ppm and the particle residence time were 1.0 second then the required Ca/S ratio would be 5.0. Increasing the pressure to 20 atmospheres would reduce the Ca/S ratio to about 3.75 based on the pressure factor in Equation 3.3. On the other hand, in an H_sS gas, at 10 atmospheres pressure and with 4 micron particle size the quantity $Ca/S H/(U-U_s) Y_o$ is equal to about 12000. If the H₂S content of the gas were 6200 ppm and the particle residence time were 1.0 second the required Ca/S ratio



Figure 3.7 — Sintered Highland and Vicron Limestones Removal Performance in SO_2 and H_2S



Figure 3.8 — Sintered Plum Run Dolomite Removal Performance in SO₂ and H₂S

would be about 2.0. Increasing the pressure to 20 atmospheres would decrease the Ca/S ratio to about 1.6 based on the pressure factor in Equation 3.12.

Figure 3.8 for sintered Highland and Vicron limestones indicates that in SO_2 the sintered limestones perform worse than the sintered dolomite. For the same hypothetical conditions as assumed above for Plum Run dolomite in SO_2 , the required Ca/S ratio would be about 13 at 10 atmospheres pressure and about 10.8 at 20 atmospheres. On the other hand, the sintered limestones compare favorably to the performance of sintered dolomite in H_2S . At the same conditions hypothesized for sintered Plum Run dolomite in H_2S , the sintered limestones require a Ca/S ratio of about 2.3 at 10 atmospheres pressure and 1.5 at 20 atmospheres.

The following conclusions are reached for the sintered sorbents based on these two figures:

- The sintered, low surface area sorbents are representative of sorbents injected into a very hot zone of a direct coal-fired turbine combustor (greater than 1500°C) before removing sulfur in a cooler combustor zone. The sintered limestones are also representative of typical commercial limes produced in high-temperature rotary kilns.

- The performance of the sintered sorbents (that is, the Ca/S ratio required to achieve the needed sulfur removal) is probably acceptable only for high sulfur coals, for cases where high sulfur removal efficiency is not required, and for combustor systems where the gas residence time can be on the order of 1 second. Their use would be more commercially acceptable in an $\rm H_2S$ gas than in an SO₂ zone of the combustor.

- The sintered dolomite performs better than the sintered limestones in SO_2 gases on a Ca/S ratio basis, but on a feed weight basis the limestones and dolomites are comparable.

- The sintered dolomite performs better in H_2S than in SO_2 gases, but only because of the potentially higher content of H_2S in the gas. On the other hand, much larger dolomite particles may be used in

an H_2S gas than in an SO_2 gas since the kinetics in H_2S are less sensitive to particle diameter.

- The sintered limestones perform much better in H_2S than in SO_2 because of both improved kinetics and higher potential H_2S concentrations compared to SO_2 concentrations. Again, much larger limestone particles may be used in H_2S than in SO_2 . While the sintered limestones and sintered dolomite are comparable in Ca/S ratio in H_2S , the limestones are much superior to dolomite on a feed weight basis. 3.7.3 Active, High-Surface Area Sorbent Performance

The objective of this section is to scale the sintered sorbent kinetics and performance results to estimate the potential performance of high surface area, freshly calcined calcium-based sorbents. This is done using available information from the literature on the behavior of the sorbent surface area with time, temperature and gas composition. There is significant uncertainty in the scaling procedure and the results provide only perspective on the potential performance of active, high surface area sorbents. Confirmation of many of the assumptions made is needed in controlled experiments as well as in small-scale integrated combustor testing.

The rate constant k in equation 3.14 is observed to be directly proportional to the surface area of the sorbent particle. For the sintered sorbents tested this surface area is a minimal value that is also stable with time, but for freshly calcined sorbents the surface area may be much larger as well as being a function of time, temperature and gas composition. The rate constant k for the sintered sorbents is given by

$$k = k_0 (d_p)^a (P)^b e^{E/T}$$
 (3-15)

where values for k_0 , a, b and E have been estimated and reported in the previous sections. For the active, high-surface area sorbents the rate constant is expressed as

$$k = k_{o} (S/S_{o}) (d_{p})^{a} (P)^{b} e^{E/T}$$
 (3-16)

The additional term (S/S_0) is the ratio of the sorbent surface area over the surface area reached on sintering. This ratio is expected to be a function of the sorbent particle diameter, the gas temperature, the pressure, the composition of the gas (mainly the carbon dioxide and water vapor content), and the time of exposure of the sorbent, but is not expected to be a strong function of the sorbent type.

The mathematical form of the ratio is expected to be

$$(S/S_0) = (S_*/S_0) a_c \eta_d + 1$$
 (3-17)

where (S_*/S_0) is the ratio of the maximum surface area that would be achieved on instantaneous calcination of the sorbent in a gas free of carbon dioxide and water vapor divided by the sintered sorbent surface area. a_c is the fraction of the calcium carbonate or calcium hydroxide calcined to calcium oxide, and η_d is a factor representing the degradation of the surface area due to sintering phenomena. It is assumed in Equation 3.17 that the sintered sorbent surface area is very close to the initial surface area of the uncalcined, raw sorbent.

The term (S_*/S_0) is observed to be a function of particle diameter. Data reported by EPA(41) and EER(42) on the calcination of fine sorbents at atmospheric pressure has been compiled and correlated to suggest that

$$(S_*/S_0) = 80 (d_p)^{-.44}$$
 (3-18)

This relation indicates that 1 micron diameter particles of limestone or dolomite will have an ultimate surface area of 80 times the sintered surface area if they are shock calcined without CO_2 or H_2O being present.

The calcination term, a_c , has a form

$$a_{c} = 1 - exo \{-K_{c}(t)^{m_{c}}(1-P_{c}/P_{e})\}$$
 (3-19)

where K_c is a calcination rate constant, t is the exposure time, m_c is an empirical constant, P_C is the partial pressure of CO_2 in the gas and P_e is the equilibrium partial pressure of CO_2 at the gas temperature. The form is suggested by the reported calcination evaluations of Borgwardt (49) and Ulerich (6). From Borgwardt's work it is also expected that

 $K_{c} = A_{c} S_{o} \exp \{-E_{c}/(T + 273)\}$ (3-20)

where A_c and E_c are empirical constants, and S_o is the initial limestone or dolomite surface area in the uncalcined state.

The data of EPA (41, 49) and EER (42) have been compiled and correlated using standard multiple regression techniques to determine the calcination factors m_c , A_c and E_c in Equations 3.19 and 3.20. The EER data was collected on an actual entrained combustor using 11 micron Vicron limestone ($S_o = 0.9 \text{ m}^2/\text{gm}$), while the EPA data was collected on a dispersed-fixed bed simulation of an entrained reactor using 10 micron Fredonia limestone ($S_o = 0.9 \text{ m}^2/\text{gm}$). The range of temperatures in the EPA testing was up to a maximum of 1000°C with particle exposure times of 0.1 to 0.7 seconds. The EER data considered a temperature range of 1360 to 1830°C at particle residence times up to 0.15 seconds.

The EPA and EER data correlations compare favorably for the factor m_c , but the predicted calcination constant is larger from the EPA data than it is from the EER data by a factor of about ten at 1200°C. This is because the particle heatup time becomes a significant portion of the total calcination time at the higher temperature range used by EER, according to the assessment of EER. The 0.5 value for m_c is representative of a diffusion-controlled reaction.

	EPA data	EER data
■_	0.5	0.45
A	136,240	81
E	13,330	5790
K (1200°C)	16.0	1.6

The particle sintering rate factor, η_d , is expected to depend on thermal sintering and sintering that is catalyzed by the presence of CO_2 and H_2O in the gas. Again, EPA and EER provide data on the sintering of limestone at atmospheric pressure (41, 42). The EPA data is at temperatures up to 1000°C with 1 micron limestone particles, while the EER data is at much higher temperatures with 11 micron limestone particles. The form used to fit the data is a product of exponential quantities, the first representing thermal sintering in a gas free of CO_2 and water vapor, and the second representing the catalytic contribution of CO_2 (no data on the effect of water vapor on sintering is available):

$$\eta_{d} = \exp\left\{-K_{t}(t)^{m}t\right\} \exp\left\{-K_{C}(P_{C})^{m}(t)^{r}\right\}$$
(3-21)

The results of the correlation are, for $K_t = A_t \exp[-E_t/{T+273}]$ and $K_c = A_c \exp[-E_c/{T+273}]$;

	EPA	EER
A _{t.}	51	222
E _{t.}	8781	8822
^m t	0.48	0.30
A _C	12	
E _C	3665	
r	0.31	
D .	0.39	

The results are quite similar considering the differences in test technique and test conditions, but the EER data tends to show greater degradation of surface area with time. Again, the value of m_t suggests a diffusion-controlled reaction.

The relative surface area factor, S/S_0 from Equation 3.17, is illustrated in Figure 3.9 for limestone and dolomite sorbents for



Figure 3.9 — Relative Surface Area of Limestones and Dolomites

temperatures of 1000, 1100, and 1200°C with particle diameters of 2, 5 and 10 microns diameter. The correlations forms from EER are used, along with the constants based on the EPA data for the catalytic sintering rate. At the moderate temperature of 1000°C the surface area is 5 to 15 times the sintered sorbent surface area within the range of times of interest. At the higher temperatures the surface area reaches a peak value early and begins to drop.

Figure 3.10 illustrates the relative surface area of a 2 micron high-surface area lime particle or a calcium hydroxide particle (S/S_*) (assuming very fast calcination of the hydrate) when injected into gases at temperatures of 1000, 1100 and 1200°C. In this figure the correlation for the sintering of surface, Equation 3.17, was used assuming the initial fraction of calcination is unity, so in these cases the surface area continuously decreases with time.

The scaling of the sintered sorbent kinetics to high-surface area sorbent was done using Equation 3.16. Specific combustor conditions and coal sulfur contents must now be included in the estimates because of the dependency of surface area on exposure time. Plum Run dolomite performance is illustrated in Figure 3.11 for the effect of coal sulfur content and particle diameter on the performance in SO_2 , Figure 3.12 for the effect of temperature, and Figure 3.13 for the performance in H_2S . It is expected that these results for Plum Run dolomite may be generalized to most dolomites because of the limited sensitivity of performance due to changes in dolomite type reported in the literature.

In Figure 3.11 Plum Run dolomite particle sizes of 2 and 5 microns are considered at a temperature of 1100°C and a pressure of 10 atmospheres. Two specific conditions are included in the figure, a 1 wt % sulfur coal requiring 70% sulfur removal, and a 4 wt % sulfur coal requiring 90 % sulfur removal. The particle residence time ranges from 0.2 to 1 second. The following conclusions can be drawn from the figure:

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Figure 3.10 — Relative Surface Area (S/S*) of Limes and Hydrates



Figure 3.11 — Plum Run Dolomite SO₂ Removal Performance at 1100°C and 10 atmospheres pressure



Figure 3.12 --- Plum Run Dolomite SO, Removal Performance: Effect of Temperature





- There is little benefit in performance from increasing the gas residence time above 0.5 seconds.
- Low sulfur coals will require small dolomite particle diameters on the order of 2 microns for acceptable sorbent consumption rates
- The performance looks promising with high sulfur coals in that Ca/S ratios of less than 2 can probably achieve 90% sulfur removal
- There is a tradeoff between Ca/S ratio, gas residence time, and particle diameter for all of the cases pictured that can only be resolved by considering operating cost, equipment cost, and operability
- Increasing the pressure will reduce the sorbent consumption by about the pressure to the 0.44 power

The effect of temperature on Plum Run dolomite sulfur removal in SO_2 is illustrated in Figure 3.12. Only the high sulfur case is considered with a particle diameter of 2 microns. Increasing the temperature to 1200°C is costly in terms of sorbent consumption, while little difference is expected between 1000 and 1100°C performance.

 H_2S removal in dolomite is illustrated in Figure 3.13 for high and low sulfur coal cases. Performance is significantly better than in SO_2 mainly because of the higher H_2S contents of the gas. The following conclusions have been drawn:

- Gas residence time greater than 0.5 seconds has no benefit for reduced sorbent consumption
- Ca/S ratios less than 2 can achieve acceptable sulfur removal for low sulfur coals using gas residence times as small as 0.35 seconds
- Ca/S ratios less than 1.5 can achieve acceptable sulfur removal for high sulfur coals using gas residence times as small as 0.3 seconds.
- Relatively large dolomite particles, up to about 25 microns, could be used for H_2S removal with little increase in the required sulfur removal efficiency because of the low

sensitivity of H_2S removal to particle size in H_2S . This may permit the use of cyclones for dolomite removal.

• Increasing the pressure reduces the dolomite consumption rate only by about pressure to the 0.2 power

Results for Highland limestone and Vicron limestone are shown in Figures 3.14 through 3.16. Again, as with the dolomites, it is expected that these results will generally represent limestones of most types within a reasonable band of variation. Figure 3.14 shows the results for limestone sulfur removal in SO_2 as a function of particle diameter, coal sulfur content, and gas residence time. The temperature is 1100°C and the pressure is 10 atmospheres. Analogous to the conclusion for dolomites, the following conclusions are drawn:

- Little benefit is gained from gas residence times greater than 0.5 seconds
- Use of small limestone particles, less than 2 microns diameter is probably needed for acceptable performance and gas residence times will probably need to be greater than 0.4 seconds
- Increasing the pressure will reduce the sorbent consumption by about the pressure to the 0.3 power

The effect of temperature on limestone SO_2 removal shown in Figure 3.15 is quite the same as for dolomite SO_2 removal. A significant increase in sorbent consumption is found when going to 1200°C, while reducing the temperature from 1100 to 1000°C reduces the sorbent consumption only slightly.

 $\rm H_2S$ removal by limestone is pictured in Figure 3.17 and shows that results comparable to dolomite $\rm H_2S$ removal on a Ca/S basis is obtained. This means that limestone $\rm H_2S$ removal is superior to dolomite on a weight basis. Also,

- Gas residence times less than 0.4 seconds will be acceptable
- Ca/S ratios less than 1.5 may be expected with high sulfur coals

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Figure 3.16 — Highland and Vicson Limestones H₂S removal performance at 1100°C and²10 atmospheres pressure





• Fairly large limestone particles could be used for \mathbb{H}_2S removal if long gas residence times are acceptable

• Increasing the pressure reduces the sorbent consumption by the 0.55 power.

The use of high surface area limes or calcium hydroxides is illustrated in Figures 3.17 through 3.19 on the same basis as previously discussed for limestones and dolomites. Lime or calcium hydroxide behaves much the same as dolomite does in SO_2 on the basis of Ca/S ratio. On a weight basis the lime or calcium hydroxide will be superior to dolomite by a factor of about 2. In H_2S the lime or calcium hydroxide is superior to dolomite and limestone and permit the use of gas residence times less than 0.3 seconds with Ca/S ratios less than 1.5. The tradeoff that exists is between the relatively high cost of high surface area lime (not commercially available) or hydrated limes (commercially available) and the relatively low cost of limestone and dolomite.

While the potential performance in H_2S for dolomites, limestones, high-sulfur area limes or calcium hydroxides appears excellent, the existence of H₂S in substoichiometric zones of combustors is not necessarily the predominant species and significant COS and SO, may also exist in these zones. Also, with lower sulfur coals in zones where water vapor content is high, equilibrium may limit the extent of sulfur removal possible, as is demonstrated in Figure 2.1. Another limiting factor may arise from the interaction of coal ash with the calcium-based sorbents (42). Fortunately, in direct coal-fired turbines the temperatures are moderate compared to conventional furnace injection situations. Also, most cases consider the use of moderately cleaned coals having relatively low ash content, so the problem of ash interaction may not be a critical problem. The injection of fine sorbents uniformly into a hot gas stream to achieve good gas-solid contacting over short residence times is a key consideration in the development of effective entrained desulfurizers.







Figure 3.19 — High-surface area lime or hydrate H₂S removal performance at 1100°C and 10² atmospheres pressure

4. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations have been extracted from the results presented:

Overall Conclusions

- Both fluidized bed and entrained desulfurizers using calcium-based sorbents have the potential to be used effectively for sulfur emissions control $(SO_2 \text{ or } H_2S)$ removal) in direct coal-fired turbine systems at temperatures as high as 1200°C. Integration of the total system design with the sulfur removal components is required to optimize the sulfur removal performance.
- Thermodynamic equilibrium may limit both the capture of SO_2 and H_2S , depending on the pressure, temperature, sulfur content of the coal and the combustion conditions (concentration of oxygen and of water vapor). The temperature limit for SO_2 removal is about 1200°C, while the limit for H_2S removal is about 1100°C, within the range of behavior for dry coal or coal-water slurries expected.
- The overall sulfur removal performance of fluidized bed and entrained desulfurizers may be quite comparable depending on the specific conditions. Fluidized bed desulfurizers can achieve high SO₂ removal efficiency at lower calcium-tosulfur ratios than entrained desulfurizers because of the nature of gas-particle mixing in these two contactors. The advantage increases for fluid bed desulfurization as the coal sulfur content decreases. Entrained desulfurizers are more effective for H₂S removal with high-sulfur coals (>3 wt %) than are fluidized bed desulfurizers, but the advantage

switches for low-sulfur coals (< 2 wt %). Some comparative sorbent consumption rates are shown below for the specific case of a 4 wt % sulfur coal, at 1100°C, 10 atmospheres pressure, achieving 90% sulfur removal in the desulfurizer. Shown in the tabulations are the mass of sorbent that must be fed to the desulfurizer per unit mass of coal. All of the fluidized bed desulfurizer cases use a 0.5 second gas residence time in the bed, while for the entrained desulfurizers a particle residence time in the desulfurizer is selected for each case that is representative of the capabilities of the specific sorbent.

Fluidized Bed Desulfurizer

1100°C; 10 atm; 90 % sulfur removal efficiency; 0.5 second gas residence time in the bed; 387 micron particle diameter; 4 wt % sulfur in coal:

Mass sorbent feed per mass coal

	For	For			
sorbent type	SO2_ removal	<u>H₂S_removal</u>			
dolomite	0.27-0.32	0.25			
limestone	0.23-0.26	0.25			

Entrained Desulfurizer

1100°C; 10 atm; 90 % sulfur removal efficiency; 5 micron particle diameter; 4 wt% sulfur coal:

	Mass	sorbent fe	ed per mass	coal
sorbent type	For SO ₂ rea	moval	For H ₂ S	removal
	time (sec)		time (se	<u>c)</u>
sintered dolomite	1.0	2.03	1.0	0.39
sinter. limestone	1.0	2.32	1.0	0.37
commercial lime	1.0	1.30	1.0	0.21
dolomite	0.5	0.32	0.3	0.25
limestone	0.5	0.55	0.3	0.17
active lime	0.5	0.15	0.3	0.07
hydrated lime	0.5	0.15	0.3	0.07

Note that the fluidized bed desulfurizer sorbent mass feed rates will be directly proportional to coal sulfur content while the entrained desulfurizer sorbent mass feed rates will be independent of the coal sulfur content.

> • A much larger range of sorbents will potentially provide acceptable sulfur removal with entrained desulfurizers (most dolomites, most limestones, all high surface area limes and lime hydrates) than will with fluidized bed desulfurizers (most dolomites, selected limestones).

Fluidized Bed Desulfurizers

• The Ca/S ratio required for a given sulfur removal efficiency in a fluidized bed desulfurizer is not effected by the coal sulfur content, while the sorbent feed rate is directly proportional to the coal sulfur content. Controlling factors are the sorbent type, the sorbent particle size, the bed voidage, the bed depth, and the bed temperature. The calcium-to-sulfur ratio is sensitive to the sulfur removal efficiency. SO₂ removal is not influenced by pressure, while the calcium-to-sulfur ratio for a given

 ${\rm H}_2{\rm S}$ removal efficiency is reduced as the pressure is increased.

- Calcium-based sorbents can be identified that are effective at temperatures as high as 1200°C. Dolomites will, in general, be acceptable sorbents, while some limestones, possibly dolomitic limestones, will be very good sorbents, and many limestones will be very poor. The variation in sorbent performance widens as the temperature is increased.
- Pretreating calcium-based sorbents by precalcination provides no sulfur removal performance advantages for the direct coal-fired turbine
- With a gas residence time of 0.5 seconds in the fluidized bed desulfurizer, and an SO_2 removal efficiency of 90 %, the Ca/S ratio will be less than about 2.0 with dolomites and less than 3.0 with selected limestones at temperatures as high as 1200°C. The sulfur removal performance in H_2S is quite comparable or better than it is with SO_2 removal, except for a lower temperature requirement due to equilibrium.
- The major concerns with fluidized bed desulfurizers are sorbent particle agglomeration and defluidization, sorbentash interaction, hot gas distribution and distributor design, relatively high pressure drops, and relatively small velocities requiring relatively large vessel diameters.
- Commercial performance estimates (Figures 2.47-2.53), and correlations have been developed showing the relation between the sulfur removal performance and the sorbent properties (Equation 2-15). Better sulfur removal is promoted by sorbents having higher magnesium content, higher surface area, and larger grain size, and additional properties such as spontaneous sorbent popping or activation on shock calcination may be additional indicators of excellent performance potential.

- Correlations for the initial reaction rate (Equation 2-11), and the sulfation (Equation 2-8) and sulfidation (Equations 2-13 and 2-14) kinetics have been developed. The sulfation reaction appears to be controlled initially by solid phase diffusion, followed by pore diffusion control.
- Further laboratory testing should be conducted to explain the observed, reproducible discontinuity in the sulfation curves, appearing to be related to particle expansion and crack formation, and the reversible temperature effect behavior, appearing to be related to adsorption phenomena.
- Bench-scale fluidized bed testing should be conducted to look at the problem of sorbent agglomeration and defluidization, as well as the possible consequences of sorbent-ash interaction.
- Engineering studies should be performed to evaluate the integrated process design and economics of fluidized bed desulfurizers in direct coal-fired turbine systems so that acceptable design and operating conditions can be identified.

Entrained Desulfurizers

• The Ca/S ratio required for a given sulfur removal efficiency in an entrained desulfurizer having generally cocurrent plug flow of gases and sorbent particles is inversely proportional to the coal sulfur content, while the sorbent feed rate is not effected by the coal sulfur content (Equation 3.14). Combustors having some backmixing will have less Ca/S ratio dependency on the coal sulfur content. Controlling factors are the sorbent type, the sorbent particle size, the temperature, the pressure, the gasparticle contact time, and the sulfur species mole fraction in the gas (SO₂ or H₂S), or equivalently, the coal sulfur

content and the combustion conditions. Increased-pressure reduces the calcium-to-sulfur ratio for SO_2 removal by the pressure to the 0.29 to 0.44 power. Similar pressure sensitivity is observed for H_0S removal.

- A wide range of acceptable calcium-based sulfur sorbents exists for entrained desulfurization at temperatures as high as $1200^{\circ}C$, with the sorbent performance variation being quite small. Dolomites and high surface area limes and lime hydrates provide the best performance in SO₂ removal, while limestones are probably best (on a weight and cost basis) for H₂S removal. Highly cintered limestones, dolomites (i.e., those exposed to very high flame temperatures prior to desulfurization) and commercial limes (i.e., those produced in typical rotary kilns) are probably only feasible for use with H₂S removal with high sulfur coals and where long residence times are available.
- Correlations of the sulfation kinetics (Equation 3-1) and the sulfidation kinetics (Equation 3-11) have been developed. The greatest uncertainty lies in the transient nature of the sorbent particle surface area. Preliminary correlations for the surface area have been developed from data reported in the literature at atmospheric pressure (Equation 3-17). The sintering rate of sorbents in the high water vapor content characteristic of direct coal-fired turbines has not been accounted for and could result in reduced sulfur removal performance relative to that estimated here.
- The major concerns with entrained desulfurizers are sorbent injection, distribution and mixing, as well as sorbent ash interaction, and sorbent particle deposition on the combustor boundaries.
- Laboratory tests should be conducted to determine the calcination rates and surface area history in high temperature, high pressure gases containing CO₂ and water

vapor representative of direct coal-fired turbines. The scaled sorbent reaction kinetics generated in this study using a dispersed particle reactor should be confirmed in an entrained reactor test unit.

• Engineering design studies should be conducted to evaluate the integrated economics and performance of direct coalfired turbine systems to determine what gas-particle contact times and what sorbent feed rates are acceptable, and to select design and operating conditions. The compact design philosophy used for conventional turbine combustors may not be appropriate or required for coal-fired systems.

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APPENDIX A

SORBENT PROPERTIES AND SUPPLIES

Table 1

SORBENT COMPOSITIONS

SAMPLE	* CALCIUM	* MAGNESIUM	AVERAGE Ca	AVERAGE Mợ
TYMOCHTEE DOLOMITE	20.38 20.04	12.60 13.13	20.21	12.87
PLUM RUN DOLOMITE (GF & LT LEDGES)	20.44 19.68	12.16 13.87	20.06	13.01
GREER LIMESTONE	37.96 37.92 37.59 37.51	.73 1.21 .96 .84	37.75	.94
CANAAN DOLOMITE	21.20 20.82	12.37 12.87	21.01	12.62
HIGHLAND LIMESTONE (11D-2)	34.06 34.07	3.87 3.65	34.07	3.76
MISSISSIPPI LIMESTONE	38.52 38.01	1.42 1.30	38.26	1.36
CARBON LIMESTONE	34.85 35.30	2.52 2.62	35.08	2.57
VICRON LIMESTONE LUCERNE VALLEY, CALIF.	37.61 38.00	1.66 1.31	37.81	1.49
VICRON LIMESTONE ADAMS. MASS.	36.90 36.81	2.38 1.65	36.86	2.02

Table 2

SORBENT SUPPLIERS

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SAMPLE	SOURCE	CONTACT
CANAAN DOLOMITE	PFIZER MINERALS.PIGMENTS AND METALS DIVISION P.O. BOX 667 CANAAN.CT. 06018	JOHN GUNTHER (203) 824-5435
GREER LIMESTONE	GERMANY VALLEY LIMESTONE CO. GREER BUILDING MORGANTOWN, W.V. 26505	RONNIE VANCE (304) 567-2141
MISSISSIPPI LIMESTONE	MISSISSIPPI LIME CO. ST. GENEVIEVE, MO. 63670	MR. BAIERLEIN (618) 465-7741
CARBON LIMESTONE	SME INDUSTRIES INC. P.O. BÓX 5250 POLAND. OHIO 44514	BRENT EDWARDS (216) 536-6275
TYMOCHTEE DOLOMITE	C.E. DUFF AND SON 9042 S.R. 117 HUNTSVILLE, OHIO 43324	DWIGHT GRANTZ (513) 686-2488
PLUM RUN DOLOMITE (GF & LT LEDGES)	DAVON INC. PLUM RUN STONE DIVISION 848 PLUM RUN ROAD PEEBLES, OHIO 45660	CRAIG MORGAN (513) 393-4211
HIGHLAND LIMESTONE (HD-2 LIMESTONE)	DAVON INC. HIGHLAND STONE DIVISION 4281 ROUSH ROAD HILLSBORO. OHIO	CRAIG MORGAN (513) 393-4211
SILICA PLANT DOLOMITIC LIMESTONE (LS-4 DOLOMITIC LST.)	FRANCE STONE CO. P.O. BOX 1928 TOLEDO. OHIO 43603	(419) 241-4101
	FRANCE STONE LABORATORIES P.O. BOX 49 WATERVILLE. OHIO 43566	BRUCE MASON V.P. PROPERTY & PRODUCT

V.P. PROPE & PRODUCT DEVELOPMENT (419) 878-9600

Table 4

MERCURY POROSIMETRY RESULTS

SAMPLE TYMOCHTEE DOLOMITE	TOTAL INTRUSION VOLUME CC/G .0407	TOTAL PORE AREA M2/G .7937	BULK DENSITY G/CC 2.4965	APPARENT SKELETAL DENSITY G/CC 2.7785
MISSISSIPPI LIMESTONE	.0493	.5474	2.3848	2.7027
GREER LIMESTONE	.0348	.4693	2.4605	2.6910
PLUM RUN DOLOMITE (GF & LT LEDGES)	.0425	.4300	2.5890	2.9095
HIGHLAND LIMESTONE (HD-2)	.0250	.7041	2.6137	2.7965
VICRON LIMESTONE LUCERNE VALLEY, CALIF.	.0123	.0318	2.6296	2.7174
CANAAN DOLOMITE	.0075	.0237	2.8032	2.8635
VICRON LIMESTONE ADAMS, MASS.	.0099	.0290	2.6399	2.7111
CARBON LIMESTONE	.0241	.4255	2.5801	2.7508

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A-4

	Sample	Total Intrusion Volume 44	Total Bre Areq ^m ³ g	Buck Dewsiry glae	Apparent (skeletal) Density g/cc.		
1	Tymochtee Downite	0.0407	0.7937	2.4965	2.7785		
2	Mississippi Linestone	0.0493	0.5474	2.3848	2.7027		
3	Greer LIMESTONE	0.0348	0.4693	2.4605	2.6910		
4	RUM RUN DOLOMITE GF-LT LEDGES	0.0425	0.4300	. 2.5890	2.9095		
5	HIGHLAND (HD-2) LIMESTONE	0.0250	0.7041	2.6137	2.7965		
6	VICRON LIMESTONE Luceme Valley, CALIF.	0.0123	0.0318	2.6296	2.7174	1	
7	Сапады Долоните	0.0075	0.0237	2.8032	2.8635		
8	, Victon Limestone Adams, Mass.	0.0099	0.0290	2.6399	2.7111		
q	Carbon LIMESTONE	0.0241	⁰ .4255	2.5801	. 2.7508		
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HITEMP-SORBENT CANAAN DOLOMITE: 16/18 MESH UNCALCINED PNTR NUMBER +385

LP EQUILIBRATION = +15.0000 SEC PNTR CONSTANT = +10.7900 MICRB-L/ HP EQUILIBRATION = +10.0000 SEC THETA = +130.0000SAMPLE WEIGHT = +5.0000 G GAMMA = +485.0000 DYNES/CM PNTR WEIGHT = +74.9400 G INITIAL PRESSURE = +0.9011 PSIA PNTR+SAMPLE WEIGHT = PORE DIAMETER = +79.9400 G +196.1730 MICRO-M PNTR+SAMPLE+MERCURY = +130.7900 6 MERCURY DENSITY = +13.5335 6/00 PNTR VOLUME = +5.5410 CC

INTRUSION (PRESSURIZATION) DATA SUMMARY

=	+0.0075	CC/G
=	+0.0237	20-M-6
=	+119.0450	MICROMETERS
=	+0.1096	MICROMETERS
=	+1.2659	MICROMETERS
=	+2.8032	G/CC
=	+2.8635	G/CC
		= +0.0075 = +0.0237 = +119.0450 = +0.1096 = +1.2659 = +2.8032 = +2.8635

% CAPILLARY = +9.7822 ++++

PAGE 1

LP 9:14:24 8/16/85

HP 9:38:24 8/16/85

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PRESSURE	PORE	INTRUSION	PORE	MEAN	
PSTA	DIAMETER	VOLUME	SURFACE	DIAMETER	DV
	MICRO-M	CC/G	SQ-M/G	MICRO-M	
+5.0	+35.4843	+0.0050	+0.0002	+115.8290	+0.0050
+9.9	+17.7814	+0.0056	+0.0003	+26.6328	+0.0006
+14.6	+12.0767	+0.0059	+0.0003	+14.9291	+0.0002
+19.9	+8.8743	+0.0060	+0.0004	+10.4755	+0.0002
+39.7	+4.4519	+0.0061	+0.0004	+6.6631	+0.0001
+60.0	+2.9462	+0.0062	+0.0005	+3.6990	+0.0001
+80.0	+2.2096	+0.0063	+0.0007	+2.5779	+0.0001
+100.4	+1.7613	+0.0064	+0.0009	+1.9855 /	+0.0001
+118.8	+1.4876	+0.0064	+0.0009	+1.6244	+0.0000
+150.5	+1.1742	+0.0064	+0.0011	+1.3309	+0.0001
+201.2	+0.8784	+0.0066	+0.0017	+1.0263	+0.0002
+252.0	+0.7014	+0.0067	+0.0023	+0.7899	+0.0001
+298.9	+0.5914	+0.0068	+0.0027	+0.6464	+0.0001
+353.6	+0.4999	+0.0068	+0.0031	+0.5457	+0.0001
+400.5	+0.4414	+0.0069	+0.0036	+0.4707	+0.0001
+455.2	+0.3883	+0.0069	+0.0037	+0.4149	+0.0000
+503.1	+0.3514	+0.0070	+0.0043	+0.3699	+0.0001
+600.7	+0.2943	+0.0070	+0.0044	+0.3228	+0.0000
+697.4	+0.2535	+0.0070	+0.0053	+0.2739	+0.0001
+799.0	+0.2212	+0.0071	+0.0064	+0.2373	+0.0001
+895.7	+0.1973	+0.0072	+0.0076	+0.2093	+0.0001
+997.3	+0.1772	+0.0072	+0.0078	+0.1873	+0.0000
+1104.8	+0.1600	+0.0072	+0.0093	+0.1686	+0.0001
+1206.3	+0.1465	+0.0072	+0.0095	+0.1533	+0.0000
+1307.0	+0.1353	+0.0073	+0.0097	+0.1409	+0.0000
+1411.5	+0.1252	+0.0073	+0.0100	+0.1302	+0.0000
+1501.3	+0.1177	+0.0073	+0.0119	+0.1215	+0.0001
+1607.8	+0.1099	+0.0073	+0.0119	+0.1138	+0.0000
+1691.8	+0.1045	+0.0073	+0.0124	+0.1072	+0.0000
+1803.2	+0.0980	+0.0073	+0.0127	+0.1013	+0.0000
42004 4	+0.0882	+0.0074	+0.0132	+0.0931	+0.0000
+2200 7	+0.0803	+0.0074	+0.0137	+0.0843	+0.0000
-2137-1	+0.0737	+0.0074	+0.0170	+0.0770	+0.0001
A2592 1	+0.0682	+0.0074	+0.0175	+0.0710	+0.0000
42814.7	+0.0628	+0.0074	+0.0181	+0.0655	+0.0000
+2995 5	+0.0590	+0.0075	+0.0186	+0.0609	+0.0000
A2189 0	+0.0554	+0.0075	+0.0191	+0.0572	+0.0000
+3388 8	+0.0520	+0.0075	+0.0196	+0.0537	+0.0000
+3520 5	+0.0493	+0.0075	+0.0196	+0.0506	+0.0000
+3800 0	+0.0465	+0.0075	+0.0207	+0.0479	+0.0000
*3863 5 *0000*C	40.044R	+0.0075	+0.0212	+0.0454	+0.0000
+3773.0 ▲4500 A	TU 0000	+0 0075	+0.0225	+0.0418	+0.0000
マテリリリ。 メモロロマーキ	TULUS70 TULUS70		+0.0238	+0.0373	+0.0000
TJUU(.1 18400 0	+0.0303 +0.0303	≠0.0075 ▲0.0075	+0.0238	+0.0337	+0.0000
T0470.7 .eqq0 4	TU.VOZI IN NOGS	+0.0075 ▲0.0075	+0 0200 +0	+0.0308	+0.0000
マジアプリ。ロ ふと言うで、4	イリーリニアリー	+0.0075 °	↓ 0 0238	+0.0283	+0.0000
TOUC(.1 12000 1	TV:VE/1 10 0959	±0.0075	+0 0229	+0.0262	+0.0000
+0707.1 .7505 5	てい。いどつび 本商 のつつち -	₹0.0070 ▲0.0075	-0.0200 -0.0200	+0.0244	+0.0000
+/3d3.2	マリュリごうつ (70.007D	TV.VE30		

PAGE 2

HITEMP-SORBENT CANAAN DOLOMITE: 16/18 MESH UNCALCINED PNTR NUMBER +385 LP 9:14:24 8/16/85* HP 9:38:24 8/16/85

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PAGE 3

PRESSURE	PORE	INTRUSION	PORE	MEAN	
PSIA	DIAMETER	VOLUME	SURFACE	DIAMETER	DV ,
	MICRO-M	CC/G	SQ-M/G	MICRO-M	
+7987.5	+0.0221	+0.0075	+0.0238	+0.0228	+0.0000
+8956.1	+0.0197	+0.0075	+0.0238	+0.0209	+0.0000
+9954.6	+0.0178	+0.0075	+0.0238	+0.0187	+0.0000
+10953.0	+0.0161	+0.0075	+0.0238	+0.0169	+0.0000
+11996.2	+0.0147	+0.0075	+0.0238	+0.0154	+0.0000
+12964.8	+0.0136	+0.0075	+0.0238	+0.0142	+0.0000
+13948.3	+0.0127	+0.0075	+0.0238	+0.0132 '	+0.0000
+14946.8	+0.0118	+0.0075	+0.0238	+0.0123	+0.0000
+15930.3	+0.0111	+0.0075 1	+0.0238	+0.0115	+0.0000
+17077.8	+0.0104	+0.0075	+0.0238	+0.0107	+0.0000
+18150.7	+0.0097	+0.0075	+0.0238	+0.0100	+0.000)
+19149.2	+0.0092	+0.0075	+0.0238	+0.0095	+0.0000
+20132.7	+0.0088	+0.0075	+0.0238	+0.0090	+0.0000
+24961.0	+0.0071	+0.0075	+0.0238	+0.0079	+0.0000
+29923.3	+0.0059	+0.0075	+0.0238	+0.0065	+0.0000
+35154.0	+0.0050	+0.0075	+0.0238	+0.0055	+0.0000
+40205.8	+0.0044	+0.0075	+0.0238	+0.0047	+0.0000
+45138.4	+0.0039	+0.0075	+0.0238	+0.0042	+0.0000
+50056.0	+0.0035	+0.0075	+0.0238	+0.0037	+0.0000
+54884.3	+0.0032	+0.0075	+0.0238	+0.0034	+0.0000
+59787.1	+0.0030	+0.0075	+0.0238	+0.0031	+0.0000

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MICROMERITICS AUTO-PORE 9200 V2.01

CANAAN DOLOMI PNTR NUMBER	∪ TE: 16×18 MESH U +385	NCALCINED		LP 9:14:24 8 HP 9:38:24 8	3/16/80 3/16/85
	CUMULATIVE POR	E VOLUME (CC/ 100% =	G) VS. PORE DI +0.0075	AMETER	
0%	20%	40%	60%	80%	100.
I			••••• I ••••	I	I
+300-	●				
+235-	•				
+184-		•			
+144-		•			
+113-			•	<i>i</i> (
+88.1-			◆ .		
+69.0-			•		
+54.0-			•		
746.37 192 19					
+25.9-	,		•	•	
+20.3-				•	
+15.9-				٠	
+12.4-				ب	
+9.72-				•	
+7.61-			•	•	
+5.96-		•		•	•
+4.66-	-			. •	
+3.65-				•	
+2.86-				•	
+2.24-			-	•	
+1.75-				•	
+1.37=				•	
±1.07≃ ⊥0.000⊥					•
+0.007- +0.457-				,	•
+0.514-					•
+0.402-	•				•
+0.315-			1		•
+11, 247+			•		•
+0.193-					+
+0.151-					•
+0.118-					•
+0.0926-					•
+0.0725-					•
+0.0567-				•	•
+0.0444-					•
≠V.V347= ★0.0272-					•
+U.UE/E- +0.0212-					
+u.9210- ▲0 0167-					
+0.0180-				•	•
+0.0102-					•
+0.00799-					•
+0.00626-	• •				•
+0.00490-	•				
+0.00383-					•
$\lambda \phi = \phi \phi \phi \phi \phi$			`		· ·

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HITEMP-SORBENT	LP	9:14:24	8/16/85
CANAAN DOLOMITE; 16/18 MESH UNCALCINED	HP	9:38:24	8/16/85
PNTR NUMBER +385			

	CUMULATIVE	SURFACE	AREA 100%	(M2/G) =	VS. +0.	PORE 0237	DIAMETER			
0%	20%		40%			60%		80%		1
1		•••••	• • • • • •	• • • • • •	• • • • •		• • • • • • • • • •		• • • • • •	• • •
+300-+ +336-+										
₩ <u>₩</u> 30-₩ 4104-4										
+184-+										
+112-+										
+113-+								•		
+57.0-+ →54 0-+										
+342.3+4										
++==;J-+ +>> 1_+										
+00.1-+ +05.0-+										
+20.7-+										
+ <u>c</u> (.3++ 15 9-4										
+10.7-+										
						•				
+7 61-4										
+5.96-+				•						
+4.66-+		•								
+3.65-+										
+2.86-+						•				
+2.24- +							,			
+1.75- +										
+1.37= +										
+1.07- +										
+0.839-	•			•						
+0.657-	•									
+0.514-	•									
+0.402-	•									
+0.315-	•									
+ <u>0,</u> 247−	•	•								
+0.195-		•								
+0.151-			•							
+0.118-				•						
+0.0926-					•					
+0.0725-							•			
+0.0567-								•		
+0.0444-									+	
+0.0347-										
+0.0272-										
+0.0213-										
+0.0167-										
+0.0130-										
+0.0102 -										
+0.00799-										-
+0.00626-										ם,
+0.00490-										
+0.00383-										
+0.00300-										

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HITEMP-SORBENT CANAAN DOLOMITE: 16/18 MESH UNCALCINED PNTR NUMBER +385

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LP 9:14:24 8/16/85 HP 9:38:24 8/16/85

DIFFERENTIAL VOLUME (CC/G-MICRO-M) VS. PORE DIAMETER 100% = +0.490555E-002

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0%	20%	40%	60%		80%	106
I	I	. I	• • • • • • • • • I • •		I	
+300-+++++	*******					
+235-+++++	**************	******				
+184-+++++	**************	*********	****			
+144-+++++	**************	**********	*********	****		
+113-+++++	**************	*********	********	• • • • • • • • • • •	◆◆	
+38.1-+++++	************* ***********************	*********	*********	• • • • • • • • • • •	******	
+69.0-+++++	**************	*********	*********	********	********	•
+54.0-+++++	*************	*********	*********	********	********	****
+42.3-+++++	*************	*********	*********	********	*********	• ••• •••
+33.1-+++++	************	*********	*********	*******	********	•
+25.9-*****	• • • • • • • • • • • • • • • • • • • •	*********	****			
+20.3	· · · · · · · · · · · · · · · · · · ·					
+10.9-*****	••					
+12.4-++				•		
+9.72-++						
+/.61-++						
+3,76-++	•					
+4,00-++						
▼3.80 - ▼ 40.04.4			•			
TC.0077 43 94-44						
+1 75-+						
+1 37 - →						
+1 87++						
+0.839+++						
+0.657-+						
+0.514-+			·			
+0.402-+	•					
+0.315-+						
+0.247-+						
÷0.103 ·•						
+0.151-+						-
+0.118-+						
+0.0926-+						
+0.0725-+						
. +0 • 0567 - ◆						
+0.0444-+						
+0,0347-+						
+0.0272-+						
+0.0213-+						
+0.0167-+						
+0.0130-+						•
+0.0102-+						
+0.00799-+						
+0.00626-+						
+0.00490-+						
+0.00383++						4
+0.00300-+		•				۹.

HITEMP-SORBENT CANAAN DOLOMITE: 16/18 MESH UNCALCINED PNTR NUMBER +385 LP 9:14:24 8/16/85 HP 9:38:24 8/16/85

DIFFERENTIAL SURFACE AREA (M2/G-MICRO-M) VS. DIAMETER 100% = +0.262426E-002

0%	20%	40%	60%	80%	10
+200-4			••••••		•••••
+225-+					
+ <u>c</u> 3.)=+					
+144-++					
+113-++					
+88.1-++				•	
+69.0-++	1				
+54.0-++	•				
+42.3-+++					
+33.1-+++					
+25.9-+++					
+20.3-***					
+15.9-++					
+12.4-++					
+9.72-++				• ,	
+7.61-++			•		
+D.96-++					
		•			
▼3.50 ▼ 19 02_44					
+2.24- ** *					
+1 75-44444					
+1.37-++					
+1.87=++++++	***				
+0.839-++++++	*********				
+0.657-+++++	*****				
+0.514-+++++	****				
+0.402-++++					
+0.315-++++++	♦ ♠				
+0.247-******	• • • • • • • • • • • • • • • • • • • •	**** .			
+0.193-+++++	••••	****			
+0.151-++++++	*****				
+0.118-++++++	***********	***********	********	◆	
+0.0926-++++++	****				
+0.0725-*******	*****************	*********	**********	***********	* **** *
+0.0367-++++++	********				
+0.0949-+++++++	•••••				
+0,034/-****** +0 0272-*	••••••				
+0.0272-+					-4
+0.0167- →					
+0.0130-+					
+0.0102-+					
0.00799-+					÷
0.00626-+					μ.
0.00490-+					
0.00383-+					
0.00300-+					
		A-3	12		
HITEMP-SORBENT CARBON LIMESTONE (8/85) 16-18 MESH PNTR NUMBER +388

285) 16-18 MESH

LP 11:34:48 8/26/85 HP 12:57:19 8/26/85

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LP EQUILIBRATION	3	+15.0000	SEC	PNTR	CONSTANT	ŧ	+10.7900	MICRO-L/F
HP EQUILIBRATION	=	+10.0000	SEC		THETA	Ξ	+130.0000	
SAMPLE WEIGHT	=	+3.5300	G		6amma	=	+485.0000	DYNES/CM
PNTR WEIGHT	=	+77.3400	G	INITIAL	PRESSURE	=	+0.9451	PSIA
PNTR+SAMPLE WEIGHT	=	+80.8700	G	PORE	DIAMETER	=	+187.0490	MICRO-M
PNTR+SAMPLE+MERCURY	Ξ	+108.5300	G	MERCURY	DENSITY	=	+13.5335	6×CC
PNTR VOLUME	æ	+3.4120	CC					

INTRUSION (PRESSURIZATION) DATA SUMMARY

TOTAL INTRUSION VOLUME	÷	+0.0241	CC/6
TOTAL PORE AREA	=	+0.4255	SQ-M/G
MEDIAN PORE DIAMETER (VOLUME)	_	+13.7645	MICROMETERS
MEDIAN PORE DIAMETER (AREA)	=	+0.0217	MICROMETERS
AVERAGE PORE DIAMETER (47/A)	=	+0.2261	MICROMETERS
BULK DENSITY	=	+2.5801	G/CC
APPARENT (SKELETAL) DENSITY	=	+2.7508	G/CC

% CAPILLARY = +22.1120 ++++

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PAGE 2

HITEMP-SORBENT CARBON LIMESTONE (8/85) 16-18 MESH PNTR NUMBER +388 LP 11:34:48 8/26/85 HP 12:57:19 8/26/85

THE PERMIT	1.0.0.0		•		
PRESSURE	PORE	INTRUSION	PORE	MEAN	
PSIA	DIAMETER	VOLUME	SURFACE	DIAMETER	DV
	MICRO-M	CC/G	SQ-M/G	MICRO-M	
+5.0	+35.4322	+0.0057	+0.0002	+111.2400	+0.0057
+9.9	+17.8208	+0.0115	+0.0011	+26.6265	+0.0057
+14.6	+12.0949	+0.0122	+0.0013	+14.9578	+0.0007
+19.9	+8.8613	+0.0128	+0.0015	+10.4781	+0.0005
+38.8	+4.5527	+0.0137	+0.0020	+6.7070	+0,0009
+58.4	+3.0275	+0.0142	+0.0025	+3.7901	÷0.0005
+78.8	+2.2446	+0.0147	+0.0033	+2.6361	+0.0005
+98.6	+1.7927	+0.0151	+0.0042	+2.0186	+0.0005
+120.8	+1.4633	+0.0156	+0.0053	+1.6280	+0.0005
+148.9	+1.1875	+0.0163	+0.0074	+1.3254	+0.0007
+198.8	+0.8890	+0.0176	+0.0126	+1.0382	+0.0014
+252.2	+0.7010	+0.0182	+0.0156	+0.7950	+0. 0006
+301.8	+0.5857	+0.0189	+0.0199	+0.6433	+0.0007
+355.6	+0.4972	+0.0192	+0.0221	+0.5414	+0.0003
+403.4	+0.4382	+0.0194	+0.0241	+0.4677	+0.0002
+454.2	+0.3892	+0.0197	+0.0264	+0.4137	+0.0002
+504.0	+0.3507	+0.0198	+0.0281	+0.3699	+0.0003
+602.7	+0.2933	+0.0202	+0.0329	+0.3220	+0.0004
+701.3	+0.2520	+0.0205	+0.0364	+0.2727	+0.0002
+803.9	+0.2199	+0.0206	+0.0392	+0.2360	+0.0002
+897.7	*0.1969	+0.0208	+0.0423	+0.2084	+0.0002
+994.4	+0.1778	+0.0210	+0.0458	+0.1873	+0.0002
+1113.6	+0.1587	+0.0211	+0.0497	+0.1683	+0.0002
+1216.1	+0.1454	+0.0212	+0.0520	+0.1521	+0.0001
+1315.7	+0.1344	+0.0214	+0.0566	+0.1399	+0.0002
+1414.4	+0.1250	+0.0215	+0.0592	+0.1297	+0.0001
+1512.1	+0.1169	+0.0215	+0.0620	+0.1209	+0.0001
+1611.7	+0.1097	+0.0216	+0.0650	+0.1133	+0.0001
+1712.3	+0.1032	+0.0217	+0.0681	+0.1065	+0.0001
+1812.0	+0.0976	+0.0218	+0.0715	+0.1004	TU.UUU1
+2008.3	+0.0880	+0.0219	+0.0754	+0.0928	+0.0001
+2204.6	+0.0802	+0.0220	+0.0797	+0.0841	TU.UUUU
+2403.9	+0.0/35	+0.0221	+0.0843	+0.0769	+0.0001 +0.0001
+25%6./	+0.0681	+0.0221	+0.0892	+0.0708	±0.0001
+2/8/.4	+0.0634	+0.0222	+0.0940	+0.0637	+0.0001
+3011.9	+0.0587	+0.0223	+0.1002	TU.U011	+0.0001
+3190.2	+0.0554	+0.0224	+0.1062	+0.0570	+0.0001
+3386.3	+0.0522	+0.0220	TU.1124	+0.0338	+0.0001
+3606.9	+0.0490	+0.0225	+0.1133	+0.0306	+0.0000
+3800.0	+0.0465	+0.0226	+0.1203	+0.0478	+0.0001 +0.0001
+3773.8	TU.U443	TU.UCCD	TV.ICIV	TV.V434 10.0417	₩0.000L ₩0.0001
+4010.3	TU.U371	TU.U228	▼V.137€ ⊥ù 4728	TU.U417 10 0070	÷0.0002 ◆0.0001
+3007.1	TU.U3D3	TU.U227	TU.1407 10 (874	TU.US/E	♦0 0001
+0013.8	★U.U321	TU.U227	TU.1375	TU.UQQ7	+0.0001 •0.0001
TOUZU.4	TU.U274		TV.107V	TU.USU/ An nooo	+0.0001
TO042.U	テリ。リピイリ エム・ヘンデン	TU.UZJI 10.0000	TU.1016	TU.VEGE	+Å. ÅÅ.
▼7018.9 .7840 -	TU.UZDZ	TU.U232	TV.1742	TU.UEDI 10 0242	+0.0001
+r340.4	+0.0234	+V.U232	40.170/	TU.UC40	••••••••

HITEMP-SORBENT CARBON LIMESTONE (8/85) 16-18 MESH PNTR NUMBER +388

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LP 11:34:48 8/26/85 HP 12:57:19 8/26/85

PORE	INTRUSION	PORE	MEAN	
DIAMETER	VOLUME	SURFACE	DIAMETER	DV
MICRO-M	CC/G	SQ-M/G	MICRO-M	
+0.0220	+0.0233	+0.2102	+0.0227	+0.0001
+0.0197	+0.0234	+0.2272	+0.0209	+0.0001
+0.0177	+0.0235	+0.2617	+0.0187	+0.0002
+0.0161	+0.0236	+0.2817	+0.0169	+0.0001
+0.0148	+0.0236	+0.2840	+0.0154	+0.0000
+0.0137	+0.0238	+0.3280	+0.0142	+0.0002
+0.0127	+0.0238	+0.3300	+0.0132	+0.0000
+0.0118	+0.0239	+0.3561	+0.0123	+0.0001
+0.0111	+0.0240	+0.3838	+0.0115	+0.0001
+0.0103	+0.0240	+0.3857	+0.0107	+0.0000
+0.0097	+0.0240	+0.3871	+0.0100	+0.0000
+0.0093	+0.0240	+0.4194	+0.0095	+0.0001
+0.0088	+0.0240	+0.4209	+0.0091	+0.0000
+0.0071	+0.0241	+0.4256	+0.0079	+0.0000
+0.0059	+0.0241	+0.4256	+0.0065	+0.0000
+0.0050	+0.0241	+0.4256	+0.0055	+0.0000
+0.0044	+0.0241	+0.4256	+0.0047	+0.0000
+0.0039	+0.0241	+0.4256	+0.0041	+0.0000
+0.0035	+0.0241	+0.4256	+0.0037	+0.0000
+0.0032	+0.0241	+0.4256	+0.0034	+0.0000
+0.0030	+0.0241	+0.4256	+0.0031	+0.0000
	PORE DIAMETER MICRO-M +0.0220 +0.0197 +0.0197 +0.0161 +0.0148 +0.0137 +0.0127 +0.0118 +0.0111 +0.0103 +0.0097 +0.0093 +0.0093 +0.0059 +0.0059 +0.0059 +0.0059 +0.0035 +0.0032 +0.0030	POREINTRUSIONDIAMETERVOLUMEMICRO-M $CC \times G$ +0.0220+0.0233+0.0197+0.0234+0.0197+0.0235+0.0161+0.0236+0.0148+0.0236+0.0137+0.0238+0.0118+0.0239+0.0111+0.0240+0.0103+0.0240+0.0097+0.0240+0.0093+0.0241+0.0059+0.0241+0.0059+0.0241+0.0050+0.0241+0.0035+0.0241+0.0035+0.0241+0.0032+0.0241+0.0030+0.0241	POREINTRUSIONPOREDIAMETERVOLUMESURFACEMICRO-MCC/6SQ-M/6+0.0220+0.0233+0.2102+0.0197+0.0234+0.2272+0.0197+0.0235+0.2617+0.0161+0.0236+0.2817+0.0148+0.0236+0.2840+0.0137+0.0238+0.3280+0.0127+0.0238+0.3300+0.0118+0.0239+0.3561+0.0111+0.0240+0.3838+0.0103+0.0240+0.3857+0.0097+0.0240+0.4256+0.0071+0.0241+0.4256+0.0059+0.0241+0.4256+0.0050+0.0241+0.4256+0.0035+0.0241+0.4256+0.0035+0.0241+0.4256+0.0032+0.0241+0.4256+0.0030+0.0241+0.4256	PORE DIAMETER MICRD-MINTRUSION VOLUME CC/GPORE SURFACE SQ-M/GMEAN DIAMETER MICRD-M $+0.0220$ $+0.0233$ $+0.0197$ $+0.0234$ $+0.2272$ $+0.0209+0.0177+0.0235+0.2617+0.0187+0.0161+0.0236+0.2817+0.0187+0.0148+0.0236+0.3280+0.3280+0.01127+0.0238+0.3280+0.01128+0.01127+0.0238+0.3300+0.01128+0.01118+0.0239+0.3561+0.0123+0.01111+0.0240+0.3857+0.0107+0.0097+0.0240+0.3857+0.0107+0.0093+0.0240+0.4209+0.0091+0.0095+0.0088+0.0240+0.4256+0.0095+0.00059+0.02411+0.4256+0.00055+0.00441+0.4256+0.00055+0.00441+0.4256+0.00411+0.4256+0.00411+0.4256+0.00411+0.4256+0.00411+0.4256+0.00411+0.4256+0.00411+0.4256+0.00411+0.4256+0.0037+0.02411+0.4256+0.0037+0.0030+0.02411+0.4256+0.0031$

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HITEMP-SORBENT CARBON LIMESTONE (8/85) 16-18 MESH PNTR NUMBER +388 LP 11:34:48 8/26/84 HP 12:57:19 8/26/85



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HITEMP-SORBENT CARBON LIMESTONE (8/85) 16-18 MESH PNTR NUMBER +388

b,

LP 11:34:48 8/26/85 HP 12:57:19 8/26/85

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CUMULATIVE SURFACE AREA (M2/G) VS. PORE DIAMETER 100% = +0.4255

0% T	20%	:	40%	60%	8	0%	100
+300-+						· · · · · · · · · · · · · · · · · · ·	
+235-+		•					
+184-+							
+112-+							
+92 1-4							
+69.0-+							
+54.0-+							
+42.3-+							
+33.1-+							
+25.9-+			•				• •
+20.3-+							
+15.9-+	•						
+12.4-+				·			-
+9.72-+							
.+7.61-+							
+5.96-+	•						
+4.66-+							
+3.65-+							
+2.86-+			•				
+2.24-+							
+1.73-+					•		
+1.37-+							•
+0.930- +							
+0.50r - + +0.514-	· . ▲						
+0.402-	•						
+0.315-	•						
+0.247-	•						
+0.193-	•						
+0.151-	•						
+0.118-	•			,			
+0.0926-	•						
+0.0725-	•					· .	
+0.0567-		•				•	
+0.0444-		•					
+0.0347-		•					
+0.0272-			•				
+0.0213-			•	•			
+0.0167-				•			
+0.0130-					•		
+0.0102-						•	-
+0.00799-							•
₽U.UU626- .a.aa454							•
+0.00490- .a.aaaaa							•
♥V.VV383- ↓0.00300						•	· •
•0.00300-							, •

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HITEMP-SORBENT CARBON LIMESTONE (8/85) 16-18 MESH PNTR NUMBER +388

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LP 11:34:48 8/26/8 HP 12:57:19 8/26/8

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DIFFERENTIAL VOLUME (CC/G-MICRO-M) VS. PORE DIAMETER 100% = +0.574866E-002

.

	0%	20%	40%	60%	80% 1	
•	I	••I•••••	••I•••••••••	••I•••••	I	
+300	-++++++++++	****				
+235		*********	◆◆◆			
+184	-++++++++++	**********	**********			
+144	-********	*********	***********	*******		
+113	-********	***********	**********	***********	◆	
+88,1	-*********	************	***********	************	*****	
+69.0	-+++++++++	************	**********	**********	********	
+54.0	-++++++++++	**********	***********	************	**********	
+42.3		•••••	••••	•••••••••••••••	••••••	-
+33.1		· • • • • • • • • • • • • • • • • • • •	••••••••••••••	••••••••••••••••	•••••••••••••••	
+20.9		••••••••	••••••••••••••	•••••••••••••••	•••••••••••••••••	
TEU.3		· • • • • • • • • • • • • • • • • • • •		************	************	
TID.7			••••	*******		
T12.4		•••				
+7.76					· · ·	
				•	•	
42 24			-			
+1.75						
+1.37	-+++++					
+1.07		•				
+0.839		***				
+0.657	-++++++					
+0.514	-++++					
+0.402	-+++					
+0.315	-+++					
+0.247	' -++		· · ·			
+0.193	-++					
+0.151	-+					
+0.118						
+0.0926	- ♦ .					
+0.0725	i - ♥					
+0.0567	· • •					
+0.0444						
+0.0347						
+0.0212						
+0.0213						
- +0.0187 - +0.0190	_ _		,			
- +0.0130 - 4 0 0109						
+0.0102 +0 00799						l
+0.00624						
+0.0028						
+0.00383						
+0.00300	-+					
• •						

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LP 11:34:48 8/26/8"

HP 12:57:19 8/26/85

HITEMP-SORBENT CARBON LIMESTONE (8/85) 16-18 MESH PNTR NUMBER +388

DIFFERENTIAL SURFACE AREA (M2/G-MICRD-M) VS. DIAMETER 100% = +0.248392E-001

	0%	20%	40%	60%	80%	10:
	1			•••••		
+2	35- •					
+1	84-+					
+1	44-+					
+1	13-+					•
+88	.1-+					
+69	.0-•					
.+54	. 0-+					
+42	.3-+					
+33	. 1+					
+25	•					
+20	K 3− + +					
+15		•			•	·
+12	.4-+			•		
+9.	72-+					
+7.	61-+				•	
+5.	94-•					
+4.	66-++					
+3.	45 - +					
+2.	86-++		•			
+2.	24-++				•	
+1-	⋎⋣ ⋍ ●●● Э⊒					
	3/					
	39			·		
	57-000000					
	14-00000	•				
+0.4	02	•				
+0.3	15	****				
+0.2	47-+++++	••••				
+0.1	93-+++++	***				
+0.1	51-+++++	▲				
+0.1	18	◆◆ _			•	
+0.09	26-+++++	****				
+0.07	25-+++++	******				
+0.05	67-+++++	*********			н. Н	
+0.04	44-+++					
+0.03	47-*****	•••••	*****			
+0.02	72-++++++	********	******			
+0.02	13-*****	• • • • • • • • • • • • • • • • • • •	***********	*******		
+0.01	67	•••••	**********	*********	************	*********
+0.01	30	•••••	*******	*****	****	
+0.01	₩2- + ++++			. ,	•	
+0.007 	╔╔╗ ╔╴╴╶╴╴╴╴	**		·		
+V.V0€.	∠₽−●●●●					
≠U.U94 ×0.005	?!! - ● 88		`			
テリ。リリボ への ののの	23 ▼ ₩₩- -					
+0.003	ųų - ≠		A-19			

PAGE 1

HITEMP-SORBENT LP 9:14:24 8/16/85 HIGHLAND (HD-2) LIMESTONE; 16/18 MESH UNCALCINED HP 11:18:58 8/16/85 PNTR NUMBER +382 LP EQUILIBRATION = +15.0000 SEC PNTR CONSTANT = +10.7900 MICRO-L/P HP EQUILIBRATION = +10.0000 SEC THETA = +130.0000 SAMPLE WEIGHT = +4.0000.G GAMMA = +485.0000 DYNES/CM PNTR WEIGHT = +76.3700 G INITIAL PRESSURE = +0.9011 PSIA PNTR+SAMPLE WEIGHT = +80.3700 G PORE DIAMETER = +196.1730 MICRO-M PNTR+SAMPLE+MERCUPY = +111.8300 G MERCURY DENSITY = +13.5335 6/00 +3.8550 CC PNTR VOLUME =

INTRUSION (PRESSURIZATION) DATA SUMMARY

TOTAL INTRUSION VOLUME	=	+0.0250	CC/G
TOTAL PORE AREA	Z	+0.7041	SQ-M/G
MEDIAN PORE DIAMETER (VOLUME)		+1.1082	MICROMETERS
MEDIAN PORE DIAMETER (AREA)	=	+0.0277	MICROMETERS
AVERAGE PORE DIAMETER (4V/A)	2	+0.1421	MICROMETERS
BULK DENSITY	=	+2.6137	G/CC
APPARENT (SKELETAL) DENSITY	=	+2.7965	G/CC

% CAPILLARY = +26.0546

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HITEMP-SORBENT HIGHLAND (HD-2) LIMESTONE; 16/18 MESH UNCALCINED PNTR NUMBER +387 LP 9:14:24 8/16/85 HP 11:18:58 8/16/85

PRESSURE	POPE	INTRUSION	PORE	MEAN	
PSIA	DIAMETER	YOLUME	SURFACE	DIAMETER	Đ٧
	MICRO-M	CC/G	SQ-M/G	MICRO-M	
+5.0	+35.4843	+0.0074	+0.0003	+115.8290	+0.0074
+9.9	+17.7814	+0.0090	+0.0005	+26.6328	+0.0015
+14.6	+12.0767	+0.0097	+0.0007	+14.9291	+0.0007
+19.9	+8.8743	+0.0101	+0.0009	+10.4755	+0.0005
+38.6	+4.5786	+0.0104	+0.0010	+6.7265	+0.0003
+58.5	+3.0237	+0.0107	+0.0014	+3.8012	+0.0003
+79.3	+2.2301	+0.0111	+0.0020	+2.6269	+0.000-
+100.7	+1.7549	+0.0115	+0.0026	+1.9925	+0.ŬPer 2
+118.4	+1.4932	+0.0117	+0.0033	+1.6240	+0.Ú
+148.6	+1.1898	+0.0121	+0.0045	+1.3415	· +0.0 : ∿
+200.5	+0.8817	+0.0135	+0.0099	+1.0358	+U.QUi+
+249.1	+0.7097	+0.0149	+0.0169	+0.7957	+0.0014
+303.8	+0.5819	+0.0155	+0.0202	+0.6458	+0.0005
+351.6	+0.5027	+0.0159	+0.0236	+0.5423	+0.0005
+404.4	+0.4371	+0.0163	+0.0271	+0.4699	+0.0004
+454.2	+0.3892	+0.0167	+0.0310	+0.4132	+0. 0004
+506.0	+0.3494	+0.0171	+0.0346	+0.3693	+0.0003
+599.8	+0.2947	+0.0176	+0.0413	+0.3221	+0.0005
+702.3	+0.2517	+0.0181	+0.0483	+0.2732	+0.0005
+802.0	+0.2204	+0.0185	+0.0552	+0.2361	+0.0004
+902.6	+0.1959	+0.0188	+0.0605	+0.2081	+0.0003
+997.3	+0.1772	+0.0191	+0.0678	+0.1866	+0.0003
+1110.6	+0.1592	+0.0194	+0.0744	+0.1682	+0.0003
+1204.4	+0.1468	+0.0196	+0.0798	+0.1530	+0.0002
+1312.8	+0.1347	+0.0199	+0.0876	+0.1407	+0.0003
+1406.6	+0.1257	+0.0201	+0.0939	+0.1302	+0.000E
+1495.5	+0.1182	+0.0202	+0.0985	+0.1219	+Ŭ.ŬŬ (†
+1609.8	+0.1098	+0.0204	± 0.1053	+0.1140	+0.0
+1699.6	+0.1040	+0.0206	+0.1110	+0.1069	+0.(
+1805.1	+0.0979	+0.0208	+0.1192	+0.1010	+0.0√
+1997.6	+0.0885	+0.0210	+Ú.1283	+0.0932	+0.0002
+2200.7	+0.0803	+0.0213	+0.1414	+0.0844	+0.0003
+2397.1	+0.0737	+Ú.Ú215	+0.1523	+0.0770	+0.0002
+2598.9	+0.0680	+0.0216	+0.1604	+0.0709	+0.0001
+2786.0	+0.0634	+0.0218	+0.1731	+0.0657	+0.0002
+2987.0	+0.0592	+0.0220	+0.1824	+0.0613	+0.ŬŬŬ1
+3199.3	+0.0553	+0.0222	+0.1969	+0.0572	+0.0002
+3400.8	+0.0520	+0.0223	+0.2074	+0.0536	+0.0001
+3584.5	+0.0493	+0.0224	+0.2184	+0.0506	+0.0001
+3814.9	+0.0463	+0.0225	+0.2247	+0.0478	+0.0001
+3993.8	+0.0443	+0.0226	+0.2311	+0.0453	+0.0 001
+4500.4	+0.0393	+0.0229	+0.2642	+0.0418	+0.0003
+5022.0	+0.0352	+0.0232	+0.2871	+0.0372	+0.0002
+5513.8	+0.0321	+0.0234	+0.3121	+0.0336	+Ů.ŬŬŬ2
+6020.4	+0.0294	+0.0235	+0.3307	+0.0307	+Ú.ÚÚÚ)]
+6512.2	+0.0271	+0.0237	+0.3601	+0.0283	+0.0002
+7033.8	+0.0251	+0.0239	+0,3817	+0.0261	+0.0001
+7540.4	+0.0234	+0.0239	+0.3939	+0.0243	+ů, ůůů)

HITEMP-SOFBENT HIGHLAND (HD-2) LIMESTONE: 16/18 MESH UNCALCINED PNTR NUMBER +387

LP	9:	14	:24	8/10	6/85
HP	11	: 1	8:5	8 873	16785

PRESSURE	POPE	INTRUSION	PORE	MEAN	
PSIA	DIAMETER	VOLUME	SURFACE	DIAMETER	DV
	MICRO-M	CC/G	SQ-M/G	MICRO-M	
+8002.4	+0.0221	+0.0241	+0.4182	+0.0228	+0.0001
+8956.1	+0.0197	+0.0242	+0.4458	+0.0209	+0.0001
+9984.4	+0.0177	+0.0244	+0.4762	+0.0187	+0.0001
+10953.0	+0.0161	+0.0245	+0.5094	+0.0169	+0.0001
+11996.2	+0.0147	÷0.0246	+0.5285	+0.0154	+0.0003
+12964.8	+0.0136	÷0.0245	+0.3489	+0.0148	+0.0000
+13948.3	+0.0127	+0.0247	+0.5706	+0.0132	+Ú.QÚÚ)
+14944.8	+ 0.0118	÷0,0248	+0.5937	+0.0123	+ŭ. ŬŬŬ
+15960.1	+0.0111	+0.0248	+0.5952	+0.0115	+0.0000
+17092.7	+0.0103	+0.0248	+0.5967	+0.0107	+0.0000
+18150.7	+0.0097	+0.0249	+0.6243	+0.0100	+0.0000
+19164.1	+0.0092	+0.0249	+0.6255	+0.0095	+0.0000
+19909.2	+0.0089	+0.0249	+0.6554	+0.0091	+0.0001
+24961.0	+0.0071	+0.0249	+0.6597	+0.0080	+0.000
+29923.3	+0.0059	+0.0250	+0.7029	+0.0065	+0.0000
+35273.2	+0.0050	+0.0250	+0.7042	+0.0055	+0.0000
+40354.8	+0.0044	+0.0250	+0.7042	+0.0047	+0.0000
+45242.7	+0.0039	+0.0250	+0.7042	+0.0041	+0.0000
+50175.2	+0.0035	+0.0250	+0.7042	+0.0037	+0.0000
+54943.9	+0.0032	+0.0250	+0.7042	+0.0034	+0.0000
+59831.8	+0.0030	+0.0250	+0.7042	+0.0031	+0.000

A-22

PHGE 3

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HITEMP-SOPBENT HIGHLAND (HD-2) LIMESTONE; 16/18 MESH UNCALCINED PNTR NUMBER +387

LP 9:14:24 8/16/01 HP 11:18:58 8/16



HITEMP-SOPBENT LP 9:14:24 8/16/85 HIGHLAND (HD-2) LIMESTONE; 16/18 MESH UNCALCINED HP 11:18:58 8/16/85 PNTR NUMBER +387

> CUMULATIVE SURFACE AREA (M2/G) VS. PORE DIAMETER 100% = +0.7041

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(0%	20%	40%	60%	80%	_ 1
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#2:3D=4	•					
+124	• -					
+144=	•					
+113-4	•				•	
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	•					
+34.0-	•					
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+20.7-1	•					-
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+0.118-	•	•				
+0.0926-		•				
+0.0725-		•				
+0.0567-		•				
+0.0444-			•			
+0.0347-			•			
+0.0372+				•		
+0.0213-				•		
+0.0167-				-	•	
+0.0130-					•	-
+0.0102-					•	
+0.00799-						٠
+0.00626-			,			-
+0.00490-						
+0.00383-						
+0.00300-	•		•			

A-24

PAGE 6

HITEMP-SORBENT LP 9:14:24 8/16/85 HIGHLAND (HD-2) LIMESTONE; 16/18 MESH UNCALCINED HP 11:18:58 8/16/80 PNTR NUMBER +387 DIFFERENTIAL VOLUME (CC/G-MICRO-M) VS. PORE DIAMETER 100% = +0.729359E-002 20% 40% 100 0% 60% 80% . . . I . . I....I.... .I. - I +235-+++++ +184-+++++++++++ -----+144-++++++++++ * +113-+++ +88.1-++++ +69.0-********** +54.0-+++++ +42.3-++++++ +33.1-*********** +20.3-*********************** +15:9-********* +12.4-++++++ +9.72-+++++ +7.61-+++ +5.96-+++ +4.66-++ +3.65-+++ +2.25-+++ +2.24-+++ +1.75-+++ +1.37-+++ +1.07-****** +0.839-********** +0.657-******** +0.514-++++ +0.402-+++ +0.315-+++ +0.247-++++ +0.193-+++ +0.151-++ +0.118-+ +0.0926-++ +0.0725-++ +0.0567-++ +0.0444-+ +0.0347-++ +0.0272-++ +0.0213-+ +0.0167-+ +0.0130-+ +0.0102-+ +0.00799-+ +0.00626-+ +0.00490-+ +0.00383-+ +0.00000-+

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HITEMP-SOPBENT LP 9:14:24 8/16/85 HIGHLAND (HD-2) LIMESTONE; 16/18 MESH UNCALCINED HP 11:18:58 8/16/85 PNTR NUMBER +387

> DIFFERENTIAL SURFACE AREA (M2/G-MICRD-M) VS. DIAMETER 100% = +0.322794E-001

	0%	20%	40%	60%	80%	1
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	+104-+ +1dd-+					
	+113- ◆		,			
+	88.1-+				•	
	89.0-+		·			
+	54.0-+					
+	42.3-+					
+(33.1-+					
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+	20.3-+			•		
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+0.	0567-+++++	******	•••••			
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÷0.	0347-+++++	************	***********	**********	•	4
+0.	0272-+++++	**********	***********	*****	***********	•
+0.	0213-+++++	•••••	•••••	***********	*****	
+0.1	0167-+++++	**************	•••••	*****	**********	*****
+0.1	0130-+++++	***********	•••••	******		5
+0.1	0102-+++++	******	· ·			
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U. U.	U383 - ♦ Ntias					
V. VI	0300−◆					

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PAGE: 7

LP 11:1:11 8/16/85 HITEMP-SOPBENT MISSISSIPPI LIMESTONE: 16/18 MESH UNCALCINED-HP 11:18:58 8/16/80 PNTR NUMBER +381 +15.0000 SEC LP EQUILIBRATION = PNTR CONSTANT = +10.7900 MICRO-L/P HP EQUILIBRATION = +10.0000 SEC THETA = +130.0000 SAMPLE WEIGHT = +4.0000 5 GAMMA = +485.0000 DYNES/CM

 PNTR WEIGHT = +74.1900 G
 INITIAL PRESSURE = +0.9158 PSIA

 PNTR+SAMPLE WEIGHT = +78.1900 G
 PDRE DIAMETER = +193.0350 MICRO-M

 PNTR+SAMPLE+MERCURY = +130.4800 G
 MERCURY DENSITY = +13.5335 G/CC

 PNTR VOLUME = +5.5410 CC
 PORE DIAMETER = +13.5335 G/CC

INTRUSION (PRESSUPIZATION) DATA SUMMARY

TOTAL INTRUSION VOLUME = +0.0493 CC/G TOTAL PORE AREA = +0.5474 SQ-M/G MEDIAN PORE DIAMETER (VOLUME) = +1.7166 MICROMETERS MEDIAN PORE DIAMETER (AREA) -+0.0834 MICROMETERS AVERAGE POPE DIAMETER (47/A) = --+0.3603 MICROMETERS BULK DENSITY = +2.3848 6/00 APPARENT (SKELETAL) DENSITY = +2.7027 6/00

% CAPILLARY = +51.3645

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HITEMP-SORBENT MISSISSIPPI LIMESTONE: 16/18 MESH UNCALCINED PNTR NUMBER +381

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LP	1	1:	1:	11	8/1	6/85
HP	1	:	18	::58	8/	16/85

PRESSURE	POPE	INTRUSION	PORE	MEAN	
PSIA	DIAMETER	VOLUME	SURFACE	DIAMETER	DV
	MICRO-M	CC/G	SQ-M/G	MICRO-M	
+5.0	+35.4843	+0.0086	+0.0003	+114.2590	+0.0086
+10.0	+17.7422	+0.0116	+0.0008	+26.6132	+0.0030
+14.6	+12.0707	+0.0132	+0.0012	+14.9064	+0.0016
+19.9	+8.8711	+0.0144	+0.0016	+10.4709	+0.0011
+38.6	+4.5786	+0.0156	+0.0023	+6.7248	+0.0012
+58.5	+3.0237	+0.0179	+0.0048	+3.8012	+Ú.ÚÚč4
+79.3	+2.2301	+0.0212	+0.0099	+2.6269 ,	+0.0033
+100.7	+1.7549	+0.0243	+0.0161	+1.9925	+0.0031
+118.4	+1.4932	+0.0265	+0.0214	+1.6240	+0.0022
+148.6	+1.1898	+0.0294	+0.0299	+1.3415	+0.0028
+200.5	+0.8817	+0.0335	+0.0460	+1.0358	+0.0042
+249.1	+0.7097	+0.0356	+0.0566	+0.7957	+0.0021
+303.8	+0.5819	+0.0364	+0.0612	+0.6458	+0.0007
+351.6	+0.5027	+0.0370	+0.0661	+0.5423	+0.0007
+404.4	+0.4371	+0.0376	+0.0712	+0.4699	+0.0006
+454.2	+0.3892	+0.0382	+0.0764	+0.4132	+0.0005
+506.0	+0.3494	+0.0387	+0.0822	+0.3693	+0.0005
+599.8	+0.2947	+0.0395	+0.0921	+0.3221	+0.0008
+702.3	+0.2517	+0.0402 .	+0.1030	+0.2732	+0.0007
+802.0	+0.2204	+0.0408	+0.1132	+0.2361	+0.UUU6
+902.6	+0.1959	+0.0415	+0.1261	+0.2081	+0.0007
+997.3	+0.1772	+0.0420	+0.1362	+0.1866	+0.0005
+1110.6	+0.1592	+0.0425	+0.1491	+0.1682	+0.0005
+1204.4	+0.1468	+0.0429	+0.1596	+0.1530	+0.0004
+1312.8	*0.1347	+0.0434	+0.1731	+0.1407	+0.0005
+1406.6	+0.1257	+0.0437	+0.1835	+0.1302	+0.0003
+1495.5	+0.1182	+0.0441	+0.1967	+0.1219	+0.0004
+1609.8	+0.1098	+0.0445	+0.2086	+0.1140	+0.0003
+1699.6	+0.1040	+0.0448	+0.2212	+0.1069	+0.0003
*1805.1	+0.0979	+0,0452	+0.2346	+0.1010	+0.0002
+1997.6	+0.0885	+0.0457	+0.2578	+0.0932	40.0005
+2200.7	÷0.0502	+0.0463	+0.2834	+0.0844 .0844	+0.0001
+2397.1	+0.0737	+0.0467	+0.3046	+0.0770	▼0.00 04 ★0.0004
+2598.9	+0.0680	+0.0470	+0.3237	↓0.0707	+0.0000 +0.0000
+2786.0	+0.0634	+0.0473	+0.3403	40.0007 +0.0410	₩0.0 002
+2987.0	+0.0592	+0.0475	+0.33554	+0.0513	+0.0000; +0.0000;
+3199.3	+0.0553	+0.0478	+0.3775	+0.0572 +0.0524	÷0.000. ≜0.000.
+3400.8	+0.0520	+0.0480	+0.3880	+0.0335 +0.0504	+0.000. +0.000.
+3584.5	+0.0493	+0.0482	+0.4042		+0,000 +0.007
+3814.9	+0.0463	+0.0483	+0.4160	+0.0450	+0.000 +0.000
+3683.8	+0.0443	+0.0484	+U.4686		• • • • • • • • • • • • • • • • • • •
+4500.4	+0.0393	+0.0487	+0.4488	TU.UHIO 1072	+0.000
+5022.0	+0.0352	+0.0489	+0.4/1/	TU.U3/4 10 0004	+0.000
+5513.8	+0.0321	+0.0490	₹U.4888 .0.4888	TU.UJUD 10.0207	+8.000
+6020.4	+0.0294	+0.0490	◆り。4岁りご 、ひ ■ひすひ	▼U,U307 ⊥A ADOD	♦ 0.000
+6512.2	+0.0271	+0.0491	+0.3010 ×∴ =+>=	TU.UECO IA 0541	♦0.000
+7033.8	+0.0251	+0.0492	TU.3120	てい。いたです よう うちょう	-0.00C
+7540.4	+0.0234	+0.0492	+0.5139	+0.0243	▼ ♥• ♥♥€

HITEMP-SORBENT MISSISSIPPI LIMESTONE: 16/18 MESH UNCALCINED PNTP NUMBER +381

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LP	11	: 1	:1	1	8/1	6/85
HP	11	: 1	8:	58	8/	16/0

: PPESSUPE	PORE	INTRUSION	PORE	MEAN	DV
PIIA	DIAMETER	VOLUME	SURFALE	MICPR-M	-
	MICRO-M	CC/G	20-410	HICKU-H	
			-0 5151	+0.0228	+0.0000
+8002.4	+0.0221	+0.0492	+0.5151	+0.0209	+0.0000
+8956.1	+0.0197	+0.0492	+0.5174	+0 0187	+0.0000
+9984.4	+0.0177	+0.0492	+0.0177	+0.0169	+0.0000
A10953.0	+0.0161	+0.0492	+0.0218	+0.0154	40.0000
+11996.2	+0.0147	+0.0492	+0.5238		+0.0001
110044 8	+0.0136	+0.0493	+0.5442	+0.0142	±0.0000
+12240 3	+0.0127	+0.0493	+0.5442	+0.0132	▲0.00000
+107+0.0 .14046 9.	+0.0118	+0.0493	+0.5475	+0.0123	A0 0000
-14740.0°	+0.0111	+0.0493	+0.5475	+0.0115	+0.0000
+10700.1	+0.0103	+0.0493	+0.5475	+0.0107	40.00 0
+1/072./	→ 0.0097	+0.0493	+0.5475	+0.0100	+0.0000
+18150.7	+0.0092	+0.0493	+0.5475	+0.0095	+0.0000
+19164,1	₹0.0076 .a acaa	+0.0493	+0.5475	+0.0091	+0.0000
+19909.5	₩0.0087 .0.0071	10 0493	+0.5475	+0.0030	+0.0000
+24961.0	◆0,0071 	±0.0493	+0.5475	+0.0065	+0.0000
+20023	+0.00⊃≓	+0.0492	+0.5475	+0.0055	÷0.0000
+35273.2	+0.0050	0.0470 	±0 5475	+0.0047	+0.0000
+40354.8	+0.0044	+0.0470	±0.0410	+0.0041	+0.0000
+45242.7	+0.0039	+0.0493	-0.5475	+0.0037	+0.0000
+50175.2	+0.0035	+0.0493	+0.0470 +0.5475	+0.0034	+0.0000
+54943.9	+0.00321	+0.0493	♥U.0♥(0 	±0.0007	+0,0000
+59831.8	+ 0.0030	+0.0493	, +U.⊃4/⊃	TO OVER	

HITEMP-SOPBENT LP 11:1:11 8/16/85 MISSISSIPPI LIMESTONE: 16/18 MESH UNCALCINED HP 11:18:58 8/16/85 PNTR NUMBER +381

> CUMULATIVE PORE VOLUME (CC/6) VS. PORE DIAMETER 100% = +0.0493



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(1997) 1997 - 1997 1997 - 1997	ITEMP-IOFBEN ISSISIIPPI L	IT .IMEITONE: 10 +381	5/18 MES	H UNCALCINE)	Ei	LF 11: HF 11:	1:11 8/10 18:58 8/	6/85 16/85
		CUMULATIVE	SUPFACE		VS. PORE	DIAMETER	· .	
				100% =	+0.5474			
	0% I	20%		40%	60% I	80 [:] 1	: 	100% 1
	+300 - +	•				•		
	+184-+							·
2	+144-+	·			·			. •
9	+88.1-+							
	+69.0-◆							
	+42.3-+							
ļ. Š	+33.1-+							
N.	+20.3-+							
	+15.9-+ +12 4-+							
2 2 2	+9.72-+							
	+7.61-* -							
	+4.6+	. •						
	+3.65-◆ +2.86-◆	•						
, F	+2.24-+							•
	+1.75- + +1.37- +				-			
	+1.07-	•						
	+0.657-	 ✓ ♦ 						
	+0.514-	 ▲ 						
	+0.402= +0.315=	•						
	+0.247- 、	•					•	•
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	·0.0567- ·0.0444-				•	•	·	
	0.0347-						•	•
	0.0272-						•	● ⁻
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3 +0	00799-		•					•
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	.00300-							•

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HITEMP-SOPBENT LP 11:1:11 8/16/85 MISSISSIPPI LIMESTONE: 16/18 MESH UNCALCINED HP 11:18:58 8/16/85 PNTR NUMBER +381

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PAGE 6.

DIFFEPENTIAL VOLUME (CC/G-MICRO-M) VS. PORE DIAMETER 100% = +0.839070E-002

0% T	20%	40%	60%	80%	10
+300-+++++	• • • • • • • • • • • • • • • • • • •		• • • • • • • • • • • • • • • •	• • • • • • • • • • • • • • •	• • • • • • • • • •
+235-+++++	***********	*******			
+184-+++++	*************	**********	*****		
+144-+++++	*************	•••••	**********		
+113-+++++	*************	•••••	*********	****** ,	
+88.1-+++++	• • • • • • • • • • • • • • • • • • •	• • • • • • • • • • • • • • • • • • •	***************	*********	
+ <u>-</u> , <u> </u> -++++++++++++++++++++++++++++++++++++	• • • • • • • • • • • • • • • • • • •	•••••	••••••••••••••	••••••••••••	••••
+34,0+++++++ +42,3+++++++		•••••	************		
+33.1-+++++	***********	***********	*********	********	••••
+25.9-*****	************	•••••	•••••		
+20.3-*****	•••••	•••••			
+15.9-****	*****	•			
+12.4-+++++	******				
+9.72-+++++	*****				
+/.51-******	· • • • •				
+1.55-++++++	****		•		
+3.65-*****	*******				
+2.86-*****	••••••	•			
+2.24-*****	•••••	*****			- •
+1.75-++++	************	*****			
+1.37======	************				
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+0.657-+++++	· • • • • • • •	•••••			
+0.514-+++++	•			•	
+0.402-++++					
+0.315-*****	•				
+0.247-++++++					
+0.193-+++++					
↓ 0.118- ↓ ♦					
+0.0926-+++					
+0.0725-+++					
+0.0567-++					
+0.0444-+					
+0.0347-++					
+V.UZ/Z=+					
+0.0210-+ +0.0167-+					
+0.0130-+					-
+0.0102-+					
+0.00799-+					
+0.00626-+					
+0.00490-+					
≠V.UU383-◆ ★A_AA2				,	
★0°00000+ ▲		·.		· ·	

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HITEMP-SOPBENT MISSISSIPPI LIMESTONE; 16/18 MESH UNCALCINED PNTP NUMBER +381 LP 11:1:11 8/16/85 HP 11:18:58 8/16/85

DIFFERENTIAL SURFACE AREA (M2/G-MICRO-M) VS. DIAMETER 100% = +0.220400E-00110 40% 60% 80% 0% 20% _ T . . 1 . - - I - . I.. +300-+ +235-+ +184-+ +144-+ +113-+ +88.1-+ +69.0-+ +54.0-+ +42.3-+ +33.1-+ +25.9-+ +20.3-+ +15.9-+ +12.4-+ +9.72-+ +7.61-++ +5.96-++ +4.65-** +3.65-++++ +2.86-******** +2,24-************* +1.75-*************** +1.37-*********** +1.07-********** +0.839-***************************** ********** +0.657-----+0.514-************* +0,402-************* +0.315-----+0.247-********** +0.193-++++++ +0.151-++++++ +0.118-***************** +0.0926-************ +0.0725-********************** +0.0213-++++ +0.0167-++++++ +0.0130-----+0.0102-+ +0.00799-+ +0.00626-+ +0.00490-+ +0.00383++ +0.00300-+

PAGE 1

HITEMP-SOPBENT LP 11:25:48 8/15/85 GREER LIMESTONE: 16/18 MESH UNCALCINED HP 11:59:34 8/15/85 PNTR NUMBER +382 PNTR CONSTANT = +15.0000 SEC LP EQUILIBRATION = +10.7900 MICRD-L/ HP EQUILIBRATION = +10.0000 SEC THETA = +130.0000 SAMPLE WEIGHT = +4.0100 6 GAMMA = +485.0000 DYNES/CM +77.2000 G PNTR WEIGHT = INITIAL PRESSURE = +0.9524 PSIA PNTR+SAMPLE WEIGHT = +81.2100 6 PORE DIAMETER = +185.6100 MICRD-M PNTR+SAMPLE+MERCUPY = +105.3300 6 MERCURY DENSITY = +13.5335 6/00

INTRUSION (PRESSURIZATION) DATA SUMMARY

PNTR VOLUME =

TOTAL INTRUSION VOLUME	Ŧ	+0.0348	CC/G
TOTAL PORE AREA	=	+0.4693	SQ-M/G
MEDIAN POPE DIAMETER (VOLUME)	=	+2.5948	MICROMETERS
MEDIAN PORE DIAMETER (AREA)	=	+0.0285	MICROMETERS
AVERAGE PORE DIAMETER (4V/A)	=	+0.2967	MICROMETERS
BULK DENSITY	=	+2.4605	6700
APPARENT (SKELETAL) DENSITY	=	+2.6910	6700

+3.4120 CC

% CAPILLARY = +36.3562

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HITEMP-SOPSENT GREER LIMESTONE: 16/18 MESH UNCALCINED PNTR NUMBER +382

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LP 11:25:48 8/15/85 HP 11:59:34 8/15/80

PRESSURE	PORF	INTRUSION	PORE	MEAN	
PSTA	NIAMETER	VOLUME	SURFACE	DIAMETER	DV
r 04m	MICRO-M	CC/G	SQ-M-G	MICRD-M	
+5. Ó	+35.6416	+0.0116	+0.0004	+110.6260	+0.0116
+9.9	+17.7683	+0.0141	+0.0008	+26.7049	+0.0025
+14.6	+12.0888	+0.0151	+0.0011	+14.9286	+0.UU1U
+19.9	+8.8678	+0.0158	+0.0014	+10.4783	+0.0008
+39.3	+4.4934	+0.0164	+0.0017	+6.6806	+0.0006
+58.5	+3.0199	+0.0171	+0.0024	+3.7566	+0.0007
+79.8	+2.2157	+0.0177	+0.0034	+2.6178	+0.0007
+99.6	+1.7742	+0.0183	+0.0046	+1.9950	+0.000
+119.6	+1.4776	+0.0190	+0.0062	+1.6259	+0.0007
+150.2	+1.1770	+0.0204	+0.0106	+1.3273	+0.0015
+201.2	+0.8786	+0.0255	+0.0303	+1.0278	+0.0051
+252.0	+0.7014	+0.0279	+0.0423	+0.7900	+0.0024
+303.8	+0.5819	+0.0285	+0.0465	+0.6417	+0.0007
+350.7	+0.5041	+0.0290	+0.0499	+0.5430	+0.0005
+401.5	+0.4403	+0.0294	+0.0533	+0.4722	+0.0004
+454.2	+0.3892	+0.0297	+0.0566	+0.4147	+0.0003
+498.2	+0.3548	+0.0299	+0.0588	+0.3720	+0.0002
+600.7	+0.2943	+0.0304	+0.0546	+0.3246	+0.0005
+701.3	+0.2520	+0.0307	+0.0587	+11.2132	+0.0003
+800.0	+0.2210	+0.0310	+0.0733	+0.2360	+0.0003
+897.7	+0.1969	+0.0312	+0.0773	+0.2089	₩0.0002
+997.3	+0.1772	+0.0313	+0.0804	+0.1871	₩0.0001
+1094.0	+0.1616	+0.0315	+U.U233	+ V. 1 8 7 4 . 0 . 1 5 4 0	+0.0001
+1202.4	- +0.1470	+U.U315 .0.0717	+0.0873 .0 0873	₩0.10₩3 ₩0.1043	+0.0001
+1301.1	+0.1339	+0.0317	70.0714 .0.0007		+0.0001
+1400.7 ••■•⊐	TU.1252	★0.0310 ★0.0310	±0.0727 ±0.0527		+0.0001 +0.0001
₹1007.2 	+V.1173 +0.1103	モリ。ひつこり また かつこう	+0.0704 ★0 1010	-0.121) -0.1127	+0.0001 +0.0001
エキロソジ・ア			+0.1010	+0.1120 +0.1070	+ů. ÚÚÚI
▼1709.0 ★1000 0		TO.OGEI 10.0000	-0.1097 -0.1097	+0.1009	+0.0001
-1002.C	-0.0701 -0.0000	+0.0323 +0.0323	+0.1127	+0.0935	+0.0001
TI707+1 A0100 0	-0,0000 -0.0000	40.00CC 40.00224	+0.1164	+0.0848	+0.0001
TE107.0	+0.0729	+0.0324 +0.0324	+0.1239	+0.0773	+0.0001
	+0.0675	+0.0326	+0.1246	+0.0707	+0.0000
+2797.1	+0.0632	+0.0326	+0.1293	+0.0653	+0.0001
+2991.7	+0.0591	+0.0327	+0.1342	+0.0611	+0.0001
+3185.3	+0.0555	+0.0328	+0.1394	+0.0573	+0.0001
+3396.0	+0.0521	+0.0329	+0.1450	+0.0538	+0.0001
+3582.8	+0.0493	+0.0329	+0.1457	+0.0507	+0.0000
+3814.9	+0.0463	+0.0330	+0.1519	+0.0478	+0.0001
+3993.8	+0.0443	+0.0330	+0.1525	+0.0453	+0.0000
+4485.5	+0.0394	+0.0331	+0.1666	+0.0418	+0.0001
+4992.2	+0.0354	+0.0333	+0.1823	+0.0374	+0.0001
+5498.9	+0.0321	+0.0334	+0.1994	+0.0338	+0.0001
+6005.5	+0.0294	+0.0336	+0.2265	+0.0308	+0.0002
+6497.3	+0.0272	+0.0337	+0.2464	+0.0283	+Ŭ.ŬUŬ1
+7004.0	+0.0252	+0.0340	+0.2779	+0.0262	+0.0002
+7495.7	+0.0236	+0.0340	+0.2900	+0.0244	+0.0001

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HITEMP-SORBENT GREER LIMESTONE: 16/18 MESH UNCALCINED ENTR NUMBER +382

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LP 11:25:48 8/15/85 HP 11:59:34 8/15/85

PRESSURE	POPE	INTRUSION	PORE	MEAN	
PSIA	DIAMETER	VOLUME	SURFACE	DIAMETER	DV
	MICRO-M	CC/G	SQ-M/G	MICRD-M	
+8002.4	+0.0221	+0.0342	+0.3143	+0.0228	+Ŭ.ÛŬŬ1
+9015.8	+0.0196	+0.0344	+0.3545	+0.0208	+0.0002
+10014.2	+0.0177	+0.0345	+0.3850	+0.0186	+0.0001
+10953.0	+0.0161	+0.0346	+0.4025	+0.0169	+0.0001
+11981.3	+0.0148	+0.0347	+0.4216	+0.0154	+0.0001
+12964.8	+0.0136	+0.0347	+0.4234	+0.0142	+0.0000
+13978.1	+0.0126	+0.0347	+0.4251	≠0.0131	+0.0000
+14931.9	+0.0118	+0.0348	+0.4695	+0.0122	+0.ÚÚÚ1
+15915.4	+0.0111	+0.0348	+0.4695	+0.0115	+0.0000
+17062.9	+0.0104	+0.0348	+0.4695	+0.0107	+0.0000
+18135.8	+0.0097	+0.0348	+0.4695	+0.0101	+0.0000
+19134.2	+0.0092	+0.0348	+0.4695	+0.0095	+0.0000
+20102.9	+0.0088	+0.0348	+0.4695	+0.0090	+0.0000
+24901.4	+0.0071	+0.0348	+0.4695	+0.0079	+0.0000
+29878.6	+0.0059	+0.0348	+0.4695	+0.0065	+0.0000
+34960.3	+0.0051	+0.0348	+0.4695	+0.0055	+0.0000
+40161.1	+0.0044	+0.0348	+0.4695	+0.0047	+0.0000
+45078.8	+0.0039	+0.0348	+0.4695	+0.0042	+0.0000
+49966.6	+0.0035	+0.0348	+0.4695	+0.0037	+0.0000
+54780.0	+0.0032	+0.0348	+0.4695	+0.0034	+0.0000
+59712.6	+0,0030	+0.0348	+0.4695	+0.0031	+0.0000

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HITEMP-SORBENT GREEP LIMESTONE; 16/18 MESH UNCALCINED PNTR NUMBER +382

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LP 11:25:48 8/15/85 HP 11:59:34 8/15/85

CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER 1 100% = +0.0348 0% 20% 40% 60% 80% 100 . 1 Ι. I. . T. .1. . I . +300-+235-+184-+144= +113-+88.1-+69.0-+54.0-+42.3-+33.1-+25.9-+20:3-+15.9-+12.4-+9.72-+7.61-+5.96-+4.66-+3.65-+2.86-+2.24-+1.75-+1.37-+1.07-+0.839-+0.657-+0.514-+0.402-+0.315-+0.247-+0.193-+0.151-+0.118 -+0.0926-+0.0725-+0.0567= +0.0444-+0.0347-+0.0272-+0.0213-+0.0167-+0.0130-+0.0102-+0.00799-+0.00626-+0.00490-+0.00383+ +0.00300HITEMP-SOPPENT -GREER LIMESTONE: 16/18 MESH UNCALCINED PNTR NUMBER +382 LP 11:25:48 8/15/85 HP 11:59:34 8/15/85

CUMULATIVE SURFACE AREA (M2/G) VS. PORE DIAMETER 100% = +0.4693

0%	20%	40%	60%	80%	10
 +300-+		•••••	• • • • • • • • • • • • • • • •		* * * * * * * *
+235-+					
+184-+					
+144-+					
+113-+					
+88.1-+					
+69.0-+					
+54.0~●					•
+42.3-+					
+33.1-+					
+25.9-+					
+20.3-+					
+15.9-+					
+12.4-+					
+9.72-+					
+7.61-+					
+5.96-+					
+4.66-+					
+3.65-+					
+2.86-+					•
+2.24-+	·				
+1.75++				×	
+1.37-+					
+1.07- +					
+0.839- •					
+0.657-	•				
+0.514-	•				
+0.402-	•				
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+0.0444-		•			
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+0.0272-			•		
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+0.0167-				•	
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+0.00799-				•	,
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HITEMP-SOPEENT

PNTR NUMBER +382

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LP 11:25:48 8/15/85 GREER LIMESTONE: 16/18 MESH UNCALCINED HP 11:59:34 8/15/85

DIFFERENTIAL VOLUME (CC/G-MICRO-M) VS. PORE DIAMETER 100% = +0.113364E-001

	0%	20%	40%	60%	80%	1000
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+30	()-++++++ ++ ~	*******				
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+18	4-******	************	•••••	****		
+14	4-******	************	•••••	***********		
+11	3-*******	***********	*********	***********	******	
+88.	1-******	************	************	**********	*********	•
+69.	Ŋ -++ ++++++	***** ~ ******	> ********** *****	***********	••••	***
+54.	()- ***** ***	************	*************	***********	**********	*****
+42.	3-*******	• • • • • • • • • • • • • • • • • •	} • • • • • • • • • • • • • • • • • • •	***********	**********	********
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+0.839		• • • • • • • • • • • • • • • •	******			•
+0.657	· ?~*******	***				
+0.514	4-***		,			
+0.408	2-++					
+0.315	5-++					
+0.24	7-++					
+0.190	-•		·			
+0.15	1-+					
+0.118	3-+		•			
+0.092	5- •					•
+0.072	5					
+0.0567	7 ~ +					
+0.0444	4-+					
+0.034						
+0.0278	2- •					
+0.0213	3-•					
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HITEMP-SORBENT GREER LIMESTONE: 16/18 MESH UNCALCINED PNTR NUMBER +382

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LP 11:25:48 8/15/85 HP 11:59:34 8/15/85

DIFFERENTIAL SURFACE AREA (M2/G-MICRD-M) VS. DIAMETER 100% = +0.294610E-001

	0%	20%	40%	60%	80%	10
	+200-+					
	+235-+					
	+184-+					
	+144-+					
	+113-+					
4	+88.1-+					
-	₩£9.0-+					
-	▶54.0-◆					•
4	+42.3-+			•		
•	F33.1-●					
	► 2 0.9~~ • 20.9~•					
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	•7.61 - •					
	►5.96- ●		· ·			• •
	t4.66-+					
-	-3.65-+					
	►2.86- + +					
4	+2.24-++					
	+1,75-+++					
4	+1.37-+++++					
4	+1.07-++++++	•••••	***			
+1	0.839-******	•••••	***********	******		
+	0.657-******	***********	••			
+	1.514-******	•				
+	║╻ ५ ╢╱─ ०००००० ० २१८-००००००	◆ ▲ ▲ ▲ ▲				
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+	0.151-++++++	••				
+	û.118 - ◆◆◆◆◆◆◆	***				
+0	.0926-******	***	,			
+0.	0725-******	++++++				•
+0.	.0567-++++++	*****				
+0.	.0444-++					
+0.	.0347-******	***********	************	**0		
+Q,	.0272-*******	***********	************	********		
+0,	.0213-++++++	***********	******	*****	**********	*******
+Ŭ.	.0167-******	***********	***********	*****	***	
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 HITEMP-SDREENT
 LP 11:25:48 8/15/85

 FLUM RUN DOLOMITE (GF< LEDGE); 16/18 MESH UNC
 HP 13:14:19 8/15/85

 FNTR NUMBER +383
 LP EQUILIBRATION = +15.0000 SEC
 PNTR CONSTANT = +10.7900 MICRO-L/F

+10.0000 SEC HP EQUILIBRATION = THETA = +130.0000 SAMPLE WEIGHT = +4.0100 G +485.0000 DYNES/CM GAMMA = PHTR WEIGHT = +75.9400 G INITIAL PRESSURE = +0.9524 PSIA +79.9500 6 PNTP+SAMPLE WEIGHT = PORE DIAMETER = +185.6100 MICRO-M +111.1600 G PNTR+SAMPLE+MEPCUPY = MERCURY DENSITY = . +13.5335 6/00 PNTR VOLUME = +3.8550 CC

INTRUSION (PRESSUPIZATION) DATA SUMMARY

TOTAL INTRUSION VOLUME = +0.0425 CC/G TOTAL POPE AFEA = +0.4300 S0-M/G MEDIAN POPE DIAMETER (VOLUME) = +14.4043 MICROMETERS MEDIAN POPE DIAMETER (APEA) = +0.0408 MICROMETERS AVERAGE POPE DIAMETER (4V/A) = +0.3958 MICROMETERS BULK DENSITY = +2.5890 G/CC APPAPENT (SKELETAL) DENSITY = +2.9095 G/CC

% CAFILLARY = +44.4326

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HITEMP-SOPBENT PLUM PUN DOLOMITE (GF< LEDGE); 16/18 MESH UNC PNTR NUMBER +383

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LP	11:25:48	8/15/85
HP	13:14:19	8/15/85

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PRESSURE	PORE	INTRUSION	PORE	MEAN	
PSIA	DIAMETER	VOLUME	SURFACE	DIAMETER	DY
	MICRO-M	CC/6	SQ-M/6	MICRO-M	
+5.0	+35.6416	+0.0172	+0.0006	+110.6260	+0.0172
+9.9	+17.7683	+0.0199	+0.0010	+26.7049	+0.0028
+14.6	+12.0888	+0.0222	+0.0017	+14.9286	+0.0023
+19.9	+8.8678	+0.0241	+0.0024	+10.4783	+0.0019
+40.0	+4.4193	+0.0256	+0.0033	+6.6436	+0.0015
+59.0	+2.9937	+0.0276	+0.0054	+3.7065	+0.0020
+79.0	+2.2383	+0.0290	+0.0075	+2.6160 /	+0.0014
+99.9	+1.7703	+0.0299	+0.0094	*2.0043	+0.0009
+121.3	+1.4571	+0.0306	+0.0112	+1.6137	+0.0007
+150.3	+1.1765	+0.0316	+0.0140	+1.3168	+0.0009
+200.3	+Ú.8826	+0.0335	+0.0217	+1.0295	+0.0020
+248.1	+0.7125	+0.0348	+0.0280	+0.7975	+0.0013
+303.8	+0.5819	+0.0353	+0.0313	+Ŭ.6472	+0.0005
+350.6	+0.4999	+0.0357	+0.0343	+0.5409	+0.0004
+398.5	+0.4436	+0.0361	+0.0371	+0.4717	+0.0003
+449.3	+0.3934	+0.0363	+0.0397	+0.4185	+0.0003
+498.2	+0.3548	+0.0366	+0.0426	+0.3741	+0.0003
+601.7	+0.2938	+0.0371	+0.0484	+0.3243	+0.0005
+699.4	+0.2528	+0.0375	+0.0544	+0.2733	+0.0004
+798.0	+0.2215	+0.0378	+0.0602	+0.2371	+0.0003
+900.6	+0.1963	+0.0381	+0.0654	+0.2089	+0.0003
+996.3	+0.1774	+0.0384	+0.0713	+0.1869	+0.0003
+1107.7	+0.1596	+0.0386	+0.0763	+0.1685	+0.0002
+1207.3	+0.1464	+0.0388	+0.0817	+0.1530	+0.0002
+1309.9	+0.1350	+0.0389	+0.0857	+0.1407	+0.0001
+1402.7	+0.1260	+0.0391	+0.0920	+0.1305	+0.0002
+1500.4	+0.1178	+0.0392	+0.0945	+0.1219	+0.0001
+1599.0	+0.1105	+0.0394	+0.1017	+0.1142	+0.0002
+1698.7	+0.1041	+0.0395	+0.1044	+0.1073	+0.0001
+1793.4	+0.0986	+0.0396	+0.1099	+0.1013	+0.0001
+1995.6	+0.0886	+0.0398	+0.1190	+0.0730	+U.UUU2
+2184.0	◆0°08 08	+0.0401	+0.1287	40.054/ .0.0774	
+2383	+0.0740	+0.0403	+0.1378	₹₩.₩ 77 9	
+2013.7	TU.U5/5	+0.0403	+U.144C		+0.0001
+2/9/.0	TU. UD32	+0.0400	+0.1327	+0.0634	+0.0001
+2989.2	+0.0591	+0.0406	+U.1521	TU.UOIE	+0.0001
+3198.6	+U.U0733	+0.0408	+0.1720	+0.0572	+0.0001
+3386.8	+0.0522	+0.0409	TU.1067		+0.0001 +0.0001
+3394.6	+0.04%2	+0.0410	+U.1883		+0.0001
+3829.8	+0.0462	+0.0411	40.1740		+0.0001
43773.X	TU.U443	TU.U411	TU. 2007	₩U. UNJE	40 00014 40 00014
********	₹U.U394	+0.0413	TU.6619		
	♥U.U3D4	+ U.Ų 4 16	TU. 299 U 10 3833		
T 3484.U	₹V.V322	+U.U416	TU. 2000	→0.0330 ▲0.000	♦0.0001
マンアプリ・ひ	エリ・リビアン	TU. 0418	TU. 2003	マロ・レンマス	+0_0001
TODIC.C	TU.UE(1 10.0553	TU.U417	TV.6711		+0.0001
▼7004.0 ▲7840 -	TU.UEDE 10.0305	TU.U421	-U.JIEJ		+0.0000
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PAGE 3

HITEMP-SOFBENT

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PLUM PUN DOLOMITE (GF< LEDGE); 16/18 MESH UNC PNTP NUMBER +383

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LP 11:25:48 8/15/85 HP 13:14:19 8/15/81

PRESSURE	POFE	INTRUSION	PORE	MEAN	•
PSIA	DIAMETER	VOLUME	SURFACE	DIAMETER	DV
	MICRO-M	CC/G	SQ-M/G	MICRO-M	
+8002.4	+0.0221	+0.0421	+0.3266	+0.0228	+0.0001
+9000.8	+0.0196	+0.0423	+0.3542	+0.0209	+0.0001
+9999 3	+0.0177	+0.0423	+0.3565	+0.0187	+0.0000
+10982.8	+0.0161	+0.0424	+0.3741	+0.0169	+0.0001
+11981.3	+0.0148	+0.0424	+0.3761	+0.0154	+0.0000
+12949.9	+0.0137	+0.0424	+0.3963	+0.0142	+0.0001
+13963.2	+0.0127	+0.0425	+0.4180	+0.0132	+0.0001
+14961.7	+0.0118	+0.0425	+0.4180	+0.0122	+0.0000
+15960.1	+0.0111	+0.0425	+0.4212	+0.0114 '	+0.000
+17048.0	+0.0104	+0.0425	+0.4227	+0.0107	+0.00
+18076.2	+0.0098	+0.0425	+0.4240	+0.0101	+0.04
+19059.7	+0.0093	+0.0425	+0.4251	+0.0095	+Ŭ.Ŭ(D)
+20073.1	+0.0088	+0.0425	+0.4262	+0.0090	+0.0000
+24871.5	+0.0071	+0.0425	+0.4303	+0.0080	+0.0000
+29968.1	+0.0059	+0.0425	+0.4303	+0.0065	+0.0000
+35079.5	+0.0050	+0.0425	+0.4303	+0.0055	+0.0000
+39892.8	+0.0044	+0.0425	+0.4303	+0.0047	+0.0000
+44825.4	+0.0039	+0.0425	+0.4303	+0.0042	+0.0000
+49936.8	+0.0035	+0.0425	+0.4303	+0.0037	+0.0000
+54884.3	+0.0032	+0.0425	+0.4303	+0.0034	+0.0000
+59787.1	+0.0030	+0.0425	+0.4303	+0.0031	+0.0000

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HITEMP-SOPBENT LP 11:25:48 8/15/85 PLUM PUN DOLOMITE (GF< LEDGE); 16/18 MESH UNC HP 13:14:19 8/15/85 PNTR NUMBER +383

> CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER 100% = +0.0425



PRGE 4

HITEMP-SOPBENT PLUM RUN DOLOMITE (GF< LEDGE); 16/18 MESH UNC PNTP NUMBER +383

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, , CUMULATIVE SURFACE AREA (M2/6) VS. PORE DIAMETER 100% = +0.4300

. 0:	*	20%	40% T	60%	80%	100
+300 - +	• • • • • • • • • • •		• • • • • • • • • • •	• • • • • • • • • • • • • • •		
+235-+						
+184-+						
+144-+	•					
+113-+					•	
+88.1-+					· · ·	
÷69.0-∳					•	
+54.0-+						
+42.3-+						
···+33.1-+						•
+25.9-+					•	
+20.3-+		•				
+15.9-+						
+12.4-+						
+9.72-+	ι.					
+7.61-+						
+5,95-+						
+4.66-+						
+3.654+						•
+2.86-+						
+2.24-+	·					
+1.75-+						
+1.3/- ●	•					
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+0.010- +1.247-	•				-	
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+0.112-		•				
+0.0926-		•			•	
+0.0725-		•				
+0.0567-		•	•			
+0.0444-			· •			
+0.0347-		•		•		
+0.0272-				•		
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+0.0167-					٠	
+0.0130-						٠
+0.0102-						•
+0.00799-						•
+0.00626-						•
+0.00490-						•
+0.00383-	•				ب	•
+0.00300-					·	•

PAGE 5

LP 11:25:48 8/15/85 HP 13:14:19 8/15/85

A-45

HITEMP-SOPBENT PLUM RUN DOLOMITE PNTR NUMBER +383	E (GF< LEDGE); 3	16/18 MESH	UNC	LP 11:25:40 HP 13:14:19	8 8/15/85 9 8/15/85
DIFF	FERENTIAL VOLUME	(CC/G-MICRO 100% = +0.	-M) VS. PORE 168108E-001	DIAMETER	
0%	20%	40%	60%	80%	10
I	. I	I	•••••I		
+300-+++++++	******				4
+235-++++++	*****	*****			
+184-+++++++	•••••	*********	****		
+144-++++++++++++++++++++++++++++++++++	•••••••••	*************	**************************************	•	
	•••••	•••••		•••••	
	· · · · · · · · · · · · · · · · · · ·	•••••	********	· · · · · · · · · · · · · · · · · · ·	
+54. 0-++++++++++++++++++++++++++++++++++++		**********	*********	***********	******
+42.3-++++++	• • • • • • • • • • • • • • • • • •	*********	**********	***********	*******
+33.1-++++++	• • • • • • • • • • • • • • • • • •	• • • • • • • • • • • • • • •	*********	••••••	•••
+25.9-+++++	• • • • • • • • • • • • • • • • • • • •	• • • • • • • • • • • • • • • •	****		•
+20.3-++++++	• • • • • • • • • • • • • • •				
+15.9-******	• • • •				

+7 61-000000	•				
+5.95-00000		• ·			
+4.65-+++++					
+0,65-++++++		÷			
+2.86-+++++	•				
+2.24-+++++					
+1.75-+++					
+1.3/-+++					
+0.229-00000					
+0.657-+++					
+0.514-++					
+0,40 <u>2</u> -+					
+0.315-++					
+0.173-+ +0.151-+					
+0.118-+					
+0.0926-+					
+0.0725-+					
+0.0567-+					
+0.0444-+					
+U.U34/-+					
+0.0167-+					
+0.0130-+					
+0.0102-+					
+0.00799-+					
+0.00626-+					
+0.00490-+ ×0.00000				,	
テリア じしつけい 二字 二					

+0.00383-+ +0.00300-+

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HITEMP-SOPPENT PLUM RUN DOLOMITE (GF< LEDGE); 16/18 MESH UNC PNTR NUMBER +383

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HP 13:14:19 8/15/85

DIFFERENTIAL	SURFACE	AREA	(M2/G-MICRO-M)	VS.	DIAMETER	
		100%	: = +0.211478E-	001		•

	0%	20%	40%		60%	80%	1.00°
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+23	35-+						
+18	34-+						
+14	44- ◆		•			•	
+11	13-+						
+83.	1-+						
+69.	,0-+						
+54.	, 0-•				•		
+42.	3-+						
+33.	1-+						
+25.	4 - •						,
+211.	, ⊰ ~●						
+10.							
+12.	.4						
+9.0	2-++			·			
+			•			•	
+2.3							
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+0.40			•				
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±0,24							
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÷0.10	8-444		••				
+0.092						•	
+0.072	5-+++	•••••		••			
+0.056	57-+++	*********	*********	•••			
+0.044	4-+++	**********	*****	-			
+0.034	7-+++	**********		********	*********	• • • • • • • • • • • • • • • • • • •	**
+0.027		**********		••••			
+0.021	3-+++			********	•••••	••••	
+0.016	7-+++				••	· · ·	
+0.013	{ =♦♦♦٩	**********		********		• • • • • • • • • • • • • • • • • •	******
+0.010	2= ++ +	••					
+0.0079	 i⊊_ ♦ ♦♦♦	****					
+0.0062		•					
+0.0049	i(i ◆						
+0.0038	(j •						
+0.0030	1 <u>1</u> -+			A _ / 7			

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LP 11:25:48 8/15/85

PAGE 1

HITEMP-SOFBENT LP 11:25:48 8/15/85 HP 11:59:34 8/15/85 TYMOCHTEE DOLOMITE: 16/18 MESH UNCALCINED PNTR NUMBER +380 +15.0000 SEC LP EQUILIBRATION = PNTR CONSTANT = +10.7900 MICRO-L/ HP EQUILIBRATION = +10.0000 SEC +130.0000 THETA = SAMPLE WEIGHT = +5.0100 6 GAMMA = +485.0000 DYNES/CM PNTR WEIGHT = +74.1600 6 INITIAL PRESSURE = +0.9524 PSIA PNTR+SAMPLE WEIGHT = PORE DIAMETER = +79.1700 G +185.6100 MICRD-M PNTR+SAMPLE+MERCURY = +127.0000 6 MERCURY DENSITY = +13.5335 6/00 PNTR VOLUME = +5.5410 CC

INTRUSION (PRESSURIZATION) DATA SUMMARY

TOTAL INTRUSION VOLUME	=	+0.0407	ČČ∕G
TOTAL PORE AREA	Ξ	+0.7937	SQ-M/G
MEDIAN PORE DIAMETER (VOLUME)	=	+1.8787	MICROMETERS
MEDIAN PORE DIAMETER (AREA)	=	+0.0320	MICROMETERS
AVERAGE PORE DIAMETER (4V/A)	=	+0.2049	MICROMETERS
BULK DENSITY	=	+2.4965	GZCC
APPARENT (SKELETAL) DENSITY	=	+2.7785	6/00

% CAPILLARY = +53.0477

A-48
HITEMP-SOPEENT TYMDCHTEE DOLOMITE: 16/18 MESH UNCALCINED PNTR NUMBER +380

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LP 11:25:48 8/15/8 HP 11:59:34 8/15/80

PRESSURE	PORE		PORE	MEAN DIAMETER	. DV
, FGAN	MICRO-M	CC/G	SQ-M/G	MICRO-M	-
+5.0	+35.6416	+0.0116	+0.0004	+110,6260	+0.0116
<u>+0</u> 0	+17.7683	+0.0137	+0.0007	+26.7049	+0.0022
414 G	A12 0888	+0.0146	+0.0010	+14,9286	+0.0009
419.9	+8.8678	+0.0161	+0.0015	+10.4783	+0.0015
+39.3	+4,4934	+0.0167	+0.0019	+6.6806	+0.0006
+58.5	+3,0199	+0.0181	+0.0034	+3.7566	+0.0014
+79.8	+2.2157	+0.0195	+0.0055	+2.6178	+0.0014
+99.6	+1.7742	+0.0206	+0.0078	+1.9950	+0.0011
+119.6	+1.4776	+0.0216	+0.0102	+1.6259	+0.0010
+150.2	+1.1770	+0.0229	+0.0140	+1.3273	+0.0013
+201.2	+0.8786	+0.0259	+0.0259	+1.0278	+0.0031
+252.0	+0.7014	+0.0280	+0.0364	+0.7900	+0.0021
+303.8	+0.5819	+0.0287	+0.0410	+0.6417	+Ů.0ÛŬ7
+350.7	+0.5041	+0.0294	+0.0457	+0.5430	+0.0006
+401.5	+0.4403	+0.0299	+0:0506	+0.4722	+0.0006
+454.2	+0.3892	+0:0305	+0.0558	+0.4147	+0.0005
+498.2	+0.3548	+0.0308	+0.0598	+0.3720	+0.0004
+600.7	+0.2943	+0.0316	+0.0697	+0.3246	+0.0008
+701.3	+0.2520	+0:0323	+0.0791	+0.2732	+0.0006
+800.0	+0.2210	+0:0328	+0.0881	+0.2365	+0.0005
+897.7	+0.1969	+0:0333	+0.0964	+0.2089	+0.0004
+997.3	+0.1772	+0:0337	+0.1056	+0.1871	+0.0004
+1094.0	+0.1616	+0.0340	+0.1132	+0.1694	+0.0000
+1202.4	+0.1470	+0;0344	+0.1230	+0.1543	+0.0004
+1301/1	+0.1359	+0:0347	+0/1306	+0.1414	+0.0003
+1400.7	+011265	+0:0349	+0.1389	+0.1310	+0.0003
+1507.2	+0.1173	+0.0352	+0.1473	+0.1217	+0.0003
+1603.9	+0.1102	+0.0354	+0.1554	+0.1137	+0.0002
+1704.5	+0.1037	+0.0356	+0.1616	+0.1070	+0.0002
+1805.2	+0.0381	+0.0358	+0.1702	+0.1009	+0.0002
+1989.7	+0.0888	+0:0361	+0.1841	+0.0935	+0.0003
+5186.0	+0:0808	+0:0365	+0.1996	+0.0848	+0.0003
+2391.2	+0.0739	+0.0367	+0.2137	+0.0773	+0.0003
+2619.3	+0.0675	+0.0369	+0.2262	+0.0707	+0.0002
+2797.1	+0.0632	+0.0372	+0.2395	+0.0653	+0.0002
+2991.7	+0.0591	+0,0374	+0.2538	+0.06II	+0,0002
+3185.3	+0:0555	+0.0375	+0.2654	+0.0573	+0.0002
+3396.0	+0.0521	+0.0378	+0.2816	+0,0538	+0.0002
+3582.8	+0.0493	+0.0379	+0.2945	+0.0507	+0.0002
+3814.9	+0.0463	+0.0380	+0.2995	+0.0478	+0.0001
+3993.8	+0.0443	+0.0382	+0.3139	+0.0453	+0.0002
+4425.5	+0.0394	+0.0384	+0.3403	+0.0418	+0.0003
+4992.2	+0.0354	+0.0387	+0.3697	+0.0374	+0.0003
+5465.6	+0.0321	+0.0385	+0.3959	+0.0338	+0.0002
+6005.5	+0.0294	+0.0391	+0.4244	+0.0308	+0.0002
+6497.3	+0.0272	+0.0393	+0.4478	+U.U233	+0.0002
+7004.0	+0.0252	+0.0394	+0.4649	+0.0252	+0.0001
+7495.7	+0.0236	+0.0396	+0.4918	≠0.0244	+0.0002

PAGE 2

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PAGE 3

HITEMPHSORBENT TYMOCHTEE DOLOMITE: 16/18 MESH UMCALCIMED PMTR NUMBER +380 LP 11:25:48 8/15/85 HP 11:59:34 8/15/85

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PRESSURE	POPE	INTRUSION	PORE	MEAN	
PSIA	DIAMETER	YOLUME	SURFACE	DIAMETER	DV
	MICRO-M	CC/G	SQ=M/6	MICRO-M	
+8002.4	+0.0221	+0:0396	+0.4929	+0.0228	+0.0000
+9015/8	+0.0196	+0.0398	+0.5352	+0.0208	+0:0002
+10014/2	+0:0177	+0:0400	+0.5709	+0.0186	+0:0002
+10953.0	+0.0161	+0.0401	+0.5974	+0.0169	+0:0001
+11981.3	+0.0148	+0.0402	+0.6262	+0.0154	+0.0001
+12964,8	+0:0136	+0:0403	+0.6425	+0.0142	+0:0001
+13978.1	+0:0126	+0:0404	+0.6759	+0.0131	+0.0001
+14931.9	+0/0118	+0:0404	+0.6943	+0,0122	+0:0001
+15915.4	+0.0111	+0.0404	+0.6954	+0:0115	+0:0000
+17062.9	+0:0104	+0:0405	+0.7359	+0:0107	+0:0001
+18135.8	+0:0097	+0.0405	+0.7369	+0:0101	+0.0000
+19134.2	+0:0092	+0.0405	+0.7379	+0.0095	+0.0000
+20102.9	+0.0088	+0:0406	+0.7620	+0.0090	+0.0001
+24901.4	+0.0071	+0:0407	+0.7918	+0.0079	+0:0001
+29878.6	+0.0059	+0:0407	+0.7939	+0.0065	+0.0000
+34960.3	+0:0051	+0,0407	+0.7939	+0.0055	+0:0000
+40161.1	+0.0044	+0:0407	+0.7939	+0.0047	+0.0000
+45078.8	+0.0039	+0:0407	+0.7939	+0.0042	+0.0000
+49966.6	+0.0035	+0.0407	+0.7939	+0.0037	+0.0000
+54780.0	+0:0032	+0:0407	+0.7939	+0,0034	+0:0000
+59712.8	+0.0030	+0:0407	+0,7939	+0.0031	+00000

HITEMP-SORBENT TYMOCHTEE DOLOMITE: 16/18 MESH UNCALCINED PNTR NUMBER +380

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		CUMULI	ATIVE P	ORE VO	LUME (CC 100% =	257 VS +0	. PORE : .0407	DIAMETÉR	2		
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+144	-		●.								
··+113	÷		٠								
+88.1	-		•								
+69.0									•		
+54.0	—			•							
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+0.839	<u> </u>						•			•	
+0.657	÷							•			
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+0:00828-			• •		,						.
►U.UJ499-	-				, .						•
FU.UU383- •A·AA3AA	-										•
+0:00300-	-									•	- -

PAGE 4

- LP 11:25:48 8/15/85

HP 11:59:34 8/15/88

A-51

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HITEMP-SORBENT TYMOCHTEE DOLOMITE: 16/18 MESH UNCALCINED PHTR NUMBER +380

LP 11:25:48 8/15/85 HP 11:59:34 8/15/85

CUMULATIVE SURFACE AREA (M2/G) VS. PORE DIAMETER 100% = +0.7937

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(0%	20%	40%	60%	80%	100
1				•••••••		
+300-4	•					
+235-4	•					
+184-4						
+144-4	•					
+113-4	•					
+88.1-4	Þ.				,	
+69.0-4	•					
+54.0-4	•					•
+42.3-4	•					
+32,1-4	•					
+25.9-4	•					
+20.3-4	•					
+15:9-4	•				•	•
+12.4-4						
+9.72-4	•					
+7.61-4	•					
+5.96-4						
+4.66-4	•					
+3.65-4	•					
+2.86-4	•					
+2.24-4	• *		•			
+1.75-4	•					
+1.37-4	•					
+1.07-	•					
+0.839-	•					
+0.657-	•					
+0.514-	•					
+0.402-	•					
+0.315-	•					
+0.247-	•					
+0.193-	•	,				
+0.151-		•				
+0.118-		•				
+0.0926-		•	•			
+0.0725-		•				
+0.0567-			•			
+0.0444-			•			
+0.0347-			٠	,		-4
+0.0272-				•		
+0.0213-				•		
+0.0167-					•	
+0.0130-					•	
+0.0102-						• •
0.00799-						• *
0.00626-						
0.00490-				-		
0.00383-			•			
0.00300-						
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HITEMP-SOPBENT. TYMOCHTEE DOLOMITE: 16/18 MESH UNCALCINED PNTR NUMBER +380

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LP 11:25:48 8/15/85 HP 11:59:34 8/15/85

DIFFERENTIAL VOLUME (CC/G-MICRO-M) VS. PORE DIAMETER 100% = +0.113418E-001

0%	20%	40%	60%	80%	100%
I	I	I	I	I	, I
- +300-++++++	******				
+235-+++++	*************	******			
+184-++++++	******	*********	*****		
+144-++++++	***********	**********	***********	•	
+113-++++++	*************	*********	***********	*******	
+88.1-+++++	***********	**********	•••••	*********	
+69.0-+++++	**********	**********	•••••	************	> + +
+54,0-++++++	************	**********	***********	************	••••
+42.3-******	************	**********	**********	*************	******
+32.1-+++++++	•••••	**********	***********	************	▶ ◆
+20.9-++++++	••••••••••	• • • • • • • • • • • • • • • •	*****		
+20.3-++++++	****				
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, +12, 4-00000 +5, 72-00000					
47 41-44444		*			
45.9x-00000	• •				
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+2.86-*****	**				
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+1.75-++++++	• ·				
+1.37-******	•				
+1.07-******	****				
+0.839-******	******				
+0.657-++++++	***				
+0.514-+++		•			
+11,4112- + ++					
+0.310-+++					
+0.151- + +					
+0.118-++					
+0.0926-++					
+0.0725-++					
+0.0567-+	·				
+0.0444-+					
+0.0347-++					
+0.0272-+	•				
+0.0213-+				_	
+0.0167-+					
+0.0130-+					
+0.0102-+					
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V. VUUUU			A-53		

HITEMP-SOPBENT TYMOCHTEE DOLOMITE: 16/18 MESH UNCALCINED PNTR NUMBER +380

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LP 11:25:48 8/15/85 HP 11:59:34 8/15/85

DIFFERENTIAL SURFACE AREA (M2/G-MICRO-M) VS. DIAMETER 100% = +0.307924E-001

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	0%	20%	40%	60%	80%	100
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	104-4					
+	113-4					
÷§	÷.1=▲					
+6	9.0-+		•			
+5	4.0-◆					
+4	2.3-+					
+3	3.1-+					
+2	5.9-+					•
+2	0.3-+					
+1	5.9-+				•	
+1	2.4-+					
+9	.72-+					
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+11.	657-+++++	**********				
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+0.	315-+++++	••••				
+0.	247-+++++	••••	•			
+0.	193-*****	•••••••				•
+0.	151-+++++	• • • • • • • • • • • • • • • •	•			
+0,	118-+++++	*********				
+0.0	1925-++++++	************	******		· .	
+0.0)725-++++++	•••••	*********			
+0.0	1567-++++++	************	******			
+0.0	444-*****	************	*********			. 📲
+0.0)347-++++++	*************	************	************	***********	***
+0.0	272-++++++	************	************	•••••	****	•
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+0.00300-+

HITEMP-SOPBENT LP 9:14:24 8/16/85 VICRON LST., LUCERNE VALLEY, CA.; 16/18 MESH UNCAL HP 9:38:24 8/16/85 PNTR NUMBER +386 LP EQUILIPRATION = +15.0000 SEC PNTR CONSTANT = +10.7900 MICRO-L/FF HP EQUILIBRATION = +10.0000 SEC THETA = +130.0000 SAMPLE WEIGHT = +4.0000 G GAMMA = +485.0000 DYNES/CM PNTR WEIGHT = +76.9800 6 INITIAL PRESSURE = +0.9011 PSIA PNTR+SAMPLE WEIGHT = +80.9800 G PORE DIAMETER = +196.1730 MICRO-M

MERCURY DENSITY =

PNTR+SAMPLE+MERCURY = +106.5700 G PNTR VOLUME = +3.4120 CC

INTRUSION (PRESSURIZATION) DATA SUMMARY.

TOTAL INTRUSION VOLUME	=	+0.0123	CC/6
TOTAL POPE AREA	=	+0.0318	SQ-M/G
MEDIAN PORE DIAMETER (VOLUME)	2	+64.1763	MICROMETERS
MEDIAN POPE DIAMETER (AREA)	=	+0.1870	MICROMETERS
AVERAGE FORE DIAMETER (47/A)	Ξ.	+1.5434	MICROMETERS
BULK DENSITY	=	+2.6296	G/CC
APPARENT (SKELETAL) DENSITY	=	+2.7174	GZCĊ

% CAPILLARY = +12.7993 ++++

PAGE 1

+13.5335 6/00

HITEMP-SOPBENT VICRON LST.,LUCEPNE VALLEY,CA.; 16/18 MESH UNCAL PNTR NUMBER +386 LP 9:14:24 8/16/85 HP 9:38:24 8/16/85

PRESSUFE PSIA	POPE DIAMETER MICRO-M	INTRUSION Volume CC/G	PORE Surface SQ-M/G	MEAN Diameter Micro-M	DV
+5.0	+35.4843	+0.0067	+0.0002	+115.8290	+0.006
+9.9	+17.7814	+0.0080	+0.0004	+26.6328	+0.001
+14.6	+12.0767	÷0.0086	+0.0006	+14.9291	+0.000
+19.9	+8.8743	+0.0089	+0.0007	+10.4755	+0.000
+39.7	+4.4519	+0.0093	+0.0009	+6.6631	+0.0004
★6 0.0	+2.9462	+0.0095	+0.0012	+3.6990	+0,000
+80.0	+2.2096	+0.0098	+0.0016	+2.5779	+0.000
+100.4	+1.7613	+0.0100	+0.0020	+1.9855	+0.000
+118.8	+1.4876	+0.0101	+0.0024	+1.6244	+0.000
+150.5	+1.1742	+0.0103	+0.0030	+1.3309	+0.000
+201.2	+0.8784	+0.0108	+0.0048	+1.0263	+0.000
+252.0	+0.7014	+0.0112	+0.0065	+0.7899	+0.000
+298.9	+0.5914	+0.0113	+0.0074	+0.6464	+0.000
+353.6	+0.1999	+0.0114	+0.0079	+0.5457	+0.000
+400.5	+0.4414	+0.0114	+0.0086	+0.4707	+0.000
+455.2	+0.3883	+0.0115	+0.0093	+0.4149	+0.000
+503.1	+0.3514	+0.0116	+0.0101	+0.3699	+0.000
+600.7	+0.2943	+0.0116	+0.0102	+0.3228	+0.000
+697.4	+0.2535	+0.0118	+0.0124	+0.2739	+0.000
+799.0	+0.2212	+0.0118	+0.0137	+0.2373	+0.000
+895.7	+0.1973	+0.0119 •	+0.0152	+0.2093	+0.000
+997.3	+0.1772	+0.0120	+0.0168	+0.1873	+0.000
+1104.8	+0.1600	+0.0120	+0.0171	+0.1686	+0.000
+1206.3	+0.1465	+0.0120	+0.0171	+0.1533	+0.000
+1307.0	+0.1353	+0.0120	+0.0177	+0.1409	+0.000
+1411.5	+0.1252	+0.0120	+0.0180	+0.1302	+0.000
+1501.3	+0.1177	+0.0120	+0.0183	+0.1215	+0.000
+1607.8	+0.1099	+0.0121	+0.0209	+0.1138	+0.000
+1691.8	+0.1045	+0.0121	+0.0212	+0.1072	+0.000
+1803.2	+0.0980	+0.0121	+0.0215	+0.1013	+0.000
+2004.4	+0.0882	+0.0121	+0.0222	+0.0991	+0.000
+2200.7	+0.0803	+0.0122	+0.0228	+0.0843	+0.000
+2397.1	+0.0737	+0.0122	+0.0234	+U.U//U .0 0710	+0.000
+2593.1	+0.0682	+0.0122	+0.0241	+0.0710	₩0.00 0
+2814.7	+0.0628	+0.0122	+0.0248	+0.0655	+0.000
+2995.5	40.0590	+0.0122	+0.0234	+V.0509 .0.0570	+0.000
+3189.0	+0.0554	+0.0122	+0.0251	+0.0572	+0.000
+3398.8	+0.0520	+0.0123	+0.0317	+0.0537	+0.000
+3588.5	+0.0493	+0.0123	+0.0317	+0.0006	+0.00 <u>0</u>
+3800.0	+0.0465	+0.0123	+0.0317	+0.0477	+0.000
+3993.8	+0.0443	+0.0123	+0.0317	+0.0434	+0.000
+4700.4	+0.0393	+0.0123	+0.0317	TU.U418	TU.UUU
+5007.1	+0.0353	+0.0123	+0.0317	◆0.0373 .4 AAA	▼0.000 ★0.000
+5498.9	+0.0321	+0.0123	+0.0319	◆0.0337 .a.a.a.a.	▼V. VUU ▲A AAA
+5990.6	+0.0295	+0.0123	+0.0319	⊕Ų.Ų⊴Ų& ⊼o opop	▼U.UUU ▲A DAK
+6527.1	+0.0271	+0.0123	+0.0319	◆U.U233 .a anin	▼U.UU U ▲A AAA
+6989.1	+0.0253	+0.0123	+U.U319	+U.UCCC	▼U.UU L
+7525.5	+0.0235	+0.0123	+0.0319	+0.0244	, +∪. ∪00

PAGE 2

LP 9:14:24 8/16/85

HP 9:38:24 8/16/85

HITEMP-SOPBENT VICRON LST.,LUCEPNE VALLEY:CA.; 16/18 MESH UNCAL PNTR NUMBER +386

PRESSURE	PORE	INTRUSION	PORE	MEAN	
PSIA	DIAMETER	VOLUME	SURFACE	DIAMETER	I)∀
	MICRO-M	CC/6	SQ-M/G	MICRO-M	
*					
+7987.5	+0.0221	+0.0123	+0.0319	+0.0228	+0.0000
+8956.1	+0.0197	+0.0123	+0.0319	,+0.0209	+0.0000
+9954.6	+0.0178	+0.0123	+0.0319	+0.0187	+0.0000
+10953.0	+0.0161	+0.0123	+0.0319	+0.0169	+0.0000.
+11996.2	+0.0147	+0.0123	+0.0319	+0.0154	+0. 0000
+12964.8	+0.0136	+0.0123	+0.0319	+0.0142	+0.0000
+13948.3	+0.0127	+0.0123	+0.0319	+0.0132	+0.0000
+14946.8	+0.0118	+0.0123	+0.0319	+0.0123 '	+0.0000
+15930.3	+0.0111	+0.0123	+0.0319	+0.0115	+0.0000
+17077.8	+0.0104	+0.0123	+0.0319	+0.0107	+0.0000
+1815.0.7	+0.0097	+0.0123	+0.0319	+0.0100	+0.0000
+19149.2	+0.0092	+0.0123	+0.0319	+0.0095	+0.0000
+20132.7	+0.0088	+0.0123	+0.0319	+0.0090	+0.0000
+24961.0	+0.0071	+0.0123	+0.0319	+0.0079	+0.0000
+29923.3	+0.0059	+0.0123	+0.0319	+0.0065	+0. 0000
+35154.0	+0.0050	+0.0123	+0.0319	+0.0055	+0.0000
+40205.8	+0.0044	+0.0123	+0.0319	+0.0047	+0.0000
+45138.4	+0.0039	+0.0123	+0.0319	+0.0042	+0.0000
+50056.0	+0.0035	+0.0123	+0.0319	+0.0037	+0.0000
+54884.3	+0.0032	+0.0123	+0.0319	+0.0034	+0.0000
+59787.1	+0.0030	+0.0123	+0.0319	+0.0031	+0.0000

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HITEMP-SOPEENT LP 9:14:24 8/16/85 VICRON LST., LUCEPNE VALLEY, CA.: 16/18 MESH UNCAL HP 9:38:24 8/16/85 PNTR NUMBER +386

> CUMULATIVE PORE VOLUME (CC/6) VS. PORE DIAMETER 100% = +0.0123

0*	20%	40%	60%	80%	10
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+235-	•				
+184-	•				
+144-	•	•		•	
+113-		•			
+85 1-		•			
+69.0-		•		÷	
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キリ。もつイー					•
+0.514-	•				•
+0.402-					•
+0.310-					
+0.247-		3			•
+0.193-					•
+0.151-					•
+0.118-					•
+0.0926-					•
+0.0725-				· · · ·	•
+0.0067-					
+0.0444-					
+0.0347-	-				-4,
+0.0272-					
+0.0213-					
+0.0167-					
+0.0130-					•
+0.0102-					۷.
+0.00799-					
+0.00626-			•		
+0.00490 -			•		
+0.00383-					
+0.00300-					
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ENERSOFIER PON LOT. (L) P NUMBER (ICERNE VALLE 1386	EY:CA.I	16/18 MESH	UNCAL		LP HP	9:38:24 9:38:24	8/16/80 8/16/85
	CUMULATIVE	SURFACE	APEA (M2/G 100% =	> VS. +0.1	PORE 0318	DIAMETER	2	
0%	20%		4.0%		60%		80%	10
I	I		I		I	,		
+300-+								
+235-+								
+144-+								
+113-+								
+88.1-+								
+69.0-+								
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+42.3-+								
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+20.3-+			•					
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+12.4-+								
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+4.66- •								
+3.65- •						•		
+2.86- +						•		
+2.24- *								
+1.73-								
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HITEMP-SOPBENT LP 9:14:24 8/16/85 VICRON LST.,LUCEPNE VALLEY,CA.; 16/18 MESH UNCAL HP 9:38:24 8/16/85 PNTR NUMBER +386

> DIFFERENTIAL VOLUME (CC/G-MICRO-M) VS. PORE DIAMETER 100% = +0.658369E+002

	0%	20%	40%	60	*	80%	10
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+2	33-*******		• • • • • • • • • • • • • •				
+1	**-********		••••••••••••	••••••••••			
+1	44-********		•••••	•••••	••••••		
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+15		•••	•••				
+12	4						
+9	72-+++						
+7.	61- ***						
+5.	96-+++	·					
+4.	66-***			•			
+3.	65-++						
+2.	86-**						
+2.	24-**						
+1.	75-++						
+1.	37-++				•		
+1.	07-+++						
+0.8	39- ****						
+0.6	57-+++						
- - ₽.5	14-+						
+0.4	₩2- +						
+0.3	10-+						
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	70-+ 51-*						
	15-▲						
#0 09	26=+						
+0.07	25-+						
+0.05	 67-+						
+0.04	44-+						
+0.03	47-+						•
+0.02	72+						
+0.02	13-+		•				
+0.01	67-+						·
+0.01	30-+						۱
+0.01	02-•						
+0.007	99- 			.*			•
+0.006	26-+		•				
+0.004	90-◆						
+0.003	83-•						
+0.003	Ú(i - ◆	,					

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HITEMP-SORBENT LP 9:14:24 8/16/85 VIORDN LST.,LUCEFNE VALLEY,CA.; 16/18 MESH UNCAL HP 9:38:24 8/16/85 PNTR NUMBER +336

> DIFFERENTIAL SURFACE AREA (M2/G-MICRD-M) VS. DIAMETER 100% = +0.194853E-002

- 0%	20%	40%	60%	80%	100%
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+300-+					
+235-++					
+184-++					
+144-++	• •				
+113-+++				,	
+88.1-***					
+ <u>6</u> 9,0-+++	· ·			4	
+54.0-+++					
+42.3~****					
+33.1-****					
+25.9-*****					
+20.3-*****	•				
+15.9-*****					
+12.4-****			i.		
+9.72-++++					
+7.61-*****					
+5.96-*****	•				
+4.66-****	**				
+3.65-*****	• • •				
+2.86-++++	****				
+2,24-+++++	*******				
+1.75-+++++	******				
+1.37-+++++	******				
+1.07-++++++	******	************	***	·	
+0.839-++++++	• • • • • • • • • • • • • • • • • • • •	***********	************	***********	***
+0.657-++++++	************	************	***********		
+0.514-+++++	• • • • • • • • • • • • • • • • • • • •				
+0.402-++++++	******	****			
+0.315-++++++	****		•		
+0.247-++++++	************	************	************	************	*******
+U, 192-+++++++	• • • • • • • • • • • • • • • • • • • •	***********	************	*****	
+0.151-+++					
+0.118-+++++++	••••				

+0.0725-++++++	•••••	••			
+0.0567-++++++	***********	* *			
+11. (1444-+					р.
+0.0347-++					
+0.0272-+					
+0.0213-+					
+0.016/-+	•				•
+0.0130-+					
+0.0102- +					
+0.00799-+				•	
+0.00525-+1					
+0.00490-+				1	
+0.00383++					

+0.00300-+

A-61

PAGE 7

HITEMP-SORBENT			LP 11:34:48 8/26/8
VICRON LST. ADAMS MASS.	(8/85) 16-18 ME	SH	HP 12:57:19 8/26/8
PNTR NUMBER +387			
LP EQUILIBRATION =	+15.0000 SEC	PNTR CONSTANT =	+10.7900 MICRO-L
HP EQUILIBRATION =	+10.0000 SEC	THETA =	+130.0000
SAMPLE WEIGHT =	+6.0800 G	GAMMA =	+485.0000 DYNES/C
PNTR WEIGHT =	+74.0600 G	INITIAL PRESSURE =	+ 0.9451 PSIA
PNTR+SAMPLE WEIGHT =	+80.1400 G	PORE DIAMETER =	+187.0490 MICRO-M
PNTR+SAMPLE+MERCURY =	+123.9600 6	MERCURY DENSITY =	+13.5335 6/CC
PNTR VOLUME =	+5.5410 CC		

INTRUSION (PRESSURIZATION) DATA SUMMARY

TOTAL INTRUSION VOLUME	=	+0.0099	CC∕G
TOTAL PORE AREA	7	÷0.0290	SQ-M/6
MEDIAN PORE DIAMETER (VOLUME)	=	+26.8138	MICROMETERS
MEDIAN PORE DIAMETER (AREA)	=	+0.1545	MICROMETERS
AVERAGE PORE DIAMETER (4V/A)	8	+1.3715	MICROMETERS
BULK DENSITY	=	+2.6399	6700
APPARENT (SKELETAL) DENSITY	=	+2.7111	6×CC

% CAPILLARY = +15.7443 ++++ -

HITEMP-SOPBENT VICRON LST. ADAMS MASS. (8/85) 16-18 MESH PNTR NUMBER +387 LP 11:34:48 8/26/85 HP 12:57:19 8/26/8

PRESSURE	POPE	INTRUSION	PORE	MEAN	•
PSIA	DIAMETER	VOLUME	SURFACE	DIAMETER	· BV
	MICRO-M	CC/6	SQ-M/G	MICRD-M	
•					
+5.0	+35.4322	+0.0044	+0.0002	+111.2400	+0.0044
+9.9	+17.8208	+0.0056	+0.0003	+26.6265	+0.0012
+14.6	+12.0949	+0.0061	+0.0005	+14.9578	+0.0005
+19.9	+8.8613	+0.0065	+0.0006	+10.4781	+0.0004
+38.8	+4.5527	+0.0070	+0.0009	+6.7070	+0.0004
+58.4	+3.0275	+0.0074	+0.0013	+3.7901	+0.0
+78.8	+2.2446	+0.0077	+0.0018	+2.6361	+0.
+98.6	+1.7927	+0.0079	+0.0022	+2.0186	+0. 4
+120.8	+1.4633	+0.0081	+0.0027	+1.6280	+Ú.Ú.
+148.9	+1.1875	+0.0084	+0.0035	+1.3254	+0.0003
+198.8	+0.8890	+0.0088	+0.0052	+1.0382	+0.0004
+252.2	+0.7010	+0.0089	+0.0059	+0.7950	+0.0001
+301.8	+0.5857	+0.0091	+0.0070	+0.6433	+0.0002
+355.6	+0.4972	+0.0092	+0.0077	+0.5414	+0.0001
+403.4	+0.4382	+0.0093	+0.0081	+0.4677	+0.0000
+454.2	+0.3892	+0.0093	+0.0086	+0.4137	+0.0000
+504.0	+0.3507	+0.0094	+0.0091	+0.3699	+0.0000
+602.7	+0.2933	+0.0094	+0.0098	+0.3220	+0.0001
+701.3	+0.2520	+0.0095	+0.0112	+0.2727	+0,0001
+803.9	+0.2199	+0.0096	+0.0121	+0.2360	+0.0001
+897.7	+0.1969	+0.0096	+0.0122	+0.2084	+0.0000
+664.4	+0.1778	+0.0096	+0.0133	+0.1873	+0.0001
+1113.6	+0.1587	+0.0097	+0.0145	+0.1683	+0.0001
+1216.1	+0.1454	+0.0097	+0.0147	+0.1521	+0.01
+1315.7	+0.1344	+0.0097	+0.0149	+0.1399	+0.0
+1414.4	+0.1250	+0.0097	+0.0164	+0.1297	+0.00
+1512.1	+0.1169	+0.0097	+0.0166	+0.1209	+0.0000
+1611.7	+0.1097	+0.0097	+0.0168	+0.1133	+0.0000
+1712.3	+0.1032	+0.0097	+0.0170	+0.1055	+0.0000
+1812.0	+0.0976	+0.0098	+0.0189	+0.1004	+0.000 0
+2008.3	+0.0880	+0.0098	+0.0194	+0.0928	+0.0000
+2204.6	+0.0802	+0.0098	+0.0198	+0.0841	+0.0000
+2403.9	+0.0735	+0.0099	+0.0220	+U.U/67 +0.0709	+0.0001
+2596.7	+0.0681	+0.0099	+0.0229	+0.0708	+0.0000
+2787.4	+0.0534	+0.0099	+0.0233	+0.0607	+0.0000
+3011.9	+U.UD87	+0.0099	TU.U230		+0.0000
+3190.2	+U.U334	+0.0099	TU.UE4E	+0.0570 +0.0578	+0.0000
+3386.3	+0.0022	+0.0099	TU,U240	+0.0506	+0.0000
+3506.9	+0.0490	+0.0099	TU.UEDI	+0.0308	+0.0000 +0.0000
+3800.0	+0.0460	+0.0099	TU.UCJJ		+0.0003 +0.00∂0
+3773.8	TU.U443	TU.UUYY	TU.UC07	▼U。U▼Jマ 上山 D417	→0.00 000
+4010.3	TU.U371	TU.UU77 10.0077	TU.VE/U An Abet		₩0.0000 ▲0.0000
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キイリージョブ	TU.UCDC 10.0334	イリ・リリアフ ・ エム ムム公公	-V.VE71 10001		+0.0000 +0.0000
+/340.4	マリーリビンチ	マリ。リリアア	TU.UC71	THETH	

HITEMP-SORBENT VICRON LST. ADAMS MASS. (8/85) 16-18 MESH PNTR NUMBER +387

LP	11:34:48	8/26/8
HP	12:57:19	8/26/8

PRESSURE PSIA	PORE DIAMETER MICRO-M	INTRUSION VOLUME CC/G	PORE Surface SQ-M/G	MEAN DIAMETER MICRO-M	עע
+8017.3	+0.0220	+0.0099	+0.0291	+0.0227	+0.000
+8985.9	+0.0197	+0.0099	+0.0291	+0.0209	+0.000
+9984.4	+0.0177	+0.0099	+0.0291	+0.0187	+0.000
+10953.0	+0.0161	+0.0099	+0.0291	+0.0169	+0.000
+11981.3	+0.0148	+0.0099	+0.0291	+0.0154	+0.000
+12949.9	+0.0137	+0.0099	+0.0291	+0.0142	+0.000
+13948.3	+0.0127	+0.0099	+0.0291	+0.0132	+0.000
+14946.8	+0.0118	+0.0099	+0.0291	+0.0123	+0.000
+15930.3	+0.0111	+0.0099	+0.0291	+0.0115	+0.000
+17122.5	+0.0103	+0.0099	+0.0291	+0.0107	+0.000
+18165.6	+0.0097	+0.0099	+0.0291	+0.0100	+0.000
+18910.7	+0.0093	+0.0099	+0.0291	+0.0095	+0.000
+20102.9	+0.0088	+0.0099	+0.0291	+0.0091	+0.000
+24975.9	+0.0071	+0.0099	+0.0291	+0.0079	+0.000
+29953.1	+0.0059	+0.0099	+0.0291	+0.0065	+0.000
+35288.1	+0.0050	+0.0099	+0.0291	+0.0055	+0.000
+40414.4	+0.0044	+0.0099	+0.0291	+0.0047	+Ů.000
+45332.1	+0.0039	+0.0099	+0.0291	+0.0041	+0.000
+50324.3	+0.0035	+0.0099	+0.0291	+0.0037	+0.000
+55107.8	+0.0032	+0.0099	+0.0291	+0.0034	+0.000
+59906.3	+0.0030	+0.0099	+0.0291	+0.0031	+0. 000

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HITEMP-SORBENT LP 11:34:48 8/26/85 VICRON LST. ADAMS MASS. (8/85) 16-18 MESH HP 12:57:19 8/26/85 PNTR NUMBER +387

1 1 1 1 1		CUMULATIVE	PORE	VOLUME 100%	(CC/G) ; =	VS. PORE +0.0099	DIAMETER			
	0% T	20%		40%		60%		80%		100 ••••I
+300-	-	•								
+235-	-	•								
+184-	-	•	•							
+144-	-		٠							
+113-	-			•					•	
+88.1-	-			. •			•			
+69.0-	-			•						
+54.0-	-			•	•					
+42.3-	-				•					
+33.1-	-				•					
+25.9-	-				•					
+20.3-	• ,			•		•				
+15.9-	-					•		•		
+12.4-						•	-			
	• ·						•			
	-						•			
	-						•			
+3.65-							•			
+2.86-	-				•		•			
+2.24-	-						•	•		
+1.75-	. .							•		
+1.37-	•					• •		٠		
+1.07-	•							•	▶ .	
+0.839-	-								•	
+0.657-	-								•	
+0.514-	-								•	1
+0.402-	-						1	• •	•	,
+0.315-	•									•
+0.247-	-			•	•					•
+0.193-	-									•
+0.151-	-									•
+0.118-	•									
+0.0725-	-									▲ .
+0.0723-	-									•
	-								•	•
+0.0347-	-		,							•
+0.0272-	-									•
+0.0213-										
+0.0167-	-			•						•.•
+0.0130-	-			-						. •
+0.0102-	-									•
0.00799-	. .									+
0.00626-	•			•					• .	•
0.00490-	•									· •
0.00383-	•									٠
0.00300-	- ·									•

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HITEMP-SDRBENT VICRON LST. ADAMS MASS. (8/85) 16-18 MESH PNTR NUMBER +387

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LP 11:34:48 8/26/85 HP 12:57:19 8/26/85

CUMULATIVE SURFACE AREA (M2/G) VS. PORE DIAMETER 100% = +0.0290

0%	20%	40%	60%	80%	1 Ŭ
۲ هـاند			••••••		• • • • • • • •
+235-+					
+184-+					
+144-+					
+113- →					
+85 1-+			•		
+69.0- +					
45 4 0 -▲					
→43 3~ →					
+32 1-+					
+25 9-4					
+20 2-4					
→15 G_★					•
	·				
+9 72-4					
+7 61- +					
45 94 - 4					
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×1 07	•				
★1 07=	· •				
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-0.007- -0.457-	· • •				
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+0.40E- +0.215-	•	•			
+0.310		• • ·			
+0.241-		•			
+0.153÷		•	•		
+0.101-			•		
			•		
+0.0725-	i		¥	•	
+0.07E0-				•	
+0.0444-				•	•
+0.0347-					
+0 0272=	•				•
+0.0212-					
◆0.0E10- ◆0.0147-					
+0.0130-					
••••••••••• ▲0.010⊇=					•
<pre>+0.0102= ▲0.00700=</pre>					•
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-V.VVD207 Aŭ dúzdo-					
-0.00470- -0.00202-					
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HITEMP-SORBENT VICRON LST. ADAMS MASS. (8/85) 16-18 MESH PNTR NUMBER +387 LP 11:34:48 8/26/85 HP 12:57:19 8/26/85

DIFFERENTIAL VOLUME (CC/G-MICRO-M) V3. PORE DIAMETER 100% = +0.428826E-002

° 0' 20% 40% 60% 80% 100 - - - I +300-++++++++++++ +20.3-********************** +15.9-************ +12.4-******** +9.72-++++++ +7.61-+++++ +5.98-+++++ +4.66-***** +3.65-****** +2.86-***** +2.24-**** +1.75-+++ +1.37-++++ +1.07-+++++ +0.839-***** +0.657-++ +0.514-++ +0.402-+ +0.315-+ +0.247=≠ +0.193-+ +0.151-+ +0.118-+ +0.0926-+ +0.0725-+ +0.0567-+ +0.0444-+ +0.0347-+ +0.0272-+ +0.0213-+ +0.0167-+ +0.0130-+ +0.0102-+ +0.00799-+ +0.00626-+ +0.00490-+ +0.00383-+ +0.00300-+

HITEMP-SOPBENT VICRON LST. ADAMS MASS. (8/85) 16-18 MESH PNTR NUMBER +387

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LP 11:34:48 8/26/89 HP 12:57:19 8/26/89

DIFFERENTIAL SURFACE AREA (M2/G-MICRD-M) VS. DIAMETER 100% = +0.224178E-002

	0%	20%	40%	60%	80%	1
	I	• • • • • • • • • I • • • • • •	1	• • • • • • • • I • • • • • •	• • • • • • • I • • • • •	••••
	300 - ● 225-●					
+c ▲1	184- 44					
+	144-++				·	
+	113-++					
+88	3.1-++					
+69	9.0-++				i.	
+54	\$. Ŭ-+++					
. +42	2.3-+++	·				
+33	3.1-+++					
+25	5.9- + +++					
+21	U.3- ●●●● ●					
+13), 4- 444 4 7 <i>4</i> -4444	•				
	72-4444				. ,	
+5.	96-***	•••	•			
+4.	66-+++	••••			•	•
+3.	65-+++					
+2.	86-***	*****	·			
+2.	.24-++++	*****	•			
+1.	,75-++++	*****				
+1.	.37-++++	• • • • • • • • • • • • • • • • • • • •				
+1.	, 07-+++++	• • • • • • • • • • • • • • • • • • • •	******	••		
+0.8	339-****	• • • • • • • • • • • • • • • • • • • •	***********	*****		
+0.6	57-++++	• • • • • • • • • • • • • • • • • • • •	****	•		
+0.5	514- *** *	•••••	***			
+ 0.4	4U2-***** 21 E-****	••••				
	313-0000			******		
+0.0 +0.1	193-4444		•••••	••••		
+0.1	151-++++					
+0.1	118-++++	****				
+0.09	926-++++		***********	**		•
+0.07	725-++++	• • • • • • • • • • • • • • • • • • • •	***********	************	**********	*****
+0.0	567-++++	• • • • • • • • • • •				
+0.04	444-++++	*****				
+0.03	347-****	• • • • • • • • • • • • • • • • • • • •	*********			0
+0.02	272-+				•	
+0.00	213-0					
+0.0	157-4					
▼0.02	130-+					
+0.01 +0.005	102-♥ 793_★					•
+0.004	; 27 - ▼ 126- ▲			•		
+0.004	1911- ●					
+0.003	383-•					
+0.000	300-+					

APPENDIX B

- COARSE SORBENT THERMOGRAVIMETRIC BALANCE DATA
- B1: Run Summaries B2: Untreated Sorbents in SO2 Pretreated Sorbents in SO_2 Untreated Sorbents in H_2S B3:
- B4:

APPENDIX B1

RUN SUMMARIES

Table Key:		
Orig. wt.	=	original weight of test sample
Final wt. calc.	=	final weight of sample after calcination
Weight loss	=	weight lost on calcination
Solid	=	% of sample remaining after calcination
Volit	=	% of sample volatile
CA	=	implied weight of calcium in sample
₩G	=	implied weight of magnesium in sample
FX. CA.	=	wt. fraction calcium in sample
FX. MG.	=	wt. fraction magnesium in sample

RUN	STONE	ORIG.	FINAL	WEIGHT	*	*	mơ.	mg.	FX.	FX.
NO.		WT.	WT.	LOSS	SOLID	VOLIT.	CÀ.	MĞ.	CA.	MG.
		(mar.)	CALC.	(mg.)						
P437	TYMOCHTEE	18.36	10.24	8.12	55.77	44.23	3.71	2.36	.2021	.1287
P438	PLUM RUN	19.02	10.04	8.98	52.79	47.21	3.82	2.48	.2006	.1302
P439	HIGHLAND	17.26	10.26	7.00	59.44	40.56	5.88	.65	.3407	.0376
P440	GREER	19.32	10.88	8.44	56.31	43.69	7.29	.18	.3775	.0094
P441	MISSISSIPPI	16.94	9.50	7.44	56.08	43.92	6.48	.23	.3827	.0136
P442	CARBON	18.24	10.32	7.92	56.58	43.42	6.40	.47	.3508	.0257
P443	VICRON	19.34	10.64	8.70	55.02	44.98	7.31	.29	.3781	.0149
P444	TYMOCHTEE	18.82	10.46	8.36	55.58	44.42	3.80	2.42	.2021	.1287
P445	PLUM RUN	18.76	9.84	8.92	52.45	47.55	3.76	2.44	.2006	.1302
P446	HIGHLAND	19.50	11.08	8.42	56.82	43.18	6.64	.73	.3407	.0376
P447	GREER	17.92	9.90	8.02	55.25	44.75	6.76	.17	.3775	.0094
P448	MISSISSIPPI	18.56	10.20	8.36	54.96	45.04	7.10	.25	.3827	.0136
P449	CARBON	19.28	11.20	8.08	58.09	41.91	6.76	.50	.3508	.0257
P450	VICRON	19.10	10.52	8.58	55.08	44.92	7.22	.28	.3781	.0149
P451	GREER	19.30	11.08	8.22	57.41	42.59	7.29	.18	.3775	.0094
P452	TYMOCHTEE	19.34	10.40	8.94	53.77	46.23	3.91	2.49	.2021	.1287
P453	PLUM RUN	19.06	9.82	9.24	51.52	48.48	3.82	2.48	.2006	.1302
P454	HIGHLAND	17.16	9.66	7.50	56.29	43.71	5.85	.65	.3407	.0376
P455	GREER	18.88	10.24	8.64	54.24	45.76	7.13	.18	.3775	.0094
P456	MISSISSIPPI	15.84	8.32	7.52	52.53	47.47	6.06	.22	.3827	.0136
P457	VICRON	18.60	10.00	8.60	53.76	46.24	7.03	.28	.3781	.0149
P458	CARBON	18.44	10.62	7.82	57.59	42.41	6.47	.47	3508	.0257
P459	TYMOCHTEE.	19.26	9.94	9.32	51.61	48.39	3.89	2.48	.2021	.1287
P460	TYMOCHTEE	18.90	10.10	8.80	53.44	46.56	3.82	2.43	.2021	.1287
P461	PLUM RUN	17.82	8.88	8.94	49.83	50.17	3.57	2.32	.2006	.1302
P462	PLUM RUN	19.04	9.84	9.20	51.68	48.32	3.82	2.48	.2006	.1302
P463	VICRON	18.00	9.70	8.30	53.89	46.11	6.81	.27	.3781	.0149
P464	VICRON	18.40	9.84	8.56	53.48	46.52	6.96	.27	.3781	.0149
P465	CARBON	18.54	10.58	7.96	57.07	42.93	6.50	.48	.3508	.0257
P466	CARBON	16.60	9.56	7.04	57.59	42.41	5.82	.43	.3508	.0257
P467	HIGHLAND	17.40	9.42	7.98	54.14	45.86	5.93	.65	.3407	.0376
P468	HIGHLAND	16.78	9.80	6.98	58.40	41.60	5.72	.63	.3407	.0376
P469	GREER	19.70	10.40	9.30	52.79	47.21	7.44	.19	.3775	.0094
P470	GREER	18.90	10.26	8.64	54.29	45.71	7.13	.18	.3775	.0094
P471	MISSISSIPPI	14.92	7.70	7.22	51.61	48.39	5.71	.20	.3827	.0136
P472	MISSISSIPPI	17.84	9.50	8.34	53.25	46.75	6.83	.24	.3827	.0136

B-3

SAMPLE NO.	STONE	ORIGINAL WT. (mg.)	FINAL WT. CALC.	WEIGHT LOSS (mg.)	PERCENT	PERCENT VOLATILES	TEMP. C	MESH SIZE
P437	TYMOCHTEE	18.36	10.24	8.12	55.77	44.23	1000	40/45
P444	TYMOCHTEE	18.82	10.46	8.36	55.58	44.42	1000	16/18
P452	TYMOCHTEE	19.34	10.40	8.94	53.77	46.23	1100	20/25
P459	TYMOCHTEE	19.26	9.94	9.32	51.61	48.39	1200	16/18
P460	TYMOCHTEE	18.90	10.10	8.80	53.44	46.56	1200	40/45
P440	GREIER	19.32	10.88	8.44	56.31	43.69	1000	40/45
P447	GREIER	17.92	9.90	8.02	55.25	44.75	1000	16/18
P451	GREIER	19.30	11.08	8.22	57.41	42.59	1000	16/18
P455	GREIER	18.88	10.24	8.64	54.24	45.76	1100	20/25
P469	GREIER	19.70	10.40	9.30	52.79	47.21	1200	16/18
P470	GREIER	18.90	10.26	8.64	54.29	45.71	1200	40/45
P443	VICRON	19.34	10.64	8.70	55.02	44.98	1000	40/45
P450	VICRON	19.10	10.52	8.58	55.08	44.92	1000	16/18
P457	VICRON	18.60	10.00	8.60	53.76	46.24	1100	20/25
P463	VICRON	18.00	9.70	8.30	53.89	46.11	1200	16/18
P464	VICRON	18.40	9.84	8.56	53.48	46.52	1200	40/45
P438	PLUM RUN	19.02	10.04	8.98	52.79	47.21	1000	40/45
P445	PLUM RUN	18.76	9.84	8.92	52.45	47.55	1000	16/18
P453	PLUM RUN	19.06	9.82	9.24	51.52	48.48	1100	20/25
P461	PLUM RUN	17.82	8.88	8.94	49.83	50.17	1200	16/18
P462	PLUM RUN	19.04	9.84	9.20	51.68	48.32	1200	40/45
P439	HIGHLAND	17.26	10.26	7.00	59.44	40.56	1000	40/45
P446	HIGHLAND	19.50	11.08	8.42	56.82	43.18	1000	16/18
P454*	HIGHLAND	17.16	9.66	7.50	56.29	43.71	1100	20/25
P467*	HIGHLAND	17.40	9.42	7.98	54.14	45.86	1200	16/18
P468*	HIGHLAND	16.78	9.80	6.98	58.40	41.60	1200	40/45
P441*	MISSISSIPPI	16.94	9.50	7.44	56.08	43.92	1000	40/45
P448*	MISSISSIPPI	18.56	10.20	8.36	54.96	45.04	1000	16/18
P456*	MISSISSIPPI	15.84	8.32	7.52	52.53	47.47	1100	20/25
P471*	MISSISSIPPI	14.92	7.70	7.22	51.61	48.39	1200	16/18
P472*	MISSISSIPPI	17.84	9.50	8.34	53.25	46.75	1200	40/45
P442	CARBON	18.24	10.32	7.92	56.58	43.42	1000	40/45
P449	CARBON	19.28	11.20	8.08	58.09	41.91	1000	16/18
P458	CARBON	18.44	10.62	7.82	57.59	42.41	1100	20/25
P465	CARBON	18.54	10.58	7.96	57.07	42.93	1200	16/18
P466*	CARBON	16.60	9.56	7.04	57.59	42.41	1200	40/45

* POPPING STONE - RESULTS IN SOME ORIGINAL WEIGHT LOSS FROM TG PAN

WEIGHT DATA IS TAKEN FROM THE TG CHARTS LIST SHOWS SAMPLE VARIABILITY OVER THE PARTICLE SIZE RANGE AND OVER THE COURSE OF THE SCHEDULED TG RUNS.

THE 40/45 MESH PARTICLE SIZES HAVE A TENDENCY TO CLUMP TOGETHER AND ADHERE TO THE PLATINUM PAN AT 1200 C. THE HIGHLAND LIMESTONE (HD-2) IS PARTICULARLY DIFFICULT TO REMOVE FROM THE TG PAN.

APPENDIX B2

UNTREATED SORBENTS IN SO2

Each run presents plot of

- fraction calcium sulfated versus time
- sulfation rate (fraction sulfated per minute) x 100 versus fraction sulfated
- Log₁₀ {sulfation rate x 100} versus fraction sulfated
- tabulation of fraction calcium sulfated versus time
- tabulation of sulfation rate (fraction calcium sulfated per minute) versus time





B-6



RUN T P43/	TIME	FRACTION	TIME	
FROOLOGE 000000000000000000000000000000000000	00000000000000000000000000000000000000	L	40000000000000000000000000000000000000	

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3821117710532206202458169737730688937048246595678 838211177105332206202458169737730688937048246595945 833333333322222255828155887100925284740407393559545 800000000000000000000000000000000000	$ \begin{array}{l} FR & 0.0974 \\ 0.0974 \\ 0.1262839200220 \\ 0.12628373800220 \\ 0.12628373800220 \\ 0.122223337097655722267771394879224 \\ 0.122223337097655791331851591333444187888888888888888888888888888888$	RATE 0.03715018998476269967669222959595959592888135 0.0373150000000000000000000000000000000000

P437 RUN

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FRACTION 0.00354 0.00355 0.00940355 0.00940355 0.00940355 0.00940355 0.0094035 0.0094035 0.0094035 0.0094035 0.0000000000000000000000000000000000	TIME 0.00 0.10 0.20 0.40 0.10 0.20 0.40 0.10 0.20 0.40 0.10 0.20 0.40 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.1	FRACTION 0.8726 0.8778 0.8844 0.8859 0.8899999 0.8899099 0.8899099 0.8899099 0.8899099 0.8899099 0.9912150 0.991329 22150 0.99122150 0.9912225 0.9912225 0.9912225 0.999335 0.8890 0.9912225 0.999335 0.889222 0.9995 0.9912225 0.999335 0.882222 0.9995 0.00000 0.00000 0.00000 0.00000 0.00000 0.000000	TIME 5.12000000000000000000000000000000000000

RUN # P438

TEMPERATURE = (1000.74 + / - 0.04) C

RUN # P438

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RA355773925773925773925773925773925773925773925773925773925773925773925773925773925773925773925773925775518288074947495083344744933339775555555555555555555555555	FRACTION 0.0690 0.1047 0.1409 0.1777 0.21506 0.28581 0.328581 0.328581 0.334897 0.44359347 0.44359347 0.44359347 0.44359347 0.44359347 0.555705 0.555005 0.555005 0.555708 0.555705 0.55570 0.55570 0.55570 0.55570 0.55570 0.55710 0.7777 7777 0.77520 0.55570 0.55570 0.55570 0.55570 0.55710 0.55710 0.55770 0.7777 7777 0.27590 0.55710 0.55710 0.55710 0.55710 0.55770 0.55710 0.55770 0.55710 0.55770 0.55710 0.55770 0.55710 0.55770 0.55770 0.55770 0.55710 0.557700 0.557700 0.557700 0.557700 0.557700 0.557700 0.557700 0.557700 0.557700 0.557700 0.557700 0.557700 0.5577000 0.55770000000000	RATE 0.03608 0.03937 0.03280 0.03281 0.02624 0.02624 0.02624 0.02624 0.02624 0.026281 0.02628 0.003281 0.013680 0.013282 0.01368 0.01368 0.01368 0.013953 0.013958 0.013958 0.013958 0.013958 0.013958 0.013958 0.013958 0.013958 0.013958 0.013958 0.013958 0.013958 0.013358 0.013358 0.013358 0.013358 0.013358 0.013358 0.013358 0.013358 0.0013558 0.0013558 0.002203 0.000558 0.00263 0.000558 0.0002203 0.000558 0.0002203 0.000558 0.0002203 0.000558 0.0002203 0.0002203 0.0002203 0.0002203 0.0002203 0.000558 0.0002203 0.0002203 0.0002203 0.000258 0.0002203 0.000220 0.000258 0.001355 0.000220 0.000220 0.000223 0.000258 0.001355 0.001355 0.000220 0.000220 0.000223 0.00023 0.001355 0.001355 0.000220 0.000223 0.00023 0.001355 0.001355 0.001355 0.000220 0.000223 0.00023 0.00005 0.000223 0.00025 0.00005 0.000000 0.0000000 0.000000 0.000000 0.000000	F0.00000000000000000000000000000000000







RUN # 194	139 TEMPERATI	JRE = (1002.54	+/- 0.01) C	
Fk4002992886211000000000000000000000000000000000	TIME 0.00 0.10 0.10 0.10 0.10 0.10 0.10 0.1	FRA.333350765533311986612010130133200088655331198764421096733333556778873000000000000000000000000000000000	TIME 55.400 000 000 000 000 000 000 000	

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$\begin{array}{l} \text{IDN} \\ \text{ID$





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FRACTION 0.0000 0.0206 0.0373	TIME 0.00 0.10	FRACTION 0.1936 0.1977 0.2018	TIME 41.40 43.20	
0.0439 0.0583 0.0700 0.0796 0.0858	0.30 0.40 0.50 0.60 0.70	0.2052 0.2094 0.2135 0.2169 0.2203	48.40 51.60 53.40 56.00 57.60	
0.0947 0.0982 0.1030 0.1050 0.1085	0.80 0.90 1.00 1.10 1.20	0.2245 0.2293 0.2327 0.2361 0.2361 0.2402	61.40 64.40 67.40 70.40 74.00	
0.1105 0.1119 0.1133 0.1146 0.1167 0.1167	1.30 1.40 1.50 1.60 1.70 1.80	0.2437 0.2478 0.2512 0.25560 0.2595 0.2629	77.80 81.40 84.40 83.60 95.00	. •
0.1191 0.1188 0.1209 0.1222 0.1222	1.90 2.00 2.10 2.20 2.30	0.2670 0.2711 0.2746 0.2737 0.2821	98.60 102.00 104.80 109.00 112.20	
0.1229 0.1236 0.1256 0.1263 0.1256	2.40 2.50 2.50 2.70 2.80	0.2862 0.2910 0.2938 0.2979 0.3020	116.40122.00126.00131.40137.80	÷
0.1270 0.1277 0.1277 0.1277 0.1290	3.00 3.10 3.20 3.40 3.40	0.3096 0.3137 0.3171 0.3212	148.20 153.00 159.00 165.40	
0.1335 0.1393 0.1435 0.1449 0.1469 0.1510	5.10 6.40 3.30 10.40 12.50	0.3288 0.3329 0.3363 0.3405 0.3453	177.80 134.00 190.20 195.40 204.00	·
0.1551 0.1586 0.1634 0.1663 0.1702	14.90 16.30 20.20 22.80 25.20	0.3480 0.3521 0.3556 0.3597 0.3638	208.80 218.20 223.80 221.20 238.20	
0.1744 0.1778 0.1826 0.1860 0.1895	29.40 30.80 35.20 37.40 39.40	0.3672 0.3714 0.3755 0.3789 0.3837	244.60 254.60 261.40 270.00 274.60	

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. RUN **#** P440.

RATE	FRACTION	RATE	FRACTIO
0.14586	0.0310	0.00179	0.1937
0.12355	0.0450	0.00175	0.1976
0.11842	0.0568	0.00155	0.2015
0.09096	0.06/5	0.00154 0.00164	0.2055 0.2094 0.2131
0.03834 0.04305 0.03432	0.0973	0.00144 0.00138	0.2209 0.2247
0.02231	0.1078	0.00131	0.2327
0.02059		0.00108	0.2365
0.01545 0.01544 0.01201	0.1134 0.1146	0.00108	0.2402 0.2440 0.2479
0.01201.	0.1159	0.00113	0.2553
0.01030	0.1170	0.00111	
0.01030	0.1182	0.00111	
0.01373	0.1205	0.00113	0.2670
0.00686	0.1234 0.1242	0.00105	0.2785
0.00515	0.1253 0.1260	0.00082	0.2902
0.00343	$0.1264 \\ 0.1267 \\ 0.1274$	0.00073	0.3019
0.00534	0.1286	0.00065	0.309/
0.00446	0.1306		0.3136
0.00365	0.1329		0.3173
0.00294	0.1360	0.00061	0.3211
0.00232	0.1396	0.00063	0.3250
0.00195	0.1435	0.00061	0.3288
0.00136	0.1472	0.00065	0.3353
0.00139	0.1510	0.00063	0.3353
0.00168	0.1550	0.00061	0.3406
0.00153	0.1590	0.00056	0.3444
0.00147	0.1629	0.00053	0.3433
0.00121	0.1667	0.00053	0.3521
0.00136	0.1705	0.00054	0.3558
0.00127	0.1744	0.00057	0.3597
0.00129	0.1782	0.00051	0.3635
0.00151	0.1820	0.00052	0.3675
0.00149	0.1859	0.00047	0.3714
0.00189	0.1899	0.00055	0.3753







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TEMPERATURE = (1001.33 +/- 0.00) C

FR00093 000093 000093 000093 000093 00000000	TINE 000000000000000000000000000000000000	N 1029 80 1029 1029 80 1029 80 1029 1029 1029 1029 1029 1029 1029 102	TIME 7.60000000555500050500505000000000000000
0.2263 0.2301 0.2340 0.2386	4.80 5.20 5.80 6.60	0.4672 0.4718 0.4765	193.15 198.55 205.45

RUN- # F441

FRACTION 0.0397 0.00584 0.09761 0.10949 0.112361300.11344339 0.11352896007111344339 0.1155896000.119935755521500 0.1199357951215008905700000000000000000000000000000000	RATE 0.00474 0.00439 0.00439 0.000311 0.00031120 0.00037120 0.0001578 0.0001578 0.0001659 0.0001784 0.00016598 0.00016598 0.0001558 0.0001558 0.0001558 0.0001558 0.0001224 0.0001224 0.0001224 0.0001223 0.00010953 0.00010953 0.000009999 0.000009999 0.000000753 0.00000753 0.00000753 0.00000753 0.00000753 0.00000753 0.00000753 0.00000753 0.00000753 0.00000753 0.00000753 0.00000753 0.00000754 0.00000754 0.00000000000000000000000000000000000
$\begin{array}{c} 0.0764\\ 0.127613\\ 0.127613\\ 0.127613\\ 0.127613\\ 0.127613\\ 0.127613\\ 0.127613\\ 0.127613\\ 0.127633\\ 0.127835\\ 0.127835\\ 0.127835\\ 0.127835\\ 0.127835\\ 0.117835\\ 0.117835\\ 0.11995013555\\ 0.11995013555\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.1199501355\\ 0.119502333\\ 0.119502333\\ 0.119502333\\ 0.119502333\\ 0.119502333\\ 0.119502333\\ 0.119502333\\ 0.119502333\\ 0.119502333\\ 0.129233\\ 0.1292333\\ 0.129$	0.00411 0.003865 0.003171 0.003712 0.001570 0.001570 0.001180 0.0011770 0.0011890 0.00118490 0.0011870 0.0011870 0.0011870 0.0011870 0.0011800 0.0011800 0.00112240 0.00112240 0.00112240 0.000123400 0.000123400 0.000123400 0.000123400 0.000122400 0.000122400 0.000123400 0.000123400 0.000123400 0.000123400 0.000123400 0.000123400 0.00000000000000000000000000000000000







	IENFERMIORE	- (1002.13	+/- 0.01) L
FRACTION 0.0041 0.0041 0.004153 0.004153 0.004153 0.004153 0.004153 0.12476 0.1255139 0.12477 0.11789 0.1289 0.02000 0.00000 0.00000 0.00000 0.00000 0.00000 0.000000	TIME 0.10 0.20 0.340 0.50 0.50 0.50 0.50 0.50 0.50 0.50 0.	F R O O O O O O O O O O	TIME 000000000000000000000000000000000000

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TEMPERATURE

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B-28

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RAI2247766669300380760264285453446715095599845488784282 920000000000000000000000000000000000
FR006730000000000000000000000000000000000
RAI0006534153358655742203709573118710009888330498839883
DN 10 10 10 10 10 10 10 10 10 10 10 10 10







	RUN 🛊 P443	TEMPERATURE	= (1001.23	+/- 0.01 > 0
-	FRACO078 00.0078 50.0078 50.0078 50.0078 50.0078 50.0055 50.006 50.0055 50.006 50.005 50.006 50.0077 7770 1128 50.0000 50.00000 50.000000 50.00000000	TIME 0.600 0.89000000000000000000000000000000000	FRACTSCOLOGO 0000000000000000000000000000000000	TIME 41.300 458.300 668.400 557.0300 668.400 557.0300 668.400 557.0300 668.400 557.0300 668.400 557.0300 668.400 557.000 5000 5000 5000 5000 5000 5000

TEMPERATURE = (1001.23 + / -

0.01) C

III RATE 92 0.0019 93 0.0009 94 0.00112 97 0.00012 98 0.00112 97 0.000112 98 0.00012 97 0.00012 98 0.00012 97 0.00012 98 0.00012 97 0.00012 97 0.00012 98 0.00012 97 0.00012 97 0.00012 97 0.00012 97 0.00012 97 0.00012 97 0.00012 97 0.00012 97 0.00012 97 0.00012 97 0.00012 97 0.00000 97 0.00000 97 0.00000 97 0.00000 97 0.00000 97 0.00000 97 0.00000 97 0.00000 97 0.00000 <td>10410000000000000000000000000000000000</td>	10410000000000000000000000000000000000
如子曰:●● 如子曰 A 子 ●子子 A 子子子 A 子子子 A 子子子 A A A A A A A	IION RATE 92 0.00109 94 0.000112 97 0.000112 98 0.000112 97 0.000112 97 0.000112 97 0.000112 97 0.000112 97 0.000112 97 0.000112 97 0.000112 97 0.0001135 97 0.000112 97 0.000111 0.000110 0.000111 0.000111 0.000000 0.000111 0.000000 0.000000 0.000000 915 0.0000000 920 0.0000000 931 0.0000000 932 0.0000000 933 0.0000000 933 0.000000 933 0.000000 933 0.000000 933 0.000000

TION









TEMPERATURE = (999.89 + / - 0.02) C

ION 9







RUN 🛊 P445	TEMPERATURE	= (1001.23	+/- 0.01) C
F0000000000000000000000000000000000000	TIME 000000000000000000000000000000000000	N F R 0000000000000000000000000000000000	TIME 6.1234000000000000000000000000000000000000

2551446411307770267147368422319912606155698846216464 59944641133299522097933699997868846216464 1000000000000000000000000000000000	F0000000000000000000000000000000000000	RAI02039711 2932939971 39329729782782446655899783461148694255556714410000000000000000000000000000000000	
0.04323	0.5702		

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FRACTION 0.0000	T IME 0.00	FRACTION 0.2170	TIME 5.10	
0.0286	0.20	0.2246 0.2291	5.70	
0.0520 0.0625 0.0708	0.40 0.50 0.60	0.2321 0.2359 0.2404	6.30 6.70 7.00	
0.0776 0.0851 0.0919	0.70 0.80 0.90	0.2457	7.50 7.80 8.30	
	1.00	0.2577 0.2607 0.2652	8.90 9.50	
0.1145 0.1183	1.30	0.2698	10.70	
0.1243 0.1273 0.1326	1.50 1.60 1.70	0.2781 0.2818 0.2863	12.20 12.90 14.20	
0.1364 0.1394 0.1439	1.80 1.90 2.00	0.2909 0.2946 0.2992	15.20	. ·
0.1469 0.1492	2.10 2.20	0.3029 0.3074	19.00	
0.1575	2.40	0.3157	22.00 23.80 26.40	
0.1635 0.1688 0.1703	2.60 2.70 2.80	0.3248 0.3285 0.3323	27.90 30.50 32.80	
0.1711 0.1756 0.1763	2.90 3.00 3.10	0.3368 0.3406 0.3451	35.80 38.20 41.50	
0.1801	3.20 3.30	0.3496 0.3534	44.40	
0.1876 0.1884	3.50	0.3617	55.50	
0.1944	3.90	0.3745 0.37290	63.80 68.50 <u>7</u> 3.90	
0.1982 0.1997 0.2019	4.00 4.10 4.20	0.3828 0.3873 0.3911	78.00 85.10 90.30	
0.2019 0.2050	4.30	0.3956 0.4001	93.30 107.20	
0.2087	4.60	0.4084 0.4122	122.60 128.20	
0.2133 0.2148	4.90 4.90 5.00	0.4167 0.4205	141.30 149.10	

RUN P446 +

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RATE 0.08140 0.07586 0.05555 0.02255 0.02255 0.022590	FRACTION 0.0223 0.0311 0.0377 0.0429 0.0466 0.0493 0.0417	RATE 0.01295 0.01110 0.01295 0.01295 0.01295 0.01480 0.01480	FRACTION 0.0568 0.0580 0.0594 0.0607 0.0619 0.0632 0.0635
0.02220	0.0517	0.01110	0.0645
0.01665	0.0537	0.00925	0.0656
0.01665	0.0554	0.00925	0.0655

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<u>B-48</u>

RUN # P447	TEMPERATURE	= (1003.42	+/- 0.00) C	
FRACTIGN 0.0000 0.0133 0.0244 0.0333 0.0407 0.0437 0.0437 0.0466 0.0503 0.0518 0.05540 0.05555	TIME 0.00 0.20 0.30 0.40 0.50 0.60 0.50 0.60 0.70 0.80 0.90 1.10 1.30	FRACTION 0.0575 0.05999 0.05999 0.0636 0.0636 0.0659 0.06659 0.06681	TIME 1.40 1.50 1.60 1.90 2.30 2.30 3.20 4.60 5.20 7.10 10.00	

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B-49

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RUN # P448	TEMPERATURE	= (1001.65	+7- 0.02) C	
FROOTION CTION COOLIGA	TIME 0.100 0.120 0.000 0.11110 0.00000 0.11110 0.00000 0.11110 0.00000 0.11110 0.00000 0.11110 0.00000000	$ \begin{array}{c} \textbf{F} \textbf{O} \textbf{O} \textbf{O} \textbf{O} \textbf{O} \textbf{O} \textbf{O} O$	TIME 4.800 4.800 55555555555555555555555555555555555	

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RUN 🛊 P448







KUN # 1449	IENFERAIORE	= (1002.51	+/- 0.05 / L
FRACTION 0.0022 0.027152 0.005218 0.005218 0.00570 0.00570 0.00570 0.008929 0.0073629 0.009929 0.009929 0.009929 0.10814 0.111462 0.1122245 0.112228864 0.112228864 0.112228864 0.112228864 0.112228864 0.112333455877 0.113335577 0.113355974 0.1144542 0.1144552 0.1145552 0.114555557 0.1145555577 0.11455555555555555555555555555555555555	TIME 00.10 0.10 0.10 0.10 0.10 0.10 0.10 0.	N F F C C C C C C C C C C C C C	TIME 57000000000000000000000000000000000000

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B-56

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RUN # P449

RUN # P449

RATE 0.01758 0.01758 0.022691 0.0225918 0.0224998 0.0224998 0.0224998 0.0225919 0.0225918 0.0225918 0.0224998 0.0225919 0.0225919 0.0022591 0.00022770 0.00000000000000000000000000	IIGG9G17272803074173839524702570358136813 C455247025702580368146924702570358136813 A1155566677778888839999000011122222222 R00000000000000000000000
	RATE 0.01758 0.01758 0.022691 0.022591 0.022591 0.0224998 0.0224998 0.022591 0.022591 0.022591 0.022591 0.022591 0.022591 0.022591 0.022591 0.00022770 0.00000000000000000000000000

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RUN # P450

TEMPERATURE = (1002.12 +/- 0.01) C

P450 RUN 4

RATE 995600000000000000000000000000000000000	FR01796 00223358 00223358 00000000000000000000000000000000000	RATE 200 00529330000633700000000000000000000000000000	F0000000000000000000000000000000000000
0.00790 0.00693 0.00607	0.0581 0.0588 0.0595	0.00289 0.00141	0.0928 0.0936

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P-63

RUN # P451	TEMPERATURE	= (1003.31	+/- 0.01) C
F0000000000000000000000000000000000000	TIME 0.10 0.20 0.30 0.40 0.40 0.40 0.40 0.40 0.40 0.4	FRACTION 0.0787 0.0787 0.08131 0.08832 0.08832 0.08856 0.08856 0.08856 0.08856 0.08904 0.099121 0.099234 0.099359 0.099599 0.10043 0.0099599 0.10043 0.10043 0.10043 0.10043 0.10043 0.10043 0.10043 0.10043 0.11120 0.11120 0.11141 0.11141	TIME 000 03000 0300000000000000000000000







RUN # P452	TEMPERATURE	= (1091.50	+/- 2.84) C
F00002100000000000000000000000000000000	TIME 000000000000000000000000000000000000	N FR000000000000000000000000000000000000	TIME 1568000000000000000000000000000000000000

RUN

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P452

F 000000000 ŏ 0 Ó Õ Ô 0000 õ Ő Ō 0 Õ Ó ō 0 4665

RA 0. 00 0000 00 ō Ō 0 Ō 0 Õ 0

F0000000000000 0







RUR & FAUS	TENFERMIORE	- (1080./5	+/- 1./3)(
N F000000000000000000000000000000000000	TIME 0005000000000000000000000000000000000	F0000000000000000000000000000000000000	TIME 790100000000000000000000000000000000000

RUN \$ P453







RUN 🕈 P454	TEMPERATURE	= (1100.36	+/- 0.00) C
FRACTION AC0090 0.001878 0.0090 0.001878 0.0090 0.001878 0.0090 0.001878 0.0090 0.001878 0.0090 0.001878 0.0090 0.001878 0.0090 0.001878 0.0000000000000000000000000000000000	TIME 0.10 0.20000000000000000000000000000000	FR000000000000000000000000000000000000	TIME 2221000000555500000055000000550505050505

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RUN

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P454

 $\label{eq:static_stat$

 $\begin{array}{l} \text{N} \\ \text{IO} \\$







FRACTIO	N TIME	FRACTION	TIME	· ·
0.0000 0.0046 0.0137	0.00 0.30 0.40	0.1254 0.1282 0.1303	97.40 102.20 104.30	
0.0211 0.0270	0.50 0.60	0.1324 0.1352	106.40 112.40	
0.0323	0.70	0.1373	115.70	•
0.0411	1.00	0.1454	129.35	
0.0485	1.20	0.1493	138.05	
0.0523	1.40 1.50	0.1542 0.1566	145.55 149.15	
0.0569 0.0583	1.60	0.1591 0.1612	153.65	
0.0611	2.00	0.1665		
0.0622 0.0625	2.2ŏ 2.3ŏ	0.1717 0.1735	169.70 171.80	
0.0636 0.0643	2.40	0.1767 0.1791	172.55 174.95	
0.0653	2.80	0.1805	176.15 178.10	
0.0727 0.0727	5.10 6.90	Ŏ.1886 0.1904	101.55 182.60	
0.0748	10.80	0.1932 0.1949 0.1900	183.65	
	20.70 26.20	0.2002	187.40 189.65 191.60	
ŏ.ŏăć7 0.0892	32.90 39.60	ŏ.2ŏ4ĕ 0.2072	194.00 195.65	
0.0917 0.0945	43.20 45.40	0.2093 0.2118	196.55 198.65	
0.0966 0.0937	48.05 51.05 57.00	$0.2142 \\ 0.2170 \\ 0.2102$	200.60	
0.1036	62.75	0.2216	208.00 207.65 209.75	
0.1085 0.1110	69.65 73.85	0.2265 0.2286	211.40 212.90	
$0.1131 \\ 0.1155$	77.30 31.20	0.2311 0.2336	216.05 217.70	
$0.1180 \\ 0.1205 \\ 0.1225$	86.00	0.2360	225.05 226.10	
V.1227	93.30			

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RUN # P455







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FRACTION 0.0037 0.0165 0.02331 0.0462 0.0462 0.0555827 0.06573 0.06573 0.06573 0.06573 0.06573 0.06573 0.007744 0.007744 0.007745	TIME 0.00 0.70 0.80 0.90 1.00 1.20 1.20 1.30 1.40 1.50 1.50 1.50 1.90 2.00 2.00	FRACTION 0.1288 0.1288 0.1338 0.1359 0.1359 0.1359 0.1408 0.1433 0.1462 0.1433 0.1462 0.14508 0.15527 0.15527 0.1557 0.1631 0.16526 0.1657	TIME 1457000000000000000000000000000000000000	
0.000000000000000000000000000000000000	00000000000000000000000000000000000000	0.177792166161 177792466161 117792466161 117888691419999144680 0000000000000000000000000000000000	05000005500555005550005555005555555555	·

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RUN # P456

	7540730V	5. A 17 17	
RAIE	FRACTION 0 0159	KAIE O OOBBC	ERACTION 0 1200
0.03/16	0.0739	0.00324	0 1312
0.07433	ŏ.ŏ325	ŏ.ŏŏž71	ŏ.1335
0.06193	ŎĨŎ <u></u> ĴŎ	0.00275	Ŏ . Ĩ359
0.05471	0.0452	0.00237	0.1384
0.04543	0.0501	0.00272	0-1409
0.03717	0.0531	0.00173	0.1458
0.02994	0.0614	0.00146	0.1482
0.02994	0.0544	0.00151	0.1506
0.02891	0.0672	0.00138	0.1529
0.02271	0.0700	0.00109	0.1553
0.022/1	0.0744	0.000113	0 1604
0.01961	0.0764	ŏ.ŏŏŏ77	Ŏ.1 <u>Ğ</u> 28
0.01959	ŎĨŎŹ <u>Ŝ</u> Ă	0.00074	0.1652
0.01858	0.0803	0.00058	0.1676
0.01002	0.0819	0.00053	0 1723
0.01652	0.0354	0.00061	0.1747
0.01549	Ŏ . Ŏ <u>8</u> 70	0.00066	0.1771
0.01445	0.0884	0.00079	0.1796
0.01342	0.0899	0.00059	0.1820
0.01133	0.0977	0.00035	0 1868
0.01136	0.0932	0.00040	0.1892
0.00826	010942	0.00045	0.1916
0.00826	0.0951	0.00073	0.1941
0.00723	0.0958	0.00071	0.1966
0.00826	0.0974	0.00070	ŏ.2ōīŝ
0.00723	0.0982	0.00053	0.2039
0.01239	0.0353	0.00050	0.2063
0.01652	0.1009	0.00052	0.2087
0.02064	0 1048	0.00054	0 2136
0.02477	0.1073	0.00049	0.2160
0.02169	Ŏ . ĨŎ97	0.00039	0.2185
0.01137	0.1120	0.00031	0.2210
0.00606	V.1143 0 1167	0.00022	0.2234 0.2257
ŏ:ŏŏ472	ŏliiší	ŏ.ŏŏŏī́7	Ŏ.ŽŽĕí
0.00431	0.1216	0.00019	0.2305
0.00551	0.1240	0.00026	0.2329
0 11121120	11 1 / 5 4	11 LILLI / M	11







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0.0434 12.25 0.0822 51 0.0441 14.50 0.0833 53 0.0452 16.15 0.0844 34 0.0459 16.75 0.0851 56 0.0459 16.75 0.0851 56 0.0470 18.70 0.0858 58	DN 1001829453758637818530304582526775996741290 C00000000000000000000000000000000000	TIME 0020000000000000000000000000000000000	FRACC48955004255630459634123377829078523416 0.00000000000000000000000000000000000	т т т т т
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RATE 314538058585 131645580585585 00003335773365719032232323 00111897922122322324425 0000000000000000000000000000000000	ION ION ION ION ION ION ION ION			
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0.0798 0.0807 0.0815 0.0824 0.0833 0.0841

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F0.0078241 00078241 00078241 00078241 00078241 00078241 00078241 00078241 00078241 00078291675551 00078291675555 000000000000000000000000000000000	TIME 0.400 0.500 0.500 0.900 0.100 0.000 0.100 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.000000	FRACES 4600 29333244443554608879710079433542465788950000000000000000000000000000000000	T IME 771469253000055000550005500505005555555555555
00000000000000000000000000000000000000	177.30 300.00 227.30 227.30 3036.860 300 227.30 306.860 300 300 300 300 300 300 300 300 300 3	733554 7455186246 7555566572885572 7665572885572 76656666666666 7565572 766666666666	55555555555555555555555555555555555555

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0.05583	0.0188	0.00318	0.3348
0.10062	0.0283	0.00313	0.3419
0.08224	0.0468	0.00243	0.3556
8:87545	0.0548		0.3621
0.06289	0.0683	0.00225	0.3751
0.05901 0.05611	0.0748	0.00228	0.3815
0.05030	0.0861	0.00220	0.3948
0.04450	0.0954	ŏ.ŏŏźŏŝ	0.4079
0.03966	0.0998	0.00208	0.4147
0.03676	0.1097	0.00192	0.4282
0.03483	0.1154	0.00192	0.4350
0.02593	0.1285	0.00179	0.4485
0.02322 0.01879	$0.1349 \\ 0.1414$	0.00185	0.4550
0.01596	0.1480	0.00164	0.4683
0.01113	0.1609	0.00174	0.4816
0.00890	0.1676	0.00164	0.4886
0.00537	ŏ.1809 ·	0.00154	ŏ.5ŏĭ5
0.00438 0.00351	0.1875 0.1943	0.00146	0.5085
0.00222	0.2008	0.00144	0.5222
0.00221	0.2141	0.00140	0.5355
0.00215	0.2210	0.00132	0.5421
0.00201	0.2342	0.00134	0.5550
0.00204	0.2409	0.00133	0.5687
0.00217		0.00130	0.5754
0.00238	0.2675	0.00124	0.5889
0.00236	0.2742	0.00122	0.5954
ŎĴŎŎŹĂŎ	Ŏ.2877	ŏ.ŏŏižé	ŏ.ĕŏヺŎ
0.00234	0.3011	0.00129	0.6136
0.00231	0.3077	0.00117	0.6291
0.00241	0.3209	0.00124	0.6424
0.00291	0.3279	0.00105	0.6491





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F0.00000000000000000000000000000000000	TIME 0.300 0.400 0.500 0.500 0.500 0.100 0.000 0.100 0.000 0.100 0.0000 0.000000	FR.000000000000000000000000000000000000	TIME 55.600000000000000000000000000000000000
0.266739220 2266739220 222277530 200000000000000000000000000000000000	30000000000000000000000000000000000000	95989989263061598882112 3222844555778862988821150 35555555555555555566121223 455555555555555566121223 46666	49.00 6300 53.520 53.520 50 53.520 50 50 50 50 50 50 50 50 50 50 50 50 50

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RA107118 19119 19118 19119 191	$ \begin{array}{l} FR.00108\\ CI368\\ CI389\\ CI389\\ CI389\\ CI388\\ CI388$	$ \begin{array}{l} \text{RATE} \\ \text{O} & \text{O} $	$ \begin{array}{l} From Signature{} Signa$	

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FR.0009239266823550194264387132438738468130581100900000000000000000000000000000000	TIME 000000000000000000000000000000000000	N 1460655118894398650983216562198321984243172108087510839 146000000000000000000000000000000000000	TIME 55556000000000000000000000000000000000

TEMPERATURE = (1183.87 +/- 2.08) C







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RUN # P461	TEMPERATURE	= (1189.08	+/- 0.89 > C
F0.001578608024286977735559953731373979153179905313799355993 A0005578608024286977735555953731373979153179905313799355993 A0005578608024286977735555953731373979153179905313799355593 A000557868024286977735555953731373979153179905313799355593 A000557868024286977735555953731373979153179905313799355593 A000557868024286977735555953731373979153179905313799355593 A000557868024286977735555953731373979153179905313799355593 A000557868024286977735555953731373979153179905313799355593 A00055786802428697773555595373137399791533179905313799355593 A00055786802428609777355559537313739979153317990553137999355593 A00055786802428609777355559537313739979153317990553137999355593 A00055648802428609777355559537313739979153317990553137999355593 A000556488024286097773555595373137399791533179905531379993555593 A0005648802442860977735555959537313739979153317990553137999355593 A000564880244286097773555595937313739979153317990553137999355593 A00056488024428869977735555959373137399791553179905531379999355593 A0005648800000000000000000000000000000000	TIME 0.10 0.20 0.450000000000000000000000000000000000	$ \begin{array}{c} FR \\ C \\ $	TIME 5.200 55.400 55.500 50.0000 50.0000 50.0000 50.0000 50.0000 50.0000 50.0000 50.0000 50.0000 50.0000 50.0000 50.00000 50.000000 50.0000 50.0000 50.000000000 50.000000

$\begin{array}{l} \text{RATE} \\ \textbf{500} \\ \textbf{5175463553342321} \\ \textbf{51756553533423321} \\ \textbf{51756553533423321} \\ \textbf{51756553533423325551} \\ \textbf{51756553533423355551} \\ \textbf{51756553533423355551} \\ 517565555555555555555555555555555555555$	FR000000000000000000000000000000000000	RATE 0.01751 0.01050 0.01401 0.00700 0.01400 0.01400 0.01400 0.01541 0.009139 0.000326 0.0002889 0.0002889 0.0002885 0.0002885 0.0002885 0.00012855 0.000012855 0.00012855 0.00012855 0.00012855 0.00012855 0.0000000000000000000000000000000000	$ \begin{array}{l} F_{0} = 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0$

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B-107

TEMPERATURE = (1175.84 +/- 1.75) C

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
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RUi	N :	ŧ	₽ı	4	G	2
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R0000000000000000000000000000000000000	FR010N 005747 000747 000747 000747 000747 000123356665260 0011235666552660 001123556665552667 001123556665552667 0011223545566677778888323730407 1718 88899901122344555667777888899901123455320977896 000000000000000000000000000000000000	RATE 940 0.002280 0.002280 0.0002260 0.00002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.0002260 0.00002260 0.00002260 0.0000000000	FRACTION 0.443482 0.445752 0.445752 0.445752 0.445752 0.445752 0.445752 0.445752 0.445752 0.445752 0.4457552 0.4457552 0.455552 0.455552 0.455552 0.455552 0.455552 0.455552 0.455552 0.5555552 0.5555555555
0.00363	0.3961	0.00369	0.8203
0.00363	0.4048	0.00312	0.8279
0.00307	0.4131	0.00316	0.8362
0.00325	0.4218	0.00300	0.8446

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RUN # P463 TEMPERATURE = (1189.94 +/-1.73) C

F0000000000000000000000000000000000000	TIME 000000000000000000000000000000000000	FRAC13099593466044000777715193399664455562693045339361777 00033009959300330013122222277771519339966445556269300000000000000000000000000000000000	TIME 55555560000000000000000000000000000000
0.0305	4.90	0.0401	33.60

RATE FRACTION RATE FRACT 0.02391 0.0032 0.00000 0.030	NOI S
)4)5
	5
0.01471 0.0166 0.00092 0.030	7
0.00827 0.0190 0.00368 0.031	2
0.00736 0.0198 0.00276 0.031 0.00736 0.0205 0.00184 0.031	.6
0.00736 0.0212 0.00184 0.031 0.00644 0.0219 0.00000 0.032	8 20
	20
0.00552 0.0236 0.00000 0.032	
0.00368 0.0248 0.00092 0.032	4
0.00460 0.0258 0.00184 0.032	7
0.00276 0.0263 0.00184 $0.0330.00000$ 0.0263 0.00092 0.033	30
00184 0.026300460 0.032 00092 0.026200460 0.032	27
00276 0.026000552 0.032 0.00368 0.026100552 0.031	20
0.00368 0.0264 0.00184 0.031 0.00460 0.0268 0.00074 0.031	2
0.00276 0.0270 0.00123 0.031 0.00276 0.0275 0.00147 0.031	. G I B
	23
0.00552 0.0281 0.00050 0.033	32
0.00092 0.0285 0.00040 $0.0330.00276$ 0.0287 0.00023 0.034	
0.00184 0.0288 0.00027 0.034 00184 0.0288 0.00017 0.034	14 17
0.00276 0.0290 0.00032 0.035 0.00276 0.0293 0.00019 0.035	50 - 55
0.00368 0.0295 0.00030 0.036 0.00460 0.0298 0.00042 0.036	50 57
0.00276 0.0303 0.00039 0.037 0.00184 0.0306 0.00184 0.037	73 77
	30
	36
	33







FR.000000000000000000000000000000000000	TIME 000000000000000000000000000000000000	FR000000000000000000000000000000000000	TIME 55555600000000000000000000000000000000
0.0475	5.00	0.0741	65.80
0.0482	5.10	0.0741	66.10

RA000000000000000000000000000000000000	$ \begin{array}{c} FR.0014940\\ 0.00123721572153328817992227924\\ 0.001222223324588917992227923570233458891799222793339399517224\\ 0.00222233345889979922279244412222233539951786\\ 0.00000000000000000000000000000000000$	RA TE 00000000000000000000000000000000000	FR.000000000000000000000000000000000000	
0.00180	0.0479	0.00034	0.0730	

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FR.00121666785241248209827160993345014036940584194001111 AC00121666785241248209827160993345014036940584199902447111 AC0020000000000000000000000000000000000	TIME 000000000000000000000000000000000000	$ \begin{array}{c} FR \\ 0.12003228 \\ 0.22003332 \\ 0.22003332 \\ 0.220033334 \\ 0.22033334 \\ 0.220333333 \\ 0.220333333 \\ 0.2203333 \\ 0.220333 \\ 0.2203333 \\ 0.2203333 \\ 0.2203333 \\ 0.2203333 \\ 0.2203333 \\ 0.2203333 \\ 0.2203333 \\ 0.2203333 \\ 0.2203333 \\ 0.220333 \\ 0.220333 \\ 0.220333 \\ 0.220333 \\ 0.220333 \\ 0.220333 \\ 0.220333 \\ 0.220333 \\ 0.220333 \\ 0.22033 \\ 0.22033 \\ 0.20$	TIME 5.200 55.300 55.600 55.1000 50.000 55.1000 50.000 55.1000 55.1000 55.1000 55.1000 55.1000 55.1000 55.1000 55.1000 55.1000 55.1000 55.1000 55.1000 55.1000 55.1000 55.0000 55.0000 55.0000 55.0000 55.0000 55.0000 55.00000000

1548973730368436144466976442797775222295990 454848973798002444444669764427977752223933455635390 0000000000000000000000000000000000	FR010226 0.023337 0.0066552748 0.0066552748 0.0066552748 0.00066552748 0.00000000000000000000000000000000000	RATE 0.007762827 0009978204009999999999999999999999999999999999	FR.2200458080051186530752985307430732944385284533074496F A2202408880051186530752985307430732944385288453307147122282800755488530711482355555 00000000000000000000000000000000
0.01155	0.2000	0.00053	0.3633

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FRACTION 0.0112 0.0241 0.0378 0.05335 0.05355 0.05457 0.05457 0.09326 0.09326 0.11264 0.1250 0.1255 0.1479 0.144955 0.14796 0.144965 0.147981 0.15625 0.1670381	TIME 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.4	FRACTION 0.2299522 0.3312428446 0.23955288446 0.332844666888 0.0000000000000000000000000000000	TIME 13.7770000000000000000000000000000000000
0.183404 183404 183404 1992436 199248 199248 199245 19925 19925 19925 19925 19925 19925 19925 19925 19925 19925 19925 19925 19925 19925 199555 199555 199555 199555 199555 199555 199555 199555 199555 1995555 199555	20000000000000000000000000000000000000	$\begin{array}{c} 0.42224\\ 0.43276\\ 0.44376\\ 0.44388\\ 0.443888\\ 0.445620\\ 0.445620\\ 0.44783922\\ 0.447839222\\ 0.4478895224\\ 4478895224\\ 447839222\\ 0.4555555555\\ 0.5555555555\\ 0.55555555555\\ 0.5555555555$	670694960000055555555555555555555555555555
RAIE 0.07614 0.133895 0.112895 0.112895 0.110312 0.09241 0.09525 0.00555 0.00773807 0.00559 0.00559 0.00559 0.00559 0.00559 0.00559 0.00559 0.00559 0.00559 0.00559 0.00559 0.0052 0.00559 0.00559 0.0052 0.0052 0.00559 0.0052 0.0052 0.00559 0.0052 0.00559 0.0052 0.0052 0.0052 0.00559 0.0052 0.0052 0.0052 0.00559 0.0052 0.00000 0.00000 0.00000 0.00000 0.00000 0.000000	FRACTION 0.0253 0.0382 0.0511 0.00744 0.00744 0.00744 0.00744 0.00744 0.00744 0.11192 0.11192 0.11192 0.11192 0.11267 0.114617 0.11267 0.114617 0.1155613 0.144617 0.1155613 0.144617 0.1155613 0.144617 0.1155613 0.1147484 0.11556226 0.1147484 0.115778 0.11887966220023389 0.120024389 0.11202317650 0.112022222222222 0.120024389 0.1200244 0.12569 0.1200244 0.12569 0.1	RATE 0.00508 0.00484 0.00457 0.00457 0.00393 0.00329 0.003294 0.002298 0.002298 0.002298 0.002298 0.002298 0.002275 0.002233 0.002233 0.002233 0.002233 0.002233 0.002233 0.0001889 0.0001227 0.0001279 0.0001279 0.0001279 0.0001277 0.0001227 0.0001227 0.0001227 0.0001227 0.0001110 0.0001112 0.0001112 0.0001112 0.0001091 0.0001195 0.0001091 0.0000000000	F0.00000000000000000000000000000000000
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0.00749 0.00768 0.00749 0.00663 0.00595 0.00595	0.2656 0.2656 0.2711 0.2769 0.2828 0.2883	0.00077 0.00077 0.00070 0.00056 0.00058	0.5426 0.5420 0.5533 0.5591 0.5591 0.5643







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F0000000000000000000000000000000000000	TIME 03400000000000000000000000000000000000	N FR000000000000000000000000000000000000	T IME 000000000000000000000000000000000000
0.2255 0.2305	8.90 9.60	0.4594	228.30

RA000000000000000000000000000000000000	FRACTION 0.0165 0.0253 0.03431 0.0510 0.0584 0.05584 0.05584 0.07179 0.08377 0.08377 0.08377 0.099591 0.0099591 0.0099591 0.10336 0.099591 0.1123701 0.112336 0.11336 0.11336 0.11336 0.114471 0.11556932 0.1259923 0.11556 0.11556 0.11556 0.11559 0.11559 0.11559 0.1159935 0.1155932 0.1159935 0.1155932 0.1159935 0.1155932 0.1159935 0.1155932 0.1159935 0.1155932 0.1155932 0.1159935 0.1155932 0.1159935 0.1155932 0.1159935 0.1155932 0.1159935 0.1155932 0.1159935 0.1155932 0.1159935 0.1155932 0.1155	RATE 0.004229 0.0003295 0.0003295 0.0003295 0.0003295 0.0003395 0.0003395 0.00032219 0.0003395 0.00032219 0.00032219 0.0003395 0.00032219 0.00000000000000000000000000000000000
0.01548 0.01478 0.01161 0.01043 0.008855 0.00771 0.00779 0.00739 0.00563	0.1944 0.1990 0.2035 0.2081 0.2126 0.2170 0.2216 0.2262 0.2305	0.00075 0.00077 0.00083 0.00078 0.00075 0.00075 0.00075 0.00075 0.00053 0.00053

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.. B-131 TEMPERATURE = (1192.33 +/-1.26) C

F0.00000000000000000000000000000000000	TIME 000000000000000000000000000000000000	F 0 0 0 0 0 0 0 0 0 0 0 0 0	TIME 100 100 13457400000000000000000000000000000000000
0.3196 0.3196 0.3199 0.3226 0.3468 0.3468 0.3525 0.3695	5.20 5.20 6.00 7.00 7.80 8.40 9.30 10.10 10.90	0.6785 0.6935 0.6935 0.7084 0.7154 0.7233 0.72373 0.7373	171.20 171.20 178.00 186.40 194.80 202.40 219.60 226.00 264.00 284.00

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755535611269113332437252443767909014782610285170251 6000000000000000000000000000000000000	FRACES 0.0056522999584 0.00565677799584 0.005677799584 0.005677799584 0.111234155642958822370659826685096079668899958 0.11123415567889628495556566777889641852997469 0.111234555666777889641852997469 0.111234555666777889641852997469 0.111233455666777889641852997469 0.111233455666777889641852997469 0.111233455982237 0.1112334555982237 0.111233455982237 0.111233455982237 0.111233455982237 0.111233455982237 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344998357 0.111233344988498 0.111233344988498 0.111233344988498 0.111233344988498 0.111233344988498 0.11123344988498 0.11123344988498 0.11123344988498 0.11123344988498 0.11123344988498 0.11123344988498 0.11123344988498 0.11123344988498 0.11123344988498 0.11123344988498 0.11123344988498 0.11123344988498 0.1112344888498 0.111234498844988449884498844988449884498778888498844888448977888844987888484888488	$ \begin{array}{l} \hbox{RATE} \\ \hbox{0.006425} \\ \hbox{0.00659520} \\ \hbox{0.0004550} \\ \hbox{0.0004550} \\ \hbox{0.0004550} \\ \hbox{0.0004538} \\ \hbox{0.0004538} \\ \hbox{0.0004538} \\ \hbox{0.0004538} \\ \hbox{0.0004538} \\ \hbox{0.00033880} \\ \hbox{0.00033880} \\ \hbox{0.00033880} \\ \hbox{0.000332880} \\ \hbox{0.0003322867} \\ \hbox{0.000332880} \\ \hbox{0.0003322867} \\ \hbox{0.000332880} \\ \hbox{0.0003322867} \\ \hbox{0.000322212170} \\ \hbox{0.00032221211097726585} \\ \hbox{0.00032221211097726585} \\ \hbox{0.00031132110977265859} \\ 0.00000000000000000000000000000000000$	$\begin{array}{l} FR & 0.101 \\ 0.$	







TEMPERATURE = (1160.80 +/+ 1.61) C

F0.00000000000000000000000000000000000	TIME 0.100 0.125000 0.125000 0.12500000000000000000000000000000000000	FRACTION 0.06646 0.06553 0.06553 0.06656 0.066536 0.066536 0.066536 0.066536 0.066536 0.066536 0.0066537 0.0077776 0.0077776 0.00888 0.008888 0.0088888 0.0000000000	TIME 34000000000000000000000000000000000000
0.00519999 005919999 005519999 005619999 005619999 005619999 00561999 00561999 0056199 00561999 0056199 0056199 0056199 005649 005640 005640 005640 005640 005640 00500 005640 00500 005640 005000 00500 000000	30000000000000000000000000000000000000	0.0821 0.08221 0.084482 0.088482 0.08868892 0.08868892 0.08858892 0.099229 0.099229 0.099299 0.09949 0.09949 0.099969 0.099969 0.09996 0.009996 0.00996 0.0000000000	4444456666667777778888888888888888888888

R0003454426 0007554426 0007554426 0007554426 0007554426 0007554426 0007554426 0007554426 0007554426 0007554426 0007554426 00075545 00075545 00075545 000000000000	FRACTION 0.00945 0.001410 0.002767 0.0027278 0.0023368 0.00423429 0.004244659 0.00423429 0.00424451233320 0.00424459 0.00424459 0.00425 0.00425 0.004234 0.00424459 0.00425 0.00555233450 0.0055555555555555555555555555555555	RATE -0.001687 0.001687 0.0001357 0.0001357 0.0001357 0.0001357 0.0001357 0.0001357 0.0001357 0.0001357 0.0001357 0.0001357 0.0001357 0.0001357 0.0001357 0.0001357 0.0000557 0.00011087 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000557 0.0000000000	FR.0665506649923309543322112010900000000000000000000000000000







RUN # P470 TEMPERATURE = (1192.05 +/- 1.92) C

FRACTION	TIME	FRACTION	TIME
0.0000 0.0112	0.00	0.0775 0.0772	5.20 5.30
0.0214 0.0302	0.30	0.0782	5.50 7.20
0.0375	0.50	0.0814	9.30
0.0477	0.70	0.0838	12.70
0.0561	0.90	0.0870	16.80
0.0603	1.10	0.0926	20.40
0.0614 0.0632	1.20 1.30	0.0923 0.0940	22.60 26.80
0.0628	1.40 1.50	0.0961 0.0975	27.30 28.20
0.0546	1.60	0.1098	33.10 37.30
0.0660 0.0674	1 00		37.40
	2.00	0.1038	42.00
0.0705	2.20	0.1063	47.60
0.0691	2.40	0.1284	59.40
0.0705	2.50 2.50	0.1123	64.10 65.10
0.0709	2.70	0.1133 0.1151	72.50 75.00
0.0709 0.0712	2.90	0.1358 0.1132	75.40 80.50
0.0712	3.10 3.20	0.1193 0.1210	83. 10 85.90
Č10723 010726	3.30 3.40		
ő.ő726	3. ŚŎ	0.1260	93.7 <u>0</u>
0.0744	3.00	0.1284	102.30
0.0747	3.20	0.1209	103.60 106.90
0.0754 0.0740	4.00 4.10	0.1326 0.1340	108.00 113.20
0.0740 0.0751	4.20 4.30	0.1354 0.1368	116.20 113.60
0.0758 0.0751	4.40 4.50	0.1386 0.1400	124.00 124.30
0.0754 0:0758	4.60	0.1438	130.40 130.50
0.0761	4.80	0.1445	
0.0751 0.0768	5.00	0.1470	139130
e e e z e e e			

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89868670485929995370584055881111965656988881578857858 50572495785268099537058570588107888511196565698888855786780 E786554691122297778855746850810788855558292988885578857858 A00000000000000000000000000000000000	FR000000000000000000000000000000000000	RATE 0.000194 0.000194 0.00008454400000000000000000000000000000	FROC.0088348638650740344442504949393939405587.4595095159 0.0088834880235507403444425049493939405582.4595095159 0.008888899999999999900001111111111222224458899995000000000000000000000000000000

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TEMPERATURE = (1160.48 +/- 1.60) C

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	RΙ	UN.	#	۲·	4	7	1	
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RA052449259999131313434346876778997889788997889780000000000000000	FR.0015121 00000000000000000000000000000000	RATE 0.00110 0.000767 0.000329 0.000548 0.000558 0.000219 0.0002268 0.0002268 0.00002268 0.000002268 0.00000737 0.00000732 0.0000002268 0.00000000000000000000000000000000000	FR.000000000000000000000000000000000000
0.00577 0.00548 0.00329 0.00438 0.00110	0.0849 0.0855 0.0860 0.0862 0.0867	0.00038 0.00032 0.00038 0.00029	0.1263 0.1276 0.1289 0.1302







F0000000000000000000000000000000000000	TIME 000000000000000000000000000000000000	R.000000000000000000000000000000000000	00000000000000000000000000000000000000
0.07752007755200000000000000000000000000	3333344444444 3333334444444 4444444 444444	0 1 1 1 1 1 1 1 1 1 1 1 1 1	505505055555000055505050 60250030458839640495887 945667888946836284789589 9456678889990041120445529 11111111111111111111111111111111111

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0999158365018818827500587805350082828707034412866 75924427583650170041252005878053500828287070344242870 7522242255324427589004125202534545486505357645486500000000 20000000000000000000000000000	FRONCON RAC1156 0.002341607779996133421864519738740640415944642232117 0.002000000000000000000000000000000000	RADOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO	FR.1007966787977480676531843348899011444456567888999013 000000000000000000000000000000000

APPENDIX B3

PRETREATED SORBENTS IN SO2







- 1

TEMPERATURE = (1101.25 +/- 0.01) C

TIME
IO63723005188027160596059482796605938274882796069182719 IO6372300518802716059605972661504827786150382748827960691827 IO637230051880278889999000112008369378615038027494403800 IO637230518802788899990001120083693786155638027494103800 IO637230518807788899990001120083693786155638027494103800 IO6372305188077888999900011200836937861556380074901011403800 IO637230518807880000000000000000000000000000000

1

RATE	FRACTION
0.03316 0.06107 0.05736 0.05367	0.0215 0.0272 0.0330
0.04811	0.0380
0.04811	0.0429
0.04442	0.0474
0.04071	0.0558
0.03146	0.0594
0103516	0.0628
0.02961	0.0660
0.02591	0.0688
0.02961	0.0715
0.02591	0.0745
0.02369	0.0773
0.02221	0.0808
0.01548	0.0885
0.01366	0.0928
0.01018	0.0928
0.00772	0.1014
0.00597	0.1060
0.00413	0.1104
0.00306	0.1149
0.00177	ŏ.1193
0.00177	o.1238
0.00154	o.1281
0.00139	0.1325
0.00138	0.1369
0.00135	0.1412
0.00142 0.00146 0.00151 0.00157	0.1498 0.1541 0.1584
0100163	0.1628
0.00174	0.1673
0.00172	0.1717
0.00189	0.1762
0.00199	0.1808
0.00208	0.1953
0.00197	0.1898
0.00200	0.1942
0.00203	0.1987
0.00203	0.2030
0.00214	0.2073
0.00222	0.2117
0.00203	0.2160







FRACTION FRACTOCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	0000000000000000000000000000000000000	FRACTION 0.113402086427864208643407553197531975346756197534 0.11445555561466925803693470036814702058649555566667777888899990000111470202020000000000000000000000000	TIME 000000000000000000000000000000000000
0.1276 0.1297 0.1325	41.50 46.50 51.20	0.2521 0.3318	

RUN 4 P474

E 4006	FRACTION
4006 6658	0.0203
5783	0.0264
4906 9694	0.0318
2979	0.0395
2979	0.0426
2629	0.0456
2804 2628	0.0482
2629	0.0536
1752	0.0555
1752	0.0593
1402	0.0611
1928	0.0625
1928	0.0646
1402	0.0678
1927	0.0697
1402	0.0728
1402	<u>0.0239</u>
0561 0701	0.0751
č57 4	ŏ.ŎŹŹŔ
0657	0.0799
0534	0.0851
0561	0.0879
0401	0.0910
0200 0267	0.0963
0193	0.0001
0122	0.1019
0107	0.1074
0088	0.1102
ŎŎŹŹ	ŏ.115š
0067	0.1135
0089 0057	0.1214
ŏŏš9	ŏ.1275
0064	0.1298
0005	Q.1335






RUN # P475	TEMPERATURE	= (1103.29	+/- 0.10) C
N 10	TIME.000000000000000000000000000000000000	F0000000000000000000000000000000000000	TIME 9000000000000000000000000000000000000

B-161

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RUN # P475

26769187740171477707074340473730 122242011400001095648360473736 1000000000000000000000000000000000000	FRACTION 0.00116755 0.001167246730642007463393911471366677770 0.00000000000000000000000000000	923246576855522610323984576032859 1000000001108775522610451032884576000000000 R0000000010087756888500000000000000000000000000000
0-000007477052556331 0-0000000000000000000000000000000000	00000000000000000000000000000000000000	00000000000000000000000000000000000000

B-162

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RUN # 9476

TEMPERATURE = (1199.90 +/- 0.02) C

00000000000000000000000000000000000000
00000000000000000000000000000000000000
N R000000000000000000000000000000000000
TI
N 106839951447949814366905784708580150047785706568087019 106839551447949814366905784708580050047880760864497819 1002444563897404878771403084456878995400477857680864497819 10002444568899514479498148687899540074807480768086498868998 100024455678889044141986905784708580057480748007480847888 10000000000000011111111111111111111

2455992275709429964647572828076948466449 110876543120018840611929119407185555951 111099876543120018810611929119407185555951 11109987775655955566000000000000000000000000000	
43456468884450 000077777770575884455 00000000000000000000000000000000	

 $\begin{array}{l} \mathsf{N} \\ \mathsf{ID} \\$





B-167

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XUN # 14//	IEMPERATURE	= (1199.95	+/- 0.00) C	
N 104 104 104 104 104 104 104 104 104 104	Т I ME 0000000000000000000000000000000000	N DN DN DN DN DN DN DN DN DN DN DN DN DN	00000000000000000000000000000000000000	

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RUN 🛊 P477

044441516871719999774448280500000000000000000000000000000000	FR0100000000000000000000000000000000000	ROIDE 80001418321325404380078509501469014098046 F0000000000000001439921486000000000000000000000000000000000000	DN 17 17 17 17 17 17 17 17 17 17 17 17 17
00011111111111111111111111111111111111	00074 100274 100251 00010087 1007 100	0.00058 0.00058 0.00054 0.00054 0.00054 0.00054 0.00054 0.00054 0.00054 0.00054 0.00054 0.00054 0.00054 0.000545 0.00044	0048534040000404 10500344490500404 447420305054449055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 44742055554 4474555554 447555554 44755554 447555554 447555554 4475555554 44755555554 44755555554 44755555554 44755555554 44755555554 44755555555





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RUN # P478

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TEMPERATURE = (1198.97 +/- 0.09) C

N 105942561744283188489147200775575844686841494949797740 10594256174428318848914720077557584468684144949797740 108659425617442883188489147200775575844868684144949797788 108000000000000000000000000000000000	00000000000000000000000000000000000000	N 10002000775555781118161441974078808419440758046346720758 100020007755557811181614440758004845467290 A00000066611102038808666666665777777777777777788888888888	UNE 566666666667777777777777777777826670000000000
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R	11	ы	4	٢	4	7	8
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56215019913399297917949474022479442474902404229 362215019977911771757667657686999876889878602404229 474622197791117717579578858780999876889878602404229 47000000000000000000000000000000000000	N HO HO HO HO HO HO HO HO HO HO HO HO HO	RATE 1900024444220760714424277244499000295879902770 90000133889009888990075502441249666322449912688979902770 000000000000000000000000000000	N 159801469225843711483000776765441010098659490210098 1999900000000000000000000000000000
0.00192 0.00769 0.00577 0.00577	0.0577 0.0581 0.0587 0.0587 0.0592	0.00077 0.00073 0.00073	0.0898 0.0898 0.0907

APPENDIX B4

UNTREATED SORBENTS IN H2S







FRACTION 0.0000 0.0361 0.0271 0.0391 0.0391	TIME 0.00 0.10 0.50 0.60	FRACTION 0.6111 0.6292 0.6412 0.6382	TIME 7-10 7-30 7-90
0.0753 0.0723 0.0873 0.0993 0.1114 0.1264 0.1385	0.80 0.90 1.10 1.20 1.30 1.40	0.6593 0.6713 0.6864 0.7014 0.7075 0.7225	8.10 8.20 8.30 8.60 8.70 8.90
0.1535 0.1776 0.1927 0.2017 0.2047 0.2077	1.50 1.60 1.70 1.80 1.90 2.00 2.10	0.7316 0.7496 0.7556 0.7677 0.7857 0.7857 0.7918 0.8098	9.00 9.50 9.70 9.90 10.40 10.50 10.50
0.2435 0.2435 0.2649 0.2770 0.2770 0.2920 0.2920	2.20 2.40 2.50 2.70 2.80 3.00 3.10	0.8189 0.8309 0.8429 0.8490 0.8610 0.8821 0.8911	10.80 10.90 11.10 11.30 11.90 12.20
0.3071 0.3312 0.3312 0.3432 0.3552 0.3733 0.3733 0.3823	3.20 3.30 3.40 3.50 3.60 3.60 3.60 3.80	0.9152 0.9152 0.9212 0.9363 0.9453 0.9453 0.9603	13.10 13.30 13.40 13.70 13.80 14.20
0.3884 0.4034 0.4185 0.4185 0.4265 0.4265	4.20 4.50 4.50 4.50 4.50 4.50	0.9814 0.9815 1.00055 1.0200 1.0296 1.0416	14.40 14.60 14.80 14.80 15.30 15.30 16.80 17.10
0.4907 0.4907 0.4937 0.5058 0.5419 0.5509	000 000 000 000 000 000 000 000 000 00	1.0567 1.0717 1.0778 1.0958 1.1018 1.1139 1.1259	17:50 18:00 18:20 19:20 19:20
0.5539 0.5539 0.5539 0.5720 0.5840 0.5870	500 6.30 6.50	1.1380 1.1500 1.1621 1.1741 1.1861	22.70 26.70 27.00 32.10 35.80

RATE 0.07741 0.05591 0.1289 0.09634 0.09031 0.07225 0.10838 0.12796 0.13557 0.16557 0.16559 0.15804 0.12796 0.12796 0.07526 0.005773 0.005773 0.08429	FRACTION 0.0313 0.04636 0.0656 0.06577 0.08993 0.11258 0.1258 0.1258 0.1415 0.1578 0.1578 0.1578 0.1578 0.1969 0.2056	RATE 0.03553 0.034635 0.033345 0.033345 0.108028 0.007311 0.064511 0.04511 0.0387 0.03817 0.03871 0.03871 0.03871 0.03871 0.03871	FRACTOS 0.6214 0.62146 0.63442 0.663422 0.667452 0.667452 0.667452 0.667452 0.70999 0.72234 0.74580 0.75801
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RUN # P481

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RUN # 484

TEMPERATURE = (1104.04 +/- 0.08) C

FRACTION 0.0000 0.0111 0.0221 0.0300 0.0411 0.04905 0.05856 0.00770 0.05856 0.00770 0.0991 0.10555 0.10555 0.10555 0.112641 0.112661 0.11256 0.11256 0.11255 0.000 0.1222 0.000 0.1222 0.000 0.000 0.11255 0.000 0.12222 0.000 0.12222 0.000 0.12222 0.000 0.000 0.000 0.0000 0.0000 0.0000 0.0000 0.00000 0.000000	TIME 0.500 0.590 1.700 0.590 1.700 7.700 3.000 4.500 4.500 4.500 5.5000 5.5000 5.5000 5.5000 5.5000 5.5000 5.5000 5.5000 5.5000 5.5000 5.5000 5.5000 5.5000 5.5000 5.5000 5.50000 5.5000 5.5000 5.50000 5.50000 5.500000000	FRACTION 0.4918 0.509032 0.552287238 0.55557238 0.55557238 0.55557238 0.55557238 0.5555789558 0.55597627 0.55599558 0.55599558 0.662353726 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.662353221 0.722722 0.723120 0.72596	TIME 21.600 2222.3334.99600000 2222.3334.99600000000000000000000000000000000000
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RATE 0.02419 0.02538 0.02538 0.02538 0.02538 0.02636 0.022536 0.022536 0.022536 0.022538 0.0022538 0.0022538 0.0022538 0.0022538 0.0022538 0.0022538 0.0022538 0.00225538 0.002225538 0.0022198 0.002298 0.002298 0.002298 0.002298 0.002298 0.002298 0.002298 0.002298 0.002298 0.0029977 0.0029977 0.0019977 0.0019977 0.0019977 0.0019977 0.0019977	FRACTION 0.0209 0.0307 0.0402 0.0497 0.0591 0.0683 0.0781 0.08824 0.0974 0.1067 0.11267 0.12657 0.12657 0.12657 0.12553 0.14553 0.15559 0.15559 0.12657 0.12657 0.12657 0.12657 0.12657 0.12657 0.12553 0.15559 0.12657 0.12655 0.12558 0.12657 0.22150 0.23150 0.2315550 0.2315550 0.23155550 0.2315550 0.2315550 0.23155550 0.23155500 0.23155500 0.231555000 0.2315550000000000000000000000000000000000	RATE 0.01732 0.01719 0.01732 0.01582 0.01582 0.01582 0.01582 0.01582 0.01582 0.01582 0.015521 0.01582 0.015521 0.01460 0.01460 0.01460 0.01460 0.014557 0.01359 0.01359 0.011359 0.011359 0.011268 0.011268 0.011359 0.011268 0.011054 0.011058 0.011058 0.011058 0.011058 0.011058 0.011058 0.011058 0.011058 0.011058 0.011058 0.011058 0.011058 0.0019949 0.0008863 0.0008863 0.00055055 0.000719 0.000885 0.000719 0.000885 0.000719 0.000885 0.000719 0.0006538 0.0005505 0.0005505 0.0005505 0.0005505 0.0005505 0.0005505 0.000550 0.00000000	FR.45515386427508380565319750594616197564949194830 C900000000000000000000000000000000000
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KUN # 485	RUN	ŧ	485
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0.2234	25.90	ŏ.4659	182.40
0.2276	26.70	o.4702	188.80
0.2340	28.10	o.4755	197.00
0.2383	29.20	o.4946	232.90

RUN # 485

RATE 0.01216 0.01216 0.01216 0.01507 0.01684 0.01444 0.01477 0.011477 0.011326 0.0112276 0.0112276 0.0112276 0.0112276 0.011229 0.011229 0.011229 0.011229 0.011229 0.011229 0.011229 0.011229 0.011068 0.0019962222 0.00099652 0.000996528 0.0007779 885973 0.000055987 0.000055987 0.000055987 0.000055987 0.000055987 0.000055987 0.00055987 0.00055548 0.00000000000000000000000000000000000	FRACTION 0.0111 0.0162 0.0204 0.0253 0.0355 0.0355 0.03455 0.04552 0.04552 0.04552 0.05500 0.05551 0.06492 0.05556 0.06492 0.07556 0.06499 0.07556 0.00999554 0.00999554 0.00999554 0.111942 0.12291 0.112491 0.112491 0.1159409 0.115982 0.1110 0.11223 0.1110 0.11223 0.1110 0.11223 0.1110 0.1110 0.11223 0.1110 0.11000 0.100000000	RATE 0.00399 0.00374 0.00374 0.00374 0.00374 0.003319 0.003319 0.003319 0.0002995 0.0002995 0.00022957 0.00022959 0.00022959 0.00022959 0.00022959 0.00022959 0.00022995 0.00022959 0.00022959 0.00022995 0.000000000 0.000000000 0.0000000000	FRACTION 0.24472787 0.22472787 0.22472787 0.22572767657657657657657657657657657657657 0.227728879727098810990 0.00000000000000000000000000000000
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APPENDIX C

SULFATION REACTION DIMENSIONAL ANALYSIS

C-1

CALCIUM-BASED SO₂ SORBENT PARTICLE REACTION MODELS DIMENSIONAL ANALYSIS

SORBENT PARTICLE DESCRIPTION

The sorbent particle is pictured as an irregularly shaped particle made up of a continuous gas phase, or pores, and a dispersed solid phase. The solid phase may be described as consisting of sorbent material grains and inert material grains that are bound together with some binding material. The gas phase can be described by either a pore structure or as intersticies between packed grains.

The raw sorbent $CaCO_3$ or $CaCO_3 \cdot MgCO_3$ structure is transformed into a much more porous CaO, $CaCO_3 \cdot MgO$, or CaO·MgO stucture by calcination, if conditions, temperature, and CO_2 partial pressure, allow calcination. The pore size distribution and internal surface area of the calcine is controlled by the calcination conditions.

 SO_2 and SO_3 diffuse into the sorbent particle through the continuous pore phase, is adsorbed on the sorbent material grain surfaces, and some active sulfur component diffuses (by solid diffusion) into the grains, reacting with the sorbent CaO by the overall reaction

$$CaO + SO_3 + CaSO_4$$

or $CaO \cdot MgO + SO_3 + CaSO_4 \cdot MgO$

or $CaCO_3 \cdot MgO + SO_3 = CaSO_4 \cdot MgO + CO_2$

CONTINUITY EQUATIONS AND ASSUMPTIONS Gas Phase Continuity

Gas phase continuity is expressed by

$$\partial c/\partial t = \nabla \cdot \{D \nabla (c)\} - \nabla \cdot \{c v\}$$

where $\partial/\partial t$ is the partial dirivative with respect to time, ∇ is the delta operator, and c is the gas phase SO₂ concentration. The diffusion coefficient D, for diffusion of SO₂ in the pores, may be a function of the pore diameter when the pore size is reduced into the Knudsen diffusion region. The gas phase molar average velocity vector is v, where

$$\nabla \cdot \underline{\mathbf{v}} = \mathbf{0} \tag{2}$$

It is assumed that

1) There is no convective bulk flow in the pores (equimolar counterdiffusion), but because of the moving boundaries in the particle (due to chemical reaction changes in volume of the solid phases) there is an imposed velocity.

2) The SO_2 is very dilute so that multicomponent diffusion may be neglected.

3) No homogeneous reactions occur in the gas phase.

Solid Product Phase Continuity

Similarly, the conservation of the diffusing species in the solid phase is given by

$$\frac{\partial s}{\partial t} = D_s \nabla^2 s - \nabla \cdot \{s \underline{v}_s\} - k_r s C_r$$
(3)

where s is the sulfur component concentration in the solid phase, D_s is the solid phase diffusion coefficient, and \underline{v}_s is the molar average velocity of the solid product phase. C_r is the concentration of solid reactant (CaO) in the solid phase, where a homogeneous reaction is assumed to occur. Other assumptions applied are

1) SO_2 is adsorbed on the solid product surface, reacts to become the diffusing species, and diffuses through the product phase as it reacts, converting CaO to CaSO₄.

C-3

(1)

2) The reaction rate is assumed to be first-order in the concentration of each of the reactant concentrations, s and C_r , with rate constant k_r .

3) The adsorption reaction is at equilibrium with the continuous gas phase concentration; $s = k_a c$ at the gas-solid interface.

CaO and CaSO₄ Continuity

The solid reactant and product species are assumed to have no diffusive flux, but are convected by the solid phase chemical reaction density changes. The continuity equations are

$$\partial C_r / \partial t = - \overline{\nabla} \cdot \{ \overline{C}_r \, \underline{v}_s \} - k_r \, s \, C_r \tag{4}$$

$$\partial C_{p}/\partial t = -\nabla \cdot \{C_{p} \underline{v}_{s}\} + k_{r} s C_{r}$$
(5)

where C_r is the molar concentration of CaO and C_p is the CaSO₄ concentration.

The product concentration at any point in the solid is related to the reactant concentration by

$$C_{\rm p} = (1 - C_{\rm r}/m_{\rm r}) m_{\rm p}$$
 (6)

 m_r is the pure reactant molar density and m_p is the pure product molar density:

CaO $m_r = 1/16.76 \text{ moles/cm}^3$ CaCO₃ $m_r = 1/36.93$ CaO·MgO $m_r = 1/28.01$ CaCO₃·MgO $m_r = 1/48.18$ CaCO₃·MgCO₃ $m_r = 1/64.34$ CaSO₄ $m_p = 1/45.94$ CaSO₄·MgO $m_p = 1/57.19$

C-4

If a calcined limestone is sulfated then $m_r/m_p = 2.74$. If a half-calcined dolomite is sulfate then $m_r/m_p = 1.19$. Finally, if a fully-calcined dolomite is sulfated $m_r/m_p = 2.04$. The differences in expansion in limestones and dolomites are significant, and if the sulfate volume is compared to the raw carbonate volume it is seen that limestone molecular volumes increase about 24% on sulfation while dolomite decreases about 11%.

The sum of equations 4 and 5 results in the following when applying equation 6:

$$\nabla \cdot \underline{\mathbf{v}}_{s} = [1 - \mathbf{m}_{p}/\mathbf{m}_{r}] \mathbf{k}_{r} \mathbf{s} \mathbf{C}_{r}/\mathbf{m}_{p}$$
(7).

Particle Pore and Grain Structure

The key particle structural factors, ε , ε_i , A_g , R_p , R_g , and R_j , the particle voidage, the inert material volume fraction, the grain surface area, the pore characteristic radius, the grain characteristic dimension, and the particle characteristic dimension, respectively, are all functions of time and position in the particle. We define the particle characteristic dimension to be the equivalent radius of the particle.

$$R = \left[V / (4/3 \pi) \right]^{1/3}$$
(8)

and the external particle surface area to be

$$A = 1/\Phi \ 4 \ \pi \ R^2$$
 (9)

where Φ is the particle sphericity. Similar definitions are made for the grain characteristic dimension, R_g , the grain surface area, A_g , and the grain sphericity, Φ_g :

$$R_{g} = [V_{g}/(4/3 \pi)]^{1/3}$$
(10)

C-5

$$A_{g} = 1/\Phi_{g} 4 \pi R_{g}^{2}$$
 (11)

The local particle content is made up of voids, inert grains, sorbent solid reactant and solid product, such that

$$\varepsilon + \varepsilon_i + \varepsilon_r + \varepsilon_p = 1$$
 (12)

Continuity equations can be written for each of these volume fractions:

$$a \epsilon_r / at = -\nabla \cdot (\epsilon_r \underline{v}_s) - \underline{k}_r s C_r / \underline{m}_r$$
 (13)

$$\partial \varepsilon_p / \partial t = - \nabla \cdot (\varepsilon_p \, \underline{v}_s) + k_r \, s \, C_r / m_p$$
 (14)

$$\partial \varepsilon_i / \partial t = - \nabla \cdot (\varepsilon_i \underline{v}_s)$$
 (15)

$$\partial \epsilon / \partial t = \nabla \cdot [(1-\epsilon) \underline{v}_s] - k_r s C_r (1/m_p - 1/m_r)$$
 (16)

We define grain and particle fractional reaction extents as

$$\alpha_{g} = 1 - V_{g} \epsilon_{r} / V_{go}$$
 (17)

$$\alpha = 1 - \int_{V}^{\varepsilon} r \frac{dV/V}{o}$$
(18)

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respectively. It can be shown that the overall particle voidage is given by

$$\frac{d}{dt} \left(\int \varepsilon \, dV \right) = \int v_{s} \cdot \underline{n} \, dS + (1/m_{r} - 1/m_{\tilde{p}}) \, d\alpha/dt \left[V_{0} (1 - \varepsilon_{0} - \varepsilon_{10}) m_{r} \right] \quad (19)$$

while the local voidage is

$$\varepsilon = 1 - \varepsilon_{i0} - (1 - \varepsilon_0 - \varepsilon_{i0}) / \{1 - \alpha_g (1 - m_r/m_p)\}$$
(20)

C-6

and

Also, the grain volume is given by

$$V_g = V_{go} [1 + (1/m_p - 1/m_r) \alpha_g m_r]$$
 (21)

The grain surface per unit total volume is roughly

$$S_{p} = A_{g} / [V_{g} / (1-\varepsilon)] (\varepsilon/\varepsilon_{o})$$

$$= 1/\Phi_{g} (12 \pi/V_{go})^{1/3} (\varepsilon/\varepsilon_{o}) (1-\varepsilon) [1 + (1/m_{r} - 1/m_{p}) \alpha_{g} m_{r}]^{-1/3}$$
(22)

Finally the mean pore radius is approximated as

$$R_{p} = \Phi_{g} 2/(12\pi)^{1/3} [\epsilon_{o}/(1-\epsilon)] V_{go}^{1/3}$$

$$[1 + (1/m_{r}^{-1/m_{p}}) \alpha_{g} V_{go} m_{r}]^{1/3}$$
(23)

Note that sintering phenomena may also interact to reduce the grain surface area, and if sintering is at a significant rate Equation 22 for $S_{_{D}}$ should be multiplied by the factor

$$exp(-k_{e}t)$$

while Equation 23 for R_p should be divided by this factor. k_s is the sintering rate constant, a strong function of temperature. Thus, sintering reduces the internal surface area and increases the average pore radius.

Boundary and Initial Condition

The particle position vector is represented by r, from some arbitrary point of origin. A position on the pore surface is represented by r_p , the position vector for the pore surface. The outer particle surface is represented by the position vector R. The flux of sulfur species across the gas-solid interface ($r = r_{p}$) is continuous with

$$-\underline{\mathbf{n}} \cdot \mathbf{D} \nabla \mathbf{c} + \underline{\mathbf{n}} \cdot \mathbf{c} \underline{\mathbf{v}} = -\underline{\mathbf{n}} \cdot \mathbf{D}_{\mathbf{c}} \nabla \mathbf{s} + \underline{\mathbf{n}} \cdot \mathbf{s} \underline{\mathbf{v}}_{\mathbf{c}}$$
(24)

where <u>n</u> is the unit normal vector at the surface at $r = r_p$. Also, with adsorption equilibrium, $s = k_a c$.

At the interface the velocity is continuous,

$$\underline{\mathbf{n}} \cdot \underline{\mathbf{v}} = \underline{\mathbf{n}} \cdot \underline{\mathbf{v}}_{\mathbf{s}}.$$
 (25)

At an inert grain surface the flux is given by

$$-D\mathbf{n} \cdot \nabla \mathbf{c} + \mathbf{n} \cdot \mathbf{c} \mathbf{v} = 0 \tag{26}$$

At time zero

$$c = 0$$

$$s = 0$$
 (27)

$$C_{r} = m_{r}$$

$$C_{p} = 0$$

Finally, at the outer surface of the particle (r = R)

$$c = c_0 \tag{28}$$

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DIMENSIONAL ANALYSIS

The dimensional analysis of the above equations can provide significant insight into the nature of the sorbent sulfur removal performance without making the sorbent model any more specific or limiting the generality further.

Dimensionless Quantities

The following dimensionless groups are defined

 $C^* = c/c_o$, the dimensionless concentration in the pores $S^* = s/(k_a c_o)$, the dimensionless concentration in the solid phase $C_r^* = C_r/m_r$, the dimensionless solid reactant concentration $C_p^* = C_p/m_p$, the dimensionless solid product concentration $t^* = t D_a/R_o^2$, the dimensionless time $\underline{v}^* = \underline{v} R_o/D_a$, the dimensionless gas phase velocity $\underline{v}_s^* = \underline{v}_s R_o/D_a$, the dimensionless solid phase velocity

where D_a is the initial average gas phase diffusion coefficient in the pores and R_o is the initial characteristic particle dimension.

Dimensionless Equations

The continuity Equations 1 through 7 become

$$\partial C^* / \partial t^* = \nabla^* \cdot (D/D_a) \nabla^* C^* - \nabla^* \cdot \{C^* \underline{v}^*\}$$
(29)

$$\nabla^{\star} \cdot \underline{v}^{\star} = 0 \tag{30}$$

$$\hat{s}^{*}/\hat{s}^{*} = (D_{s}/D_{a}) (R_{o}/R_{go})^{2} \nabla^{*2} \hat{s}^{*}$$

$$(31)$$

$$(R_{o}/R_{go}) \nabla^{*} \cdot \{\hat{s}^{*} \underline{v}_{s}^{*}\} - \{k_{r} m_{r} R_{o}^{2}/D_{a}\} \hat{s}^{*} C_{r}^{*}$$

$$\partial C_{r}^{*}/\partial t^{*} = -\nabla^{*} \cdot \{C_{r}^{*} \underline{v}_{s}^{*}\} - \{k_{r} R_{o}^{2} k_{a} c_{o}/D_{a}\} S^{*} C_{r}^{*}$$
 (32)

$$\partial C_{p}^{*} / \partial t^{*} = - \nabla^{*} \cdot \{C_{p}^{*} \underline{v}_{s}^{*}\} + \{k_{r} R_{o}^{2} k_{a} c_{o} / D_{a}\} S^{*} C_{r}^{*}$$
(33)

$$\bar{c}_{r}^{*} = 1 - \bar{c}_{p}^{*}$$
 (34)

$$\nabla^{\star} \cdot \underline{v}_{s}^{\star} = \{k_{r} R_{o}^{2} k_{a} c_{o}/D_{a}\} \{m_{r}/m_{p}-1\} S^{\star} C_{r}^{\star}$$
 (35)
The particle structure factors can be written

$$\varepsilon = 1 - \varepsilon_{io} - (1 - \varepsilon_o - \varepsilon_{io}) / \{1 - \alpha_g (1 - m_r/m_p)\}$$
(36)

$$V_g^* = V_g/V_{go} = 1 - (m_r/m_p - 1) \alpha_g$$
, the grain volume (37)

$$S_{p}^{*} = S_{p}/S_{po} = \epsilon/\epsilon_{o} (1-\epsilon)/(1-\epsilon_{o}) [1 + (1-m_{r}/m_{p})\alpha_{g}]^{-1/3} \exp(-k_{s} t), (38)$$

the dimensionless internal surface area per unit volume,

$$R_{\mu}^{*} = R_{\bar{\mu}}/R_{\mu\bar{\nu}} = (1-\epsilon_{\bar{\nu}})/(1-\epsilon) [1 + 1 m_{\mu}/m_{\mu}) \alpha_{\bar{g}}]^{1/3} \exp(k_{s} t), (39)$$

and the dimensionless pore radius, where the sintering effect has been included.

The boundary and initial conditions, Equations 24-28, become

$$(D/D_{a}) \underline{n} \cdot \nabla^{*} C^{*} - \underline{n} \cdot C^{*} \underline{v}^{*} = (D_{s}/D_{a}) k_{a} \underline{n} \cdot \nabla^{*} S^{*}$$

$$- \underline{n} \cdot S^{*} k_{a} \underline{v}_{s}^{*} \text{ at } r^{*} = r_{\bar{p}}/R_{o}$$

$$(40)$$

$$S^{*} = C^{*}$$
 at $r^{*} = r_{p}/R_{o}$ (41)

$$\underline{\mathbf{n}} \cdot \underline{\mathbf{v}}^{\star} = \underline{\mathbf{n}} \cdot \underline{\mathbf{v}}_{\mathrm{s}}^{\star} \quad \text{at } \mathbf{r}^{\star} = \mathbf{r}_{\mathrm{p}}/\mathrm{R}_{\mathrm{o}}$$
(42)

$$(D/D_{\underline{a}}) \underline{n} \cdot \nabla C^{*} - \underline{n} \cdot C^{*} \underline{v}^{*} = 0$$
 on inert surfaces (43)

$$C^{*} = 0 \quad \text{at } t^{*} = 0$$

$$S^{*} = 0 \quad \text{at } t^{*} = 0 \quad (44)$$

$$C_{r}^{*} = 1 \quad \text{at } t^{*} = 0$$

$$C_{p}^{*} = 0 \quad \text{at } t^{*} = 0$$

$$C^{*} = 1 \quad \text{at } r^{*} = R/R_{o} \quad (45)$$

Interpretation

The dimensionless equations indicate that the dimensionless concentration fields, velocity fields and structural factors



are functions of the following variables:

t["], dimensionless time

 r/R_o , dimensionless position

 D/D_a , dimensionless gas phase diffusion coefficient, potentially a function of time and position if in the Knudsen difusion regime

 $D_s/D_a (R_o/R_{go})^2 k_a$, ratio of solid phase diffusion rate to gas phase diffusion rate

 $k_r m_r R_0^2/D_a$, chemical reaction rate over gas phase diffusion rate

 $k_a c_0/m_r$, ratio of diffusing sulfur species concentration in the solid to molar density of pure solid phase reactant CaO

 m_r/m_p , ratio of pure CaO molar density to pure CaSO₄ molar density

k_a, adsorption coefficient

and the dimensionless geometry of the particle, $r_{\rm p}/R_{\rm o}$.

The geometric factors relate to the following dimensionless groups:

ε _o	initial particle voidage
ε _{io}	initial volume fraction of inert grains
R _{go} /R _o	initial average grain diameter over initial particle characteristic dimension

A _{go} /A _o	initial internal surface area over external initial surface area
R _p /R _o	average initial pore diameter over the initial particle characteristic dimension
S _{go} R _o	initial surface area per unit volume times the initial particle characteristic dimension

The total fraction of the particle solid phase reacted, a_t , is given by

$$\alpha_{t} = 1 - \int_{V} c_{\tau}^{*} / \{(1 - \varepsilon_{0} - \varepsilon_{10})\} dV^{*}$$
(46)

where V^* is the dimensionless particle volume, V/V_0 . V_0 is the initial particle volume.

The general equation for the overall particle reaction rate is

$$d \alpha_t / dt^* = k_r k_a c_o^2 R_o / D_a \int_{V^*} S^* C_r^* / \{1 - \varepsilon_o - \varepsilon_i_o\} dV^*$$
(47)

This equation indicates that in general

$$d \alpha_t/dt^* = function \{t^*, D(t^*)/D_a, D_s/D_a (R_o/R_{go})^2 k_a,$$
 (48)

 $k_r m_r R_o^2/D_a$, $k_a c_o/m_r$, m_r/m_p , and structural factors (ϵ_o , ϵ_{io} , R_{go}/R_o , R_{po}/R_o , A_{go}/R_o)

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and its complex form, while informative, is not directly useful.

In order to look at more limiting cases than that above, the overall particle reaction rate, d a_t/dt , is given by the following three equations for pore diffusion control, chemical reaction control, and solid diffusion control, respectively:

If the rate is diffusion controlled

$$d \alpha_{t}/dt = D_{a} c_{o}/m_{r} A_{o}/\{(R_{o} V_{o})(1-\epsilon_{o}-\epsilon_{io})\}$$
(49)
$$x \int_{A}^{\star} - (D/D_{a}) \underline{n} \cdot \nabla^{\star} C^{\star} d A^{\star}$$
$$= D_{a} c_{o}/m_{r} A_{o}/\{(R_{o} V_{o})(1-\epsilon_{o}-\epsilon_{io})\}$$
$$x \text{ function } \{t^{\star}, D/D_{a}\}$$

where

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$$D/D_a = function \{R_{po}/R_o, m_r/m_p, k_s\}$$
(50)

 A^* is the surface area of the shrinking reaction surface, and D is the diffusion coefficient in the solid product layer, a potential function of time due to sintering.

If the rate is chemical reaction.controlled

$$d \alpha_{t}/dt = k_{r} k_{a} c_{o} \int_{v}^{*} S^{*} C_{r}^{*} / \{(1 - \varepsilon_{o} - \varepsilon_{io})\} dV^{*}$$
(51)
$$= k_{r} k_{a} c_{o} / \{1 - \varepsilon_{o} - \varepsilon_{io}\}$$

$$x \text{ function } \{t k_{r} m_{r}\}$$

The definition of reaction rate control implies that S^* and C_r^* have values everwhere in the solid phase of 1 and 1-a, respectively. Thus,

 $d \alpha_t / dt = k_r k_a c_0 (1 - \alpha_t) V / V_g$ (52)

for the chemical reaction controlled case.

If the rate is solid diffusion controlled

$$d \alpha_t/dt = D_s k_a c_0/m_r A_{go}/(R_{go} V_{go})$$
 (53)

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$$x \int_{A_p} \dot{x} - \underline{n} \cdot v^* S^* dA_p^*$$

= $D_s k_a c_0/m_r A_{go}/(R_{go} V_{go})$
x function {t $D_s R_{go}^{-2}, m_r/m_p, k_s$ }

where A_p^* is the pore reaction surface over A_{go} .

These dimensionless equations tell us several things about the influence of time, particle diameter, external reactant gas concentration, pressure, temperature, pore surface area, etc on the overall reaction rate.

1) time

For particles having identical values of all of the dimensionless groups, the dimensionless reaction rate is the same function of dimensionless time:

$$d \alpha_{t}/d t^{*} = function \{t^{*}\}$$
 (54)

Û

2) particle size

For particles of similar sorbent materials at the same temperature and pressure, having the same values of dimensional quantities except for the particle size, R_o , A_o , V_o

 $d \alpha_t/dt^{w} = function \{t^{w}, k_r m_r R_0^2/D_a, A_{g0}/A_0, R_{p0}/R_0\}$ (55)

With limestone or dolomite particles it is not possible to change the particle size and maintain the last three of the quantities within the brackets fixed, but the limiting cases can be assessed.

a) if the pore diffusion rate is very much smaller than the chemical reaction rate or the solid diffusion rate, i.e.,

$$k_r m_r R_o^2/D_a$$
 very large (56)

$$D_s/D_a (R_o/R_{go}^2) k_a$$
 very large (57)

then Equation 49 becomes

$$d \alpha_{t}/dt = D_{a} c_{o}/m_{r} A_{o}/\{(R_{o} V_{o})(1-\epsilon_{o}-\epsilon_{io})\}$$
(58)

x function {t^{*}, R_p/R_o}

or, with respect to the particle size, using $A_0/(R_0 V_0)$

 $= 3/(\Phi R_0^2),$

$$(d \alpha_t/dt) \Phi R_0^2 = function (t/R_0^2, R_p/R_0)$$
 (59)

where the term R_p/R_o , the characteristic pore radius in the product layer, can be neglected unless in the Knudsen diffusion regime.

b) if the chemical reaction rate is very much smaller than the pore diffusion or solid diffusion rates, i.e.,

$$k_r m_r R_0^2 / D_a + 0$$
 (60)

 $k_r m_r R_o^2/D_s + 0$ (61)

then, from Equation 51,

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$$(d a_{t}/dt) = function (t)$$
 (62)

and the rate is independent of particle size.

c) if the solid diffusion rate is much smaller than the chemical reaction or pore diffusion rates, i.e.,

$$D_{s}/D_{a} (R_{o}/R_{go}) k_{a} + 0$$
 (63)

$$k_r m_r R_0^2/D_s$$
 very large (64)

then, from Equation 53,

$$d \alpha_t/dt = D_s k_a c_o/m_r A_{go}/(R_{go} V_{go})$$

(65)

x function (t/R_{go}²)

and

$$(d \alpha_{+}/dt) = function (t)$$
 (66)

The three special cases, pore diffusion control, reaction control, and solid diffusion control, are characterized by a dependency on R_0^n where n is 2, 0, and 0 respectively. Also, very large particles should approach pore diffusion control behavior, while very small particles should approach chemical reaction rate control.

3) external reaction gas concentration

For particles that are identical except for the SO_2 concentration they react in, Equation 17, 18 and 19 indicate that

$$d a_t/dt = c_0 function \{t\}$$
(67)

and the overall reaction rate is first order with respect to c_0 for all cases.

4) pressure

For particles that are identical except for the pressure of the

reaction gas and the resulting gas concentration c_0 , the following cases can be determined:

a) for pore diffusion control

$$d \alpha_t/dt = D_a c_0$$
 function {t D_a , D/D_a } (68)

With the diffusion coefficient being some function of pressure given approximately by a series model of molecular and Knudsen diffusion

$$D_{a} = 1 / [1/D_{k} + 1/D_{m}]$$
(69)

where the Knudsen diffusion coefficient, D_k , is

$$D_k = D_{kr} T^{1/2} / (A_g/V)$$
 (70)

and the molecular diffusion coefficient, D_m , is

$$D_{m} = D_{mr} T^{1.8} / P$$
 (71)

T is the absolute temperature, P is the absolute pressure, and D_{kr} and D_{mr} are constants.

We see that if Knudsen diffusion controls then D_a is independent of P and the overall reaction rate is directly proportional to the pressure.

 $d \alpha_t/dt = P$ function {t} (72)

The Knudsen diffusion control is promoted by larger values of the internal surface area, A_g/V , lower ε , and lower gas pressures.

If molecular diffusion controls then D_a is inversely proportional to the pressure. This makes the overall reaction rate relate to pressure as

$$d a_t/dt = function \{t/P\}$$
 (73)

Molecular diffusion is promoted by small values of the internal surface area (large pores), higher ε , and higher pressures.

b) for chemical reaction rate control

$$d \alpha_t/dt = c_0$$
 function { $t k_r m_r$ } (74)

or, with respect to pressure

$$d \alpha_r/dt = P$$
 function {t} (75)

c) for solid diffusion control

$$d a_t/dt = c_0 \text{ function } \{t D_s/R_{g0}^2\}$$
 (76)

or, with respect to pressure

$$d a_{t}/dt = P \text{ function } \{t\}$$
 (77)

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While these equations indicate a rather simple pressure dependence, the pressure also has a great impact on the initial calcine pore and grain structure which is not considered in these equations. Higher pressures promote larger pores while smaller pressures promote smaller pores.

5) temperature

Following a similar procedure to find the impact of temperature yields these results:

a) pore diffusion control

$$d a_t/dt = D_a c_o function \{t D_a/R_o^2, D/D_a\}$$
 (78)

The temperature dependence of D_a is given above. If the diffusion is in the Knudsen regime then the temperature dependence of D_a is T to the 1/2-power and

$$d \alpha_t/dt = T^{-1/2}$$
 function {t $T^{1/2}$, $k_s(T)$ } (79)

The sintering rate constant is assumed to be given by

$$k_{s} = k_{s0} \exp(-E_{s}/T)$$
 (80)

If the diffusion is in the molecular diffusion regime then the temperature dependence of D_a is $T^{1.8}$ and

$$d \alpha_t/dt = T^{0.8}$$
 function {t $T^{1.8}$ } (81)

The Knudsen regime is promoted by higher temperatures, and the molecular regime by lower temperatures.

b) chemical reaction rate control

$$d \alpha_t/dt = k_r k_a c_0$$
 function {t $k_r m_r$ } (82)

With the reaction rate and adsorption terms having exponetial temperature dependence

$$d a_t/dt = exp \left\{-\left(E_r + E_a\right)/T\right\} / T$$
(83)

c) solid diffusion rate control

$$d \alpha_t/dt = D_s k_a c_0 \text{ function } \{t D_s/R_{g0}^2, k_s\}$$
(84)

The solid diffusion coefficient has a limited understanding with respect to temperature, although it is expected to increase with temperature as $D_s=D_{so} \exp \{-Es/T\}$. Thus,

$$d \alpha_t/dt = exp \{-(Ea+Es)/T\} / T$$
(85)

x function [t exp{-Es/T}, k_(T)]

It should be pointed out that the temperature dependence is more complex than that indicated by these equations because the temperature effects the initial calcine pore and grain structure, as well as having a transient impact on the structure if significant sintering is occuring.

6) pore and grain structure

For particles identical except for their internal pore and grain structure the following is indicated:

a) pore diffusion control

$$d a_t/dt = 1/(1 - \epsilon_0 - \epsilon_{i0})/m_r$$
 function {t, R_{p0}/R_0 , m_r/m_p } (86)

where the quantity R_{po}/R_o is only important if in the Knudsen diffusion regime.

b) chemical reaction control

$$d a_t/dt = 1 / (1 - \epsilon_0 - \epsilon_{i0})$$
 function $\{t m_r\}$ (87)

~

c) solid diffusion control

$$d_{a_t}/dt = 1/(\phi_g R_{go}^2)/m_r$$
 function $\{t/R_{go}^2, m_r/m_p\}$ (88)

and the rate is directly proportional to the initial internal surface area per unit volume squared because

$$1/(\phi_{g} R_{go}^{2}) = S_{po}^{2} \phi_{g}/\{9(1-\varepsilon_{o})\}$$
 (89)

7) ultimate sorbent utilization

Little can be deduced about the ultimate extent of reaction, α^* , from the dimensional analysis except

- All sorbent particles having the same dimensionless groups will have the same a^{*}.
- 2) In the pore diffusion controlled regime the sorbent utilization is limited by the reduction in the ratio D/D_a as the pore volume is reduced due to solid product expansion.
- 3) In the chemical reaction controlled regime there is no limitation to the utilization and $\alpha^* = 1$.
- 4) In the solid diffusion controlled regime the sorbent utilization is limited by the loss in internal surface area due to solid product expansion and sintering.

APPENDIX D

MODEL DEVELOPMENT FOR CALCIUM-BASED SORBENT SULFUR REMOVAL IN EXTERNAL DESULFURIZERS

1.1 INTRODUCTION

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Kinetic data collected on laboratory devices require the use of a commercial process model in order to apply the data for process evaluation. Such models are used as engineering tools to select design and engineering conditions for commercial design studies. They are not substitutes for full-scale data, but should be used with full-scale data as it becomes available to evolve improved process performance correlations.

Simple models are developed here for fluidized and entrained bed external desulfurizers, using several simplifying assumptions. External desulfurizers are defined to be desulfurization stages of a gasification process or a combustion process that follow either the complete gasification or combustion process or follow an intermediate step, but are not insitu with the gasification or combustion process. Thus, they do not interact with the carbon conversion process directly. The models are suitable for use in sorbent evaluations and to predict performance for conceptual designs.

1.2 CALCIUM-BASED SORBENT SULFATION KINETICS

While sulfation kinetics for individual limestones, dolomites and other calcium-based sorbents must be determined experimentally, it is convenient to use an empirical form to fit the kinetics. The sulfation reaction kinetics are a function of the temperature, pressure, the gas composition $(0_2, C0_2, H_2 0 \text{ and } S0_2 \text{ or } H_2 S)$, particle size, fraction of the sorbent calcium content sulfated, and the particular sorbent type. A form that fits the experimental kinetics well is

$$d a/dt = k (1 - a) {}^{m}C$$
(1)

where a is the fraction of the calcium reacted, t is the time, k is the rate constant, m and empirical constant, and C is the SO_2 or H_2S concentration. The rate is found to be zero order in the O_2 concentration while the rate constant k is dependent on temperature, pressure, CO_2 concentration, particle size and sorbent type in a very complex way.

With the form of equation (1) the fraction sulfated for a constant SO_2 or H_2S concentration becomes

$$a = 1 - \{ 1 + (m-1) \ k \ C \ t \}^{1/(1-m)}$$
(2)

or if the sulfur gas concentration is a function of time

$$a = 1 - \{1 + (m-1) \ k \int_{0}^{t} C(t)^{1/(1-m)} \ dt\}$$
(3)

 $\{\boldsymbol{\varphi}_{\boldsymbol{\gamma}}\}$

In some cases this form will have to be fit to the kinetic data in two or three sections, so that multiple values of m and k will be needed.

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1.3 GENERAL DIFFERENTIAL MATERIAL BALANCES

A general, steady-state material balance on SO_2 or H_2S in either a fluidized bed or an entrained desulfurizer is shown below:

$$U dC/dx = -R + G$$
 (4)

where U is the superficial gas velocity, x is the axial distance from the base of the bed, R is the desulfurization reaction rate and G is the SO, generation rate per unit bed volume.

In Equation (4)

$$\mathbf{R} = \mathbf{p} \, \mathbf{N} \, \mathbf{k} \, \left(\mathbf{1} - \boldsymbol{\alpha} \right)^{\mathbf{m}} \, \mathbf{C} \tag{2}$$

where p is the number of particles per unit volume, and N is average number of moles of calcium per particle. The generation term G is a function of axial position that depends on the nature of the coal, the coal size, the coal feed location, the bed temperature, the pressure and the excess air level. For the case of external desulfurization the generation term is assumed to be zero.

1.4 SPECIFIC SOLUTIONS

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Bubbling Fluidized Bed Desulfurizer

The following assumptions are applied to the development of a fluidized bed desulfurizer process model, and are based on, in part, modeling conclusions developed for fluidized bed combustion:

- The prior combustion, pyrolysis or gasification reactions have been essentially completed and the composition does not change significantly due to carbon conversion within the desulfurizer. Gas compositions will change within the desulfurizer due to calcination of the sorbent (release of CO_2) and due to sorbent sulfur species reactions. If secondary reactions of gases do occur in the bed this will have only a small influence on the sulfur removal performance.
- The gas temperature is at the temperature of the prior gas temperature entering the desulfurizer and will change due to heat releases from the calcination and sulfur reaction only to a small extent. The gas and particle temperature is essentially uniform within the desulfurizer because of good particle mixing.
- The gas flows through the desulfurizer both in the bubble phase and in the emulsion phase of the fluid bed. Because the particles are relatively coarse, the gas mixing rate between the bubble and emulsion phases is high and simple plug flow of the gas may be assumed with little error. That is, the gas composition is approximately uniform across any horizontal cross-section of the bed. Design correlations are available to estimate the emulsion voidage and bubble volume fraction in the bed.
- Particles in the sorbent feed of a size having terminal velocity less than the bed superficial velocity (in their calcined state) will be elutriated from the bed. These particles will be partially sulfated or sulfided. It is assumed that this represents a small portion of the total sorbent.

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- Significant sorbent particle attrition may occur in the bed. It is assumed that the fine sorbent particles attrited will not be recycled to the desulfurizer. The attrition occurs mainly during the initial period of the particles residence in the bed and generally sulfated or sulfided sorbent is not highly attrited. The attrited and elutriated particles are assumed to be reacted to an extent very similar to the coarse particles remaining in the bed.
- The sorbent particles reside in the bed with a perfectly-mixed age distribution. Because of the high rate of mixing versus the slow rate of sulfur reaction, the sorbent particles see only the average sulfur-gas species (SO₂ or H_2S) concentration in the bed.

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- Significant sorbent reaction may occur in the bed "splash zone" directly above the bed surface. Design correlations are available to estimate the height and particle concentration in the splash zone. The splash-zone sorbent particle inventory is assumed to be included in the bed inventory in this model.
- Negligible sulfur release or sulfur removal occurs in the freeboard region of the desulfurizer.
- Coal ash passes through the desulfurizer with little accumulation in the bed.
- The sulfur reaction rate of the sorbent particles is very slow compared to the calcination rate of the particles. That is, the rate of calcination has little influence on the rate of sulfur reaction of the sorbent. The correlation forms developed in this test program will be utilized to represent the sulfur reaction rate as a function of the operating parameters:

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$$\mathbf{r} = \mathbf{N} \mathbf{k} (1 - \alpha)^{\mathbf{m}} \mathbf{C}$$
(6)

where r is the reaction rate per sorbent particle of diameter d_p . N is the number of moles of calcium in a particle (based on the average particle diameter in the bed), C is the sulfur species concentration in the gas, and k is the sulfur rate constant. The model is based mainly on a differential material balance on sulfur in the bed. The material balance is

$$U d C/dx = G - R$$
⁽⁷⁾

where U is the gas superficial velocity, C is the sulfur gas-phase concentration, x is the axial distance above the distribution plate, G is the rate of sulfur release per unit volume of the bed, and R is the rate of sulfur capture per unit bed volume. The sulfur generation term, G, is zero based on the assumptions stated above, and the sulfur reaction term is given by

$$\mathbf{R} = \mathbf{p} \ \bar{\mathbf{R}} \ \mathbf{C} / \bar{\mathbf{C}} \tag{8}$$

where p is the total number of sorbent particles per unit volume of the bed, R is the average particle reaction rate in the bed, and C is the average sulfur gas concentration in the bed. The term p is given by

$$p = 6 (1 - \epsilon) (1 - \delta) / [\pi d_p^3]$$

where n is the voidage in the bed emulsion phase and k is the bubble volume fraction in the bed.

Equations 7 and 8 may be combined and integrated to yield the simple concentration profile

$$C = C \exp \{-p \times \overline{R}/(U\overline{C})\}$$
(10)

(9)

with the inlet sulfur gas concentration being C_{o} .

The bed sulfur removal efficiency is defined as

$$E = 1 - C(x=H)/C = 1 - \exp \{-p H/U\bar{R}/\bar{C}\}$$
(11)

The average sulfur gas concentration is defined as

$$\bar{C} = 1/H \int_{0}^{H} C dx$$
 (12)

and becomes

$$\bar{C} = C_0 / H U / p \bar{C} / \bar{R} [1 - \exp \{ -p H / U \bar{R} / \bar{C} \}]$$

$$= - C_0 E / Ln \{1 - E\}$$
(13)

The average reaction rate in the bed may be estimated for a perfectly mixed fluid bed using the residence time frequency distributions F:

$$\mathbf{F} = 1/\tau \exp\{-t/\tau\}$$
(14)

where τ is the average particle residence time, and t is the time. By definition the average sorbent utilization in the bed is

$$a = \int_0^\infty a \ 1/\tau \exp\left\{-t/\tau\right\} dt \tag{15}$$

Since each particle in the bed effectively sees only the average sulfur gas concentration in the bed, then

$$a = 1 - 1/\{1 + (m-1) \ k \ C \ t\}^{-1/(m-1)}$$
(16)

The procedure applied to predict sulfur removal performance is:

1) Identify the bed operating conditions (T, P), the average diameter of particles in the bed (d_p) and ρ_{ca} .

2) Determine m and k for the given sorbent at its appropriate conditions of CO_2 concentration, average particle diameter, pressure and temperature from laboratory data.

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3) Specify the bed sulfur removal efficiency, E, calculate C_{o} (from the coal properties and the conversion characteristics on the prior processing stage) and C from Equation (13).

4) Define the parameter $\sigma = C \tau$ and assume any positive value for it. This parameter is

$$\sigma = \bar{C} \tau = -C_{\tau} \tau E/Ln [1 - E] \text{ from Equation 13}$$
(17)

5) Calculate the term a from Equations (15) and (16) for the assumed value of σ . In general a numerical integration is required.

6) Calculate C τ from Equation (17).

7) Calculate the key bed design term $H/U_{-}(1-\epsilon)$ (1- δ) from

$$H/U (1 - \epsilon) (1 - \delta) = C_{\tau} \tau E/\bar{a}/\rho_{\tau}$$
(18)

45.18g

This is the average gas residence time in the bed (H/U) times the volume fraction of particles in the bed, and must be determined to completely specify the desulfurizer design. The voidage terms ϵ and δ must be estimated from available fluidized bed correlations.

8) Calculate the calcium-to-sulfur ratio from

 $Ca/S = E/\bar{a}$

This of course represented the sorbent feed rate required to achieve the specified sulfur removal efficiency for the calculated value of H/U. 9) Repeat this set of calculations for a series of assumed σ values to generate a set of corresponding calcium-to-sulfur ratios versus H/U (1- ϵ) (1- δ) values. The best design point can then be selected from this family of curves.

Entrained Desulfurizer

The following assumptions are applied for the development of a sulfur removal model of an entrained desulfurizer:

- No significant combustion, pyrolysis or gasification occurs within the desulfurizer and only minor gas composition changes occur due to calcination and sulfation or sulfidation. Thus, this model does not strictly apply within a combustion or gasification stage.

- The gas temperature is constant except for minor changes due to the calcination and desulfurization reactions.

- The sorbent is either precalcined or calcination is extremely fast and can be neglected.

- There is plug flow of both the particles and gases, with the relative velocity between the two being U_s . The model neglects the possibility of gas or particle backflow due to internals in the gas stream that may be inserted to increase the slip velocity.

- There is no size segregation in the system and particle attrition is negligible.

- The gas composition is uniform across any horizontal plane of the desulfurizer. Thus, perfect gas-solid contacting is assumed in the model.

*

The model of the entrained desulfurizer is considerably simpler than that for the fluidized desulfurizer because of the simple plug flow assumption and the resulting uniform residence time for all sorbent particles.

The model of the entrained desulfurizer with the above assumptions starts with material balances on both the gas and sorbent phases:

$$U d C/dx = -R$$
(19)

$$(\mathbf{U} - \mathbf{U}_{\mathbf{n}}) \mathbf{d} (\mathbf{p} \mathbf{N} \mathbf{a}) / \mathbf{d}\mathbf{x} = \mathbf{R}$$
(20)

where U_s is the particle slip velocity at the reactor conditions and R is the rate of the desulfurization reaction as is given by

$$\mathbf{R} = \mathbf{p} \, \mathbf{N} \, \mathbf{k} \, \mathbf{C} \, \left(\mathbf{1} - \boldsymbol{\alpha} \right)^{\mathbf{m}} \tag{21}$$

for fine sorbent particles. Note that the assumption that "m" is zero in Equation (21) holds only up to some level of sorbent conversion beyond which the rate drops significantly.

Adding Equations (19) and (20) and integrating yields

$$C - C_{o} = (1 - U_{o}/U) p N a$$
 (22)

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The gas phase concentration profile may also be solved for directly from Equation (19) to give

$$C = C \exp \{-p N k x/U\}$$
(23)

The sulfur removal efficiency is by definition

$$E = 1 - 0_{e}^{\prime} / 0_{o}$$
 (24)

where C_e is the exit gas sulfur concentration, and from Equation (23), noting that $p = \rho_{ca}$ (1- ϵ), an expression for the gas passage length is obtained:

$$H/U (1 - \epsilon) = -Ln (1 - E)/(\rho_{ca} k)$$
 (25)

The exit utilization of the sorbent particles becomes

$$\boldsymbol{\alpha}_{e} = (\mathbf{C}_{e} - \mathbf{C}_{o}) / [\mathbf{p} \ \mathbf{N} \ (\mathbf{1} - \mathbf{U}_{s} / \mathbf{U})]$$

$$= \mathbf{0}_{o} \ \mathbf{E} / [\boldsymbol{\rho}_{ca} \ (\mathbf{1} - \boldsymbol{\epsilon}) \ (\mathbf{1} - \mathbf{U}_{s} / \mathbf{U})]$$
(26)

The calcium=to=sulfur ratio is

$$Ca/S = E/a_{g} = (1 - U_{g}/U) p N/C_{o}$$

= [-Ln (1 - E)][(U - U_{s})/II][1/(k C_{o})] (27)

1×

Ĝ

Equation (27) is the main design equation, giving the calciumto-sulfur ratio as a function of the sulfur removal efficiency specified (E), the particle residence time in the gas stream $[H/(U-U_s)]$, the sorbent reaction rate constant (k), and the gas initial sulfur content (C_o). In using this design equation, the resulting level of conversion, a_e , should be checked to see that the conversion has not exceeded the value at which the reaction rate begins to fall, thus violating the basic assumption of the model.

1.5 NOMENCLATURE

C:	Concentration of SO_2 or H_2S in the gas.
C _e :	Concentration at the exit of the desulfurizer.
¢.	Concentration at the entrance of the desulfurizer.
Č :	Average concentration in the fluid bed.
d_:	Average particle diameter.
E:	Fraction of sulfur removed in the desulfurizer.
F :	Particle residence time frequency distribution in the fluid bed.
G:	Rate of SO ₂ generation per unit volume.
H :	Fluid bed height or length of entrained desulfurizer.
k:	Reaction rate constant.
m:	Reaction order with respect to function of calcium reacted.
N:	Average number of moles of calcium per particle.
p:	Number of particles per unit volume.
r :	Reaction rate per sorbent particle.
R:	Reaction rate per unit volume.
t:	Time
Ē:	Average reaction rate per unit volume.
U:	Superficial gas velocity.
U _s :	Particle velocity.
X:	Distance coordinate.
C_a/S :	Calcium-to-sulfur molar feed ratio.

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GREEK

a: Fraction of calcium reacted.

 \bar{a} : Average fraction of calcium reacted in the fluid bed.

a_e: Fraction of calcium reacted at the desulfurizer exit.

 δ : Volume fraction of bubbles in the fluid bed.

 ϵ : Voidage in the fluid bed emulsion phase or total voidage in the entrained desulfurizer.

 τ : Average particle residence time in the fluid bed.

 σ : Defined by Equation 17.

 ρ_{ca} : Moles of calcium per unit particle volume.

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LABORATORY EVALUATION OF HIGH-TEMPERATURE SULFUR REMOVAL SORBENTS FOR DIRECT COAL-FIRED TURBINES

DOE