

II. BASIC PROCESS DESCRIPTIONS

Two distinct desulfurization processes were simulated, the Direct Sulfur Recovery Process (DSRP) -based process and the Advanced Hot-Gas Process (AHGP). A complete collection of process flowsheets and stream summaries is contained in Appendix E. The defining characteristic of the DSRP -based process is that a slipstream of clean coal gas is used to produce the elemental sulfur from an intermediate regeneration off-gas stream containing sulfur dioxide (SO₂). The defining characteristic of AHGP is that a SO₂ stream (in a recycle loop) is used to regenerate the sorbent and produce elemental sulfur. Base case simulations for both HGD processes, referred to as “DSRP” and “AHGP”, have 0.85 mol% H₂S in the coal gas feed. Both base cases also generate 260 MW from the clean coal gas. Simulations that deviate from the base cases use suffixes to denote the changes. Table 1 displays the significance of the suffixes. In all cases the coal gas feed pressure is 275 psia and its temperature is 482°C. Simulations changes were strongly dependent on the quantity of sulfur removed from the coal gas. There is little distinction between HGD processes deviating the total sulfur removal by changing H₂S concentration and those changing sulfur removal by varying the power production.

Table 1: Coal Gas Characteristics of Simulations

<u>Simulations</u>	<u>H₂S Feed Molar Concentration</u>	<u>MW Produced</u>
DSRP, AHGP (base cases)	0.85 %	260
DSRP-b, AHGP-b	2.50 %	260
DSRP-c, AHGP-c	0.25 %	260
DSRP-100, AHGP-100	0.85 %	110
DSRP-500, AHGP-500	0.85 %	540

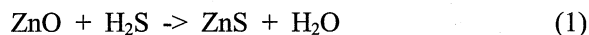
Table 2 shows the composition and flow rate of the “raw” coal gas feed to the base case HGD processes. After sulfur is removed from the streams the coal gas can produce 260 MW.

Table 2 : Raw Coal Gas Feed to Base Case Simulations

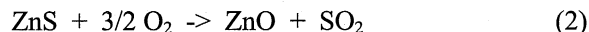
Component	DSRP (lb/hr)	AHGP (lb/hr)
H ₂ S	6,300	6,100
H ₂ O	70,500	69,000
H ₂	11,800	11,500
CO	218,200	213,400
CO ₂	117,400	114,800
N ₂	36,300	35,500
Total	460,500	450,500

1. Direct Sulfur Recovery Process Sorbent Cycle

The term DSRP, strictly speaking, refers only to that part of the entire HGD process that produces elemental sulfur. For convenience, the process simulations were made by assuming a kind of “generic” process (Figure 2) utilizing a ZnO sorbent, with Al₂O₃ support, to remove sulfur (present in the form of H₂S) via reaction 1. The reader should note that in this report “DSRP” is often used as shorthand for the entire “DSRP-based HGD process,” while the novel DSRP reactions to form elemental sulfur occur in what this report refers to as the “DSRP Reactor.” Reaction 1 occurs in the desulfurization reactor (DESULF, Figure 2).

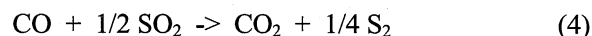
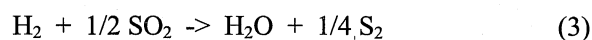


The spent sorbent is regenerated in an oxidizing environment, forming SO₂. Reaction 2 occurs in the regenerator reactor (REGEN, Figure 2), it is driven to completion by oxygen.



The SO₂ exits the regenerator in a stream designated regenerator off-gas (ROG). The ROG flows to the DSRP Reactor. A slipstream of clean coal gas is also fed to the DSRP Reactor. The H₂ and CO in the coal gas slipstream participate in catalyzed reactions (3 and 4), converting SO₂

into elemental sulfur. The reactions 3 and 4 are the simplified overall reactions of a more complex series of reactions.



The heats of reaction for converting SO₂ to elemental sulfur have been calculated by RTI (Portzer, 1996). Comparing RTI calculated values with experimental results indicated the RTI values were reasonable. Table 2 shows that ASPEN calculated heats of reaction are in general agreement with those calculated by RTI. The ASPEN model does an accurate job determining the heat evolved during reactions and therefore will predict correct heat transfer requirements in the process simulations.

Table 3: Heats of Reaction Calculated by RTI and ASPEN Model

Reaction	Temp (°C)	ΔH_{RTI} (BTU/mole)	ΔH_{ASPEN} (BTU/mole)	difference
3	550	-28,000	-28,700	2.5 %
3	650	-28,300	-29,000	2.5 %
3	750	-28,600	-29,200	2.1 %
4	550	-43,900	-44,100	0.5 %
4	650	-43,700	-44,000	0.7 %
4	750	-43,800	-43,600	0.5 %

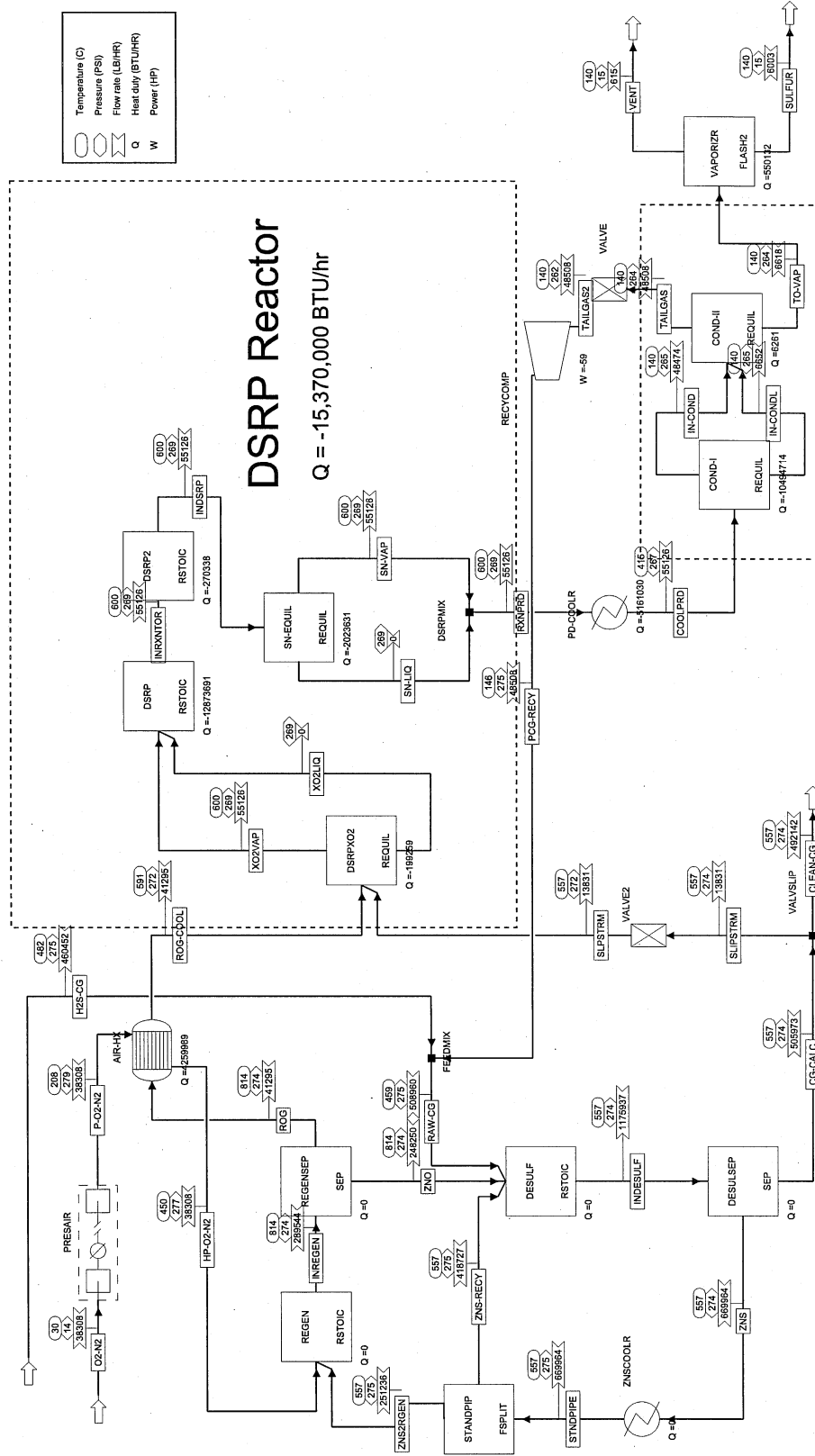
-Heat of reaction values adjusted to match stoichiometry written, P=300 psig for calculations

2. Sorbent Composition - DSRP

The oxidized sorbent, a mixture of ZnO and Al₂O₃, was assumed to contain 15 wt% zinc metal. This distribution is based on an assumed, "generic" sorbent defined by RTI, and results in an oxidized sorbent containing 18.671 wt% ZnO with the balance as inert Al₂O₃ support. While developing the process model and adjusting the stream flow rates to achieve the desired heat balance, it became desirable to increase sorbent circulation rates above the stoichiometric requirements. For these models, the ratio of Zn to Al remained unchanged. The excess Zn sorbent circulating through the system was assumed to remain in the sulfide state (ZnS).

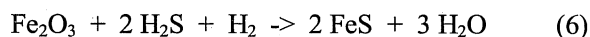
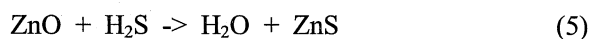
DSRP - based Desulfurization

12/20/97 DSRP

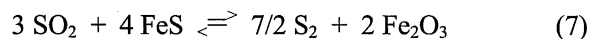


3. Advanced Hot Gas Process Sorbent Cycle

The AHGP (Figure 3) uses a sorbent containing a mixture of ZnO and Fe₂O₃ on Al₂O₃ support for removing H₂S from the coal gas and converting it into elemental sulfur. Both zinc and iron components react with the H₂S present in the coal gas. The desulfurization reactions are represented below.



The sulfided sorbent is sent to a three-stage regenerating reactor that reoxidizes the sorbent and generates elemental sulfur. Sorbent and a SO₂ gas stream flow counter-currently through the regenerator (Figure 3) (Figure 6). The sorbent enters the regenerator at the HX-STAGE (the third and highest elevated stage) where the sorbent is heated by the effluent gas stream. Sorbent descends to REGEN2 (the second stage) where SO₂, present in great excess, oxidizes the majority of the FeS sorbent.



It has been assumed that two-thirds of the FeS oxidizes in REGEN2. Calculated equilibrium conversions for reaction 7 are listed in table 4. Sorbent enters the second stage of the regenerator at 512°C and gas enters the second stage at 715°C. Table 3 shows equilibrium conversions varies significantly over the range of temperatures possible in stage 2, a stage for which it is unclear what value represents its temperature the best. Simulated stage 2 exit temperatures were 580°C, this exit temperature assumes perfectly mixed behavior in the stage 2. In reality there will likely be higher temperatures at lower elevations in the stage. The ASPEN model uses an RSTOICH block to simulate this stage so that the conversion can be arbitrarily fixed at 67%. This value was defined by RTI, based on experimental data. The information in Table 4 suggests that the assumed two-thirds conversion probably overestimates the actual conversion. In commercial practice, increasing the Fe:Zn ratio could compensate for lower than simulated reaction 7 conversions (conversion written in terms of FeS). Another aspect of this reactor stage is that the

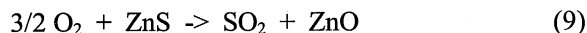
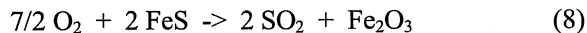
extent that FeS oxidizes by SO₂ will vary with temperature fluctuations and increase the difficulty in balancing SO₂ consumption and generation.

Table 4: Equilibrium Conversion for FeS Oxidation by SO₂

<u>Regenerator Temperature (°C)</u>	<u>Equilibrium Fractional Conversion</u>
500	0.43
550	0.53
600	0.65
650	0.77
700	0.90

Equilibrium calculated from ASPEN REQUIL block, P = 275 psia

Sorbent oxidization approaches completion in the bottom regenerator stage (REGEN1, Figure 3). REGEN1 oxidizes the sorbent using pure oxygen (reactions 8 and 9). The oxidation generates SO₂, making up for SO₂ used in reaction 7.



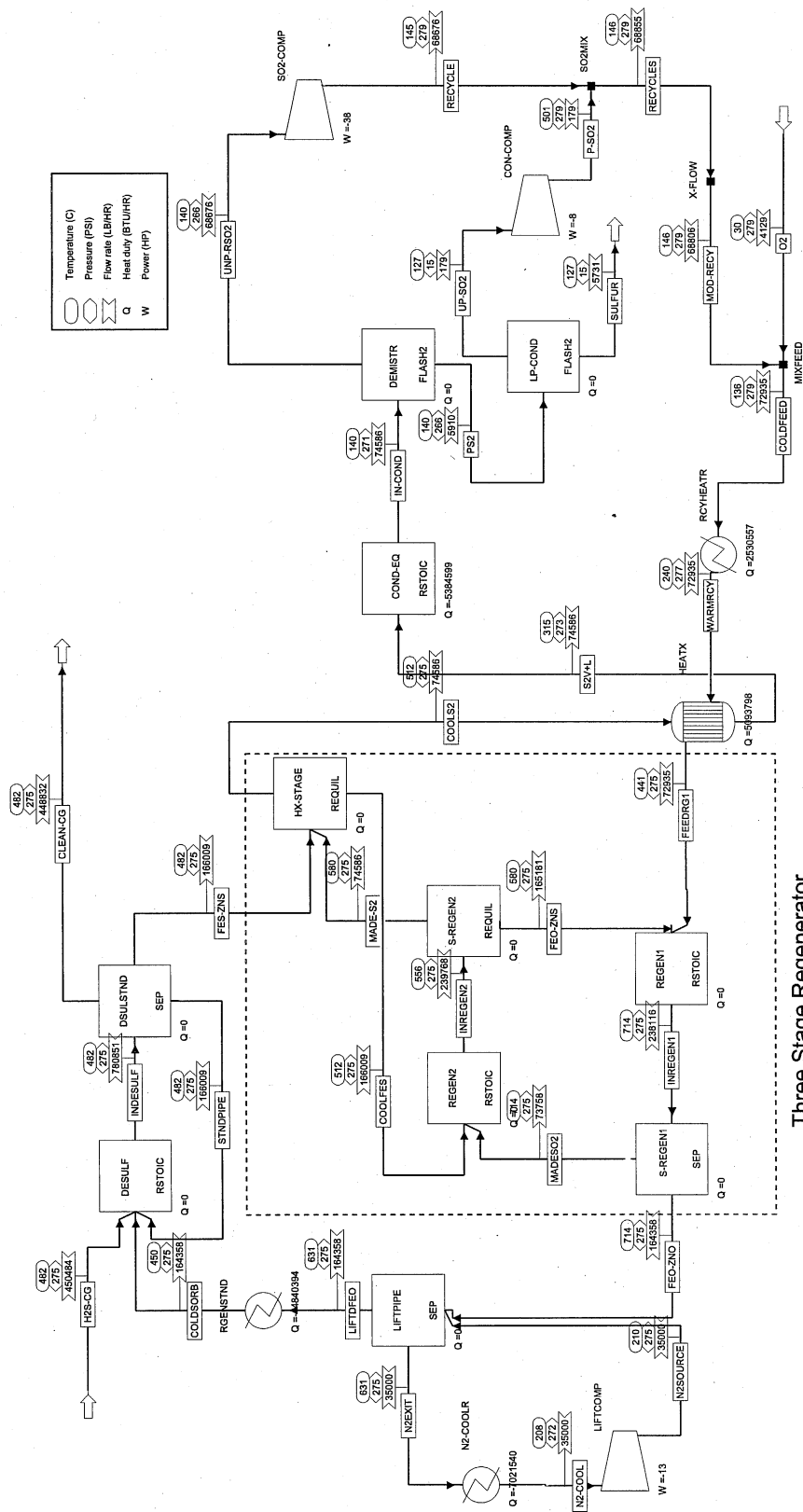
This modeling assumes that SO₂ does not oxidize sorbent in REGEN1, since equilibrium conversion for SO₂ oxidation is approached in REGEN2. The equilibrium regeneration of sorbent by SO₂ will be quickly superseded by oxygen regeneration.

4. Sorbent Composition - AHGP

AHGP sorbent composition was defined by RTI to contain 3 wt% Zn and 12 wt% Fe, which corresponds to 3.734 wt% ZnO and 17.154 wt% Fe₂O₃. The balance, 79.109 wt%, was inert Al₂O₃. As discussed above, the ratio of Fe to Zn will need to be increased if the actual conversion for reaction 7 is lower than 0.667, its assumed value.

AHGP Advanced Hot Gas Process

AHGP 1/19/98



Three Stage Regenerator

During subsequent simulation development and adjustment of stream flow rates to achieve the desired heat balance, it became apparent the defined sorbent composition was not optimal. To run the reactors adiabatically, it was necessary to increase sorbent flow. Circulating more sorbent increased the heat capacity of the reactive stream and reduced the adiabatic temperature rise. Such a sorbent increase required an increase in Al₂O₃ flow. Increasing Fe or Zn flow would have upset the SO₂ generation and consumption balance created by reactions 7, 8 and 9. Therefore, alumina flow was increased. The effect would be the same as adding pure alumina sorbent to the reactor system, or by manufacturing a sorbent that has a lower active metal content and increasing the total flow to match the amount of alumina added.

The Al₂O₃ circulation was increased until an adiabatic regenerating reactor would operate below 716°C. The effects of changing Al₂O₃ circulation ripple through the process. The required SO₂ circulation rate was affected by varying the Al₂O₃ flow. The desired SO₂ volumetric flow rate increased with increasing sorbent flow rate because of increased reactor size. Increasing the SO₂ circulation helped reduce the adiabatic temperature rise, lessening the need to increase sorbent flow. Table 5 shows how Al₂O₃ flow was increased until an acceptable adiabatic regeneration temperature was achieved. The table displays the stepwise approach used to determine the Al₂O₃ circulation needed in the AHGP-b simulation (-b signifies a 2.5 mol% H₂S in the feed). In the simulation, ZnS and FeS flow rates (leaving the desulfurization reactor) were constant at 7,600 lb/hr and 41,000 lb/hr, respectively.

Table 5: Al₂O₃ Circulation Rate Effect on Regenerator Stage 1 Temperature

<u>Al₂O₃ (lb/hr)</u>	<u>T_{REGEN1} (°C)</u>	<u>Desired SO₂ flow (ft³/hr)</u>
165,297	1025	102,000
330,594	787	181,000
400,000	759	214,000
450,000	715	238,000

III. PHYSICAL PROPERTIES

1. Equation of State

All simulations discussed in this report used the Peng Robinson cubic equation of state with the Boston-Mathias alpha function (PR-BM).

1.a. *Equation of State's Importance*

Modeling unit operations requires physical property information for all compounds present. In calculating thermodynamic equilibrium, fugacity coefficients are used to determine phase equilibrium. An equation of state can be used for the calculation of fugacity, as well as other important physical properties. The equation of state also relates pressure, temperature, and molar volume so that only two need to be specified and the third can be calculated. Phase equilibrium is established when the fugacity of each component is the same in all phases.

A two-phase (vapor and liquid) system is at equilibrium when:

$$f_i^v = f_i^l \quad i = 1, 2, \dots, N \text{ where } N \text{ is the number of compounds}$$

Where:

$$f_i^v = \phi_i^v y_i P \quad \text{Fugacity of component } i \text{ in the vapor phase}$$

$$f_i^l = \phi_i^l x_i P \quad \text{Fugacity of component } i \text{ in the liquid phase}$$

$$\ln \phi_i^\alpha = -\frac{1}{RT} \int_{\infty}^{V_i^\alpha} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} - \frac{RT}{V} \right] dV - \ln Z_m^\alpha$$

Notation:

α	=	vapor or liquid (v or l)	P	=	Pressure
n_i	=	Mole number of component i	T	=	Temperature
x_i	=	Liquid mole fraction of component i	R	=	Gas Constant
y_i	=	Vapor mole fraction of component i	V	=	Total volume
Z	=	Compressibility factor			

The equation of state also is used to determine other properties via departure functions.

- Enthalpy departure:

$$(H_m - H_m^{ig}) = - \int_{\infty}^V \left(P - \frac{RT}{V} \right) dV - RT \ln \left(\frac{V}{V^{ig}} \right) + T(S_m - S_m^{ig}) + RT(Z_m - 1)$$

- Entropy departure:

$$(S_m - S_m^{ig}) = - \int_{\infty}^V \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV + R \ln \left(\frac{V}{V^{ig}} \right)$$

- Gibbs Free Energy departure:

$$(G_m - G_m^{ig}) = - \int_{\infty}^V \left(P - \frac{RT}{V} \right) dV - RT \ln \left(\frac{V}{V^{ig}} \right) + RT(Z_m - 1)$$

Notation:

H = Enthalpy S = Entropy G = Gibbs Free Energy

ig (superscript) denotes variable's value for ideal gas

m (subscript) denotes variable's value for the mixture

1.b. Selection

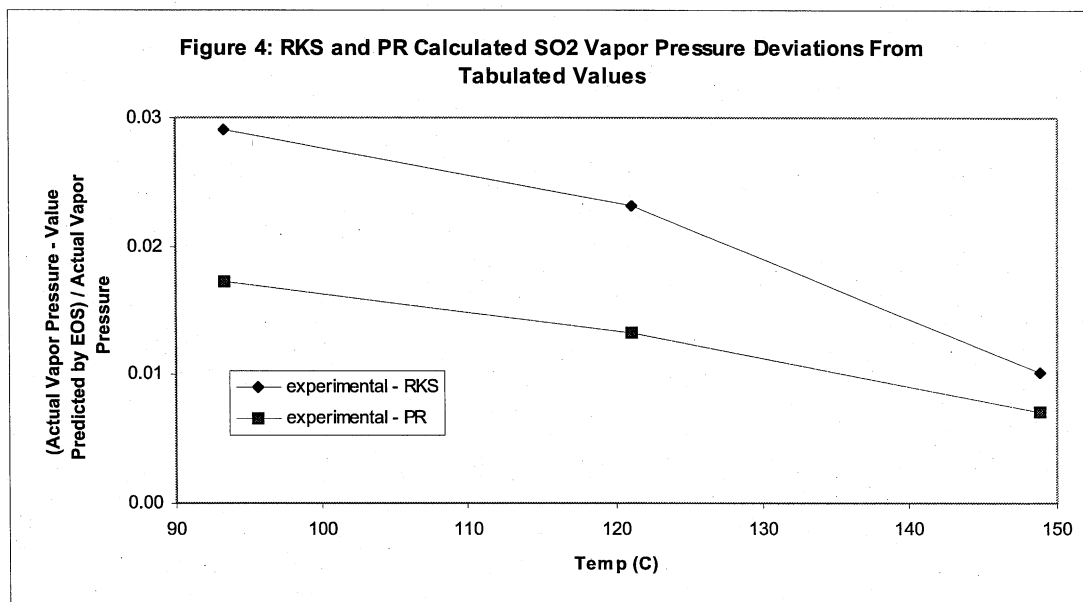
The Peng Robinson cubic equation of state with the Boston-Mathias alpha function (PR-BM) was used in these simulations because it was recommended for gas-processing, refinery, and petrochemical applications (ASPEN PLUS- Reference Manual 2). It was recommend for modeling nonpolar and mildly polar mixtures, including hydrocarbons and light gases like: carbon dioxide, hydrogen sulfide, and hydrogen. Reasonable results can be expected for all temperatures and pressures. The Peng-Robinson equation of state is:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)}$$

Variables 'a' and 'b' account for attractive forces and the space occupied by all species present, R is the ideal gas constant, T is temperature and V_m is the mixture's specific molar volume.

The Boston Mathias extrapolation is used for supercritical components. Boston and Mathias derived an alpha function that is particularly good at modeling decreasing attraction between molecules at high temperatures (ASPEN PLUS- Reference Manual 2).

The above descriptions also apply to the Redlich-Kwong-Soave cubic equation of state with Boston-Mathias alpha function (RKS-BM). The decision to use the PR-BM over RKS-BM was made after comparing literature phase data (Braker) with simulations using both property option sets. Figure 4 shows the fractional deviation of simulated vapor pressures compared to literature values. Both equations of state calculate values in good agreement with actual values, and the Peng-Robinson equation of state gives the best results.



2. Elemental Sulfur

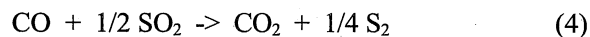
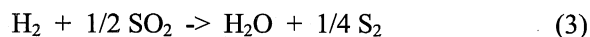
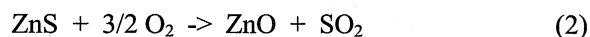
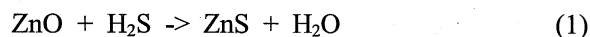
Accurately predicting elemental sulfur properties requires knowing which allotropes of sulfur will be formed. For the conditions occurring in the HGD process S_8 , S_6 , and S_2 are the predominant allotropes (Barnett; Cotton). Temperature is the dominant variable affecting the equilibrium sulfur distribution. The ASPEN simulations concurred with literature distributions, predicting S_2 predominance at high temperatures (reactor temperatures), and a shift towards S_8 and S_6 at lower temperatures (condenser temperatures). Accurate sulfur distributions are important for the integrity of phase equilibrium predictions. In addition, correctly simulating sulfur equilibrium increases the accuracy of energy balances.

It is worth noting some unusual properties of liquid elemental sulfur. Recovered sulfur should not be raised to temperatures above 159°C , as above that temperature the liquid sulfur becomes increasingly viscous (Cotton). Sulfur melts around 114°C ; it does not have a sharp melting point due to the presence of various allotropes (Barnett).

IV. EQUIPMENT

1. DSRP- Based Process Equipment

For the purposes of this process simulation and economic evaluation, the DSRP - based HGD process was defined to have a desulfurization and regeneration transport reactor network as shown in Figure 5. Sulfur is removed from coal gas (Reaction 1) in the desulfurization reactor and sorbent regeneration (Reaction 2) takes place in the regeneration reactor. There is also a DSRP Reactor in which the elemental sulfur is formed via Reactions 3 and 4. Other major pieces of equipment in the DSRP include compressors, condensers, and heat exchangers.



In addition to Reactions 3 and 4, intermediate and side reactions occur in the DSRP Reactor. They are discussed later in the report.

1.a. *Desulfurization and Regeneration Transport Reactors - DSRP*

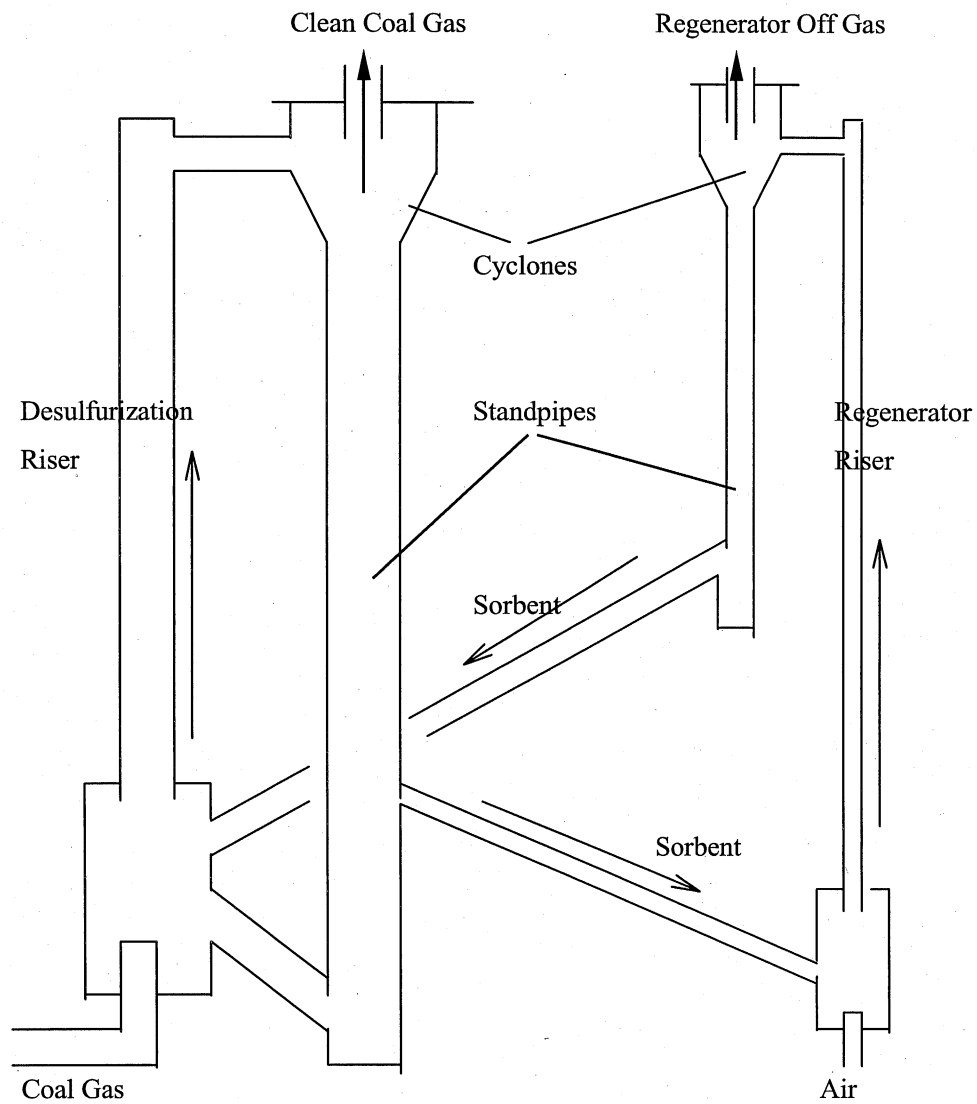
The DSRP - based HGD process is assumed to use transport reactors for the desulfurization and regeneration reactions. The Sierra Pacific hot-gas desulfurization system (Cambell) has been the basis for the reactor system design (Figure 5). Cyclones separate the sorbent from the exiting gas streams. Sorbent settles from the cyclones into standpipes. The sorbent has a relatively high residence time in the standpipes. Standpipe residence times are several minutes while reactor residence times are only several seconds long. Standpipe heat exchangers remove heat from the reactor system. During startup, sending steam through the standpipe heat exchanger could heat the sorbent partially up to reactor temperatures.

The regeneration reaction releases a substantial amount of heat. Feeding a stoichiometric amount of sorbent in the ASPEN simulation to an adiabatic regeneration reactor results in predicted temperatures surpassing 1,000°C (DSRP base case). RTI guidelines stated that HGD sorbents would experience substantial sintering at temperatures above 815°C. The strategy adopted to control reactor temperature is recycling excess sorbent. The additional sorbent increases the total heat capacity of the reactive streams. The additional sorbent will not result in additional reactions and the increased heat capacity will decrease the adiabatic temperature rise. The adiabatic temperature rise can be expressed by the following relationship:

$$\Delta T_{\text{adiabatic}} \approx \frac{\Delta H_{\text{rxn}}}{C_{p \text{ stream}}}$$

Increased sorbent flow was selected as the preferred strategy over that of using a reactor heat exchanger, since it simplifies reactor design. Furthermore, hot spots are more likely to occur in a reactor containing a heat exchanger. Limiting reactor temperature by reducing reactor feed stream temperatures (without additional sorbent circulation) was also investigated. This approach was discarded because the reactions would be extinguished at feed temperatures low enough to keep the reactor temperature below 815°C.

Figure 5: Schematic of DSRP - Based HGD Process Desulfurization and Regeneration Reactors



The transport reactors exhibit numerous advantages over fixed-bed, fluid-bed and moving-bed reactors. The transport reactor has lower capital cost, its high flowrate of sorbent controls reactor temperatures, and the high velocities prevent hot spots from occurring on the sorbent (Campbell). The transport reactor's superior temperature control allows undiluted air to be used during regeneration.

The equations used for sizing and costing the DSRP - based process desulfurization and regeneration transport reactor system are described in Appendix G-Calculation of Reactor Size. The actual calculations can be found in Appendix H-Sizing Reactors for the DSRP.

1.b. *DSRP Reactor - DSRP*

The DSRP Reactor itself is a fast fluidized bed reactor with its catalyst modeled as Al_2O_3 . There are several ASPEN blocks used to model what will be only one DSRP Reactor, a dashed box has been drawn around the series of blocks used (Figure 2). The catalyst is circulated through the reactor and an external heat exchanger. Heat is removed by cooling the catalyst while it is outside the reactor. The heat exchanger cools the catalyst to 500°C and the catalyst is then reintroduced to the reactor at a rate that is high enough to keep the DSRP Reactor effluent near 600°C . (Appendix D- Calculation of DSRP Catalyst Cycling Rate)

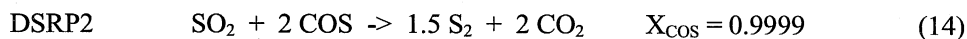
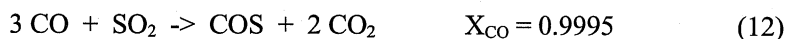
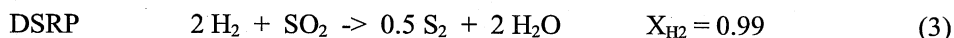
Figure 2 shows that several blocks were used for the simulation of the DSRP Reactor: DSRPX02, DSRP, DSRP2, and SN-EQUIL.

In DSRPX02, any oxygen that enters the DSRP as a contaminant in the ROG consumes coal gas by a conventional combustion reaction. The oxygen combines with CO forming CO_2 . It is not necessary to model combustion of H_2 since the ratio of CO to H_2 will be set by the Water Gas Shift (WGS) reaction. Also in DSRPX02 the WGS reaches equilibrium. The WGS reaction is known to reach equilibrium before the reactions of SO_2 with H_2 or CO begin (Chen,

1994). DSRPXO2 uses a Gibbs Free Energy calculation to establish equilibrium for reactions 10 and 11.



The key DSRP reactions have been modeled in the following blocks.



SN-EQUIL establishes the allotropic distribution of elemental sulfur using a Gibbs Free Energy calculation. Including this block more accurately models the heat generated inside the DSRP Reactor.



1.c. *PRESAIR - DSRP*

The transport reactor design for the regenerator in the DSRP - base HGD process model allows the use of undiluted air (“neat air”) to regenerate the desulfurization sorbent. Introducing air at the required pressure can be accomplished using either an axial-flow or centrifugal compressor. In most applications, including this process simulation, it is preferable to use a centrifugal compressor. Centrifugal compressors have the advantage of a larger operating range (Dimoplom). Centrifugal compressors typically operate below 225°C (Brown; Dimoplom) in order to avoid equipment damage.

The large increase in pressure (ambient to 275+ psia) in the PRESAIR air compressor generates a considerable temperature rise. Interstage cooling, between the compressor's 6 stages, is necessary to maintain an air temperature below 225°C and to prevent mechanical damage to the compressor (Brown; Dimoplou). The temperature increase across the first stage does not require cooling stage 1 effluent and there is no need to cool the effluent of the final stage as well. Therefore, there will be four interstage coolers needed for the six-stage compressor. Pressure drop during interstage cooling can be approximated as 2% of the pressure entering the cooler or 2 psia, whichever is larger (Brown). For pressuring to 280 psia estimating a 2 psia drop for each cooler is reasonable; these pressure losses are included in the ASPEN PLUS compressor block calculations.

Significant capital will be spent on the purchase of an air compressor. Increasing pressure to 280 psia for an feed of 8,800 ft³/min (DSRP base case) requires a compressor made of steel as opposed to cast iron (Bloch). Compressors made of low value steel should be both mechanically durable and economical. For simplicity, the cost estimates in this report assume electric drive.

Steam turbines could drive the compressors. Steam turbines are historically the most popular means of driving centrifugal compressors. They have the ability to operate over a wide speed range. Electric motors have experienced increasing favor due to a typically lower operating cost. Buying electricity is more economical than small scale steam generation for a specific piece of equipment (Brown). However, with the desulfurization processes generating steam and with steam available from the power plant, a steam turbine may be the best means of driving the compressors.

Air Compressor Costs

Compressor costs were determined from a budgetary quotation obtained from Ingersoll-Rand. Ingersoll-Rand stated a cost of \$241,000 for the Centac Model 2CV23M3EPPF. This model Centac is a centrifugal air compressor (drive and motor) capable of raising 2,250 acfm to

280 psia. Extrapolation was used to determine the cost of compressors needed for the different flow rates. Figures in Peters and Timmerhaus (1991) were used to determine the rate at which compressor costs change with varying flow rates.

The compressor, PRESAIR, is modeled as a six stage compressor. It has been assumed that the interstage coolers lower the air temperature to 115°C. Calculation of stage efficiency was performed using a procedure outlined in Brown (1986). The polytropic efficiencies calculated range from 0.65 to 0.787, which are consistent with other values found in literature (Brown; Dimoplon). PRESAIR pressurizes 8,800 acfm (in the DSRP base case); for such a flow ASPEN predicts a 3,280 HP power requirement. Directly scaling up the Centac (2,250 acfm, 800 HP) compressor predicts a 3,130 HP power requirement. The similar horsepower requirements suggest that ASPEN is realistically simulating the air compressor.

1.d. *RECYCOMP - DSRP*

The compressor RECYCOMP repressurizes the vapor stream leaving the sulfur condenser (the tailgas of the DSRP reaction) and sends it back to the desulfurization reactor. Recycling this stream eliminates an emissions stream while causing a minor load increase for the reactor network. The pressure increase between the condenser and the desulfurization reactor should be within the capabilities of a single stage centrifugal compressor, and RECYCOMP was modeled as such.

1.e. *High Pressure Condenser - DSRP*

The High Pressure Condenser condenses sulfur out of the DSRP Reactor effluent stream. It is high pressure in the sense that it operates near the pressure of the DSRP Reactor. Reducing the temperature to 140°C condenses the sulfur. At this temperature, the vast majority of sulfur condenses, and there is no risk of freezing.

The High Pressure Condenser is simulated using two blocks (Figure 2). The first, COND-I, is an equilibrium block that establishes equilibrium between S_2 and S_8 . At high temperatures like those in the DSRP reactor, sulfur is predominately in the S_2 form (Barnett; Chen; Cotton). At the cooler condensation temperatures, the S_8 and S_6 sulfur species predominate. The second block, COND-II, establishes equilibrium between the S_8 and S_6 sulfur species and phase equilibrium. The S_8 and S_6 sulfur species are easier to condense. Calculation of the sulfur equilibrium, in addition to more accurately simulating the phase equilibrium, also increases the accuracy of the heat transfer requirements. The low temperature in the condenser makes it unsuitable for the direct production of high pressure steam. The condenser could be used to preheat the feedwater to other steam-generation units (Appendix F).

1.f. *VAPORIZR - DSRP*

Reducing the sulfur product stream's pressure to ambient will cause the water present in the stream to vaporize. The vaporizing water can cool the sulfur stream enough to cause freezing. The VAPORIZR accomplishes three tasks: a) it reduces sulfur pressure to ambient; b) it supplies heat to the sulfur stream so that the temperature will be maintained at 140°C and sulfur will remain molten; and, c) it also helps purify the product stream by removing water from the sulfur.

1.g. *PD-COOLR - DSRP*

Prior to entering the condenser, the DSRP Reactor effluent ("RXNPRD") is sent through the Product Cooler (PD-COOLR) heat exchanger. Cooling the reactor products in this heat exchanger reduces the condenser heat duty and PD-COOLR operates at temperatures suitable for generating high pressure steam. Sulfur condensation inside the PD-COOLR should be avoided. Condensation would create the undesirable situation of two phase flow and would require removing the sulfur during shutdown so that it will not freeze inside the heat exchanger. Operating the PD-COOLR above the product stream's dew point would prevent sulfur condensation. Dew point calculations were made for the various reactor effluent distributions.

The allotropic sulfur distribution (S_2 , S_6 , S_8) changes with temperature, however the speed at which equilibrium is reached is unknown. It is not known how closely sulfur allotrope distribution will approach equilibrium in the cooler. Therefore, calculations were made for the dew point temperatures at both the equilibrium distribution of sulfur allotropes, and at the allotrope distribution that leaves the reactor (Table 6).

For the simulations, the PD-COOLR was defined to cool reaction products to 415°C. Table 6 shows that at 415°C sulfur condensation will not occur if the sulfur allotrope equilibrium is reached instantaneously (Sulfur Equilibrium = yes) and also will not occur if the sulfur allotrope distribution is still at the DSRP Reactor temperature distribution (Sulfur Equilibrium = no).

Table 6: Dew Point Temperatures for DSRP Product Distributions

<u>Product distribution</u>	<u>Sulfur Equilibrium</u>	<u>Pressure (psia)</u>	<u>Temperature (°C)</u>
DSRP	yes	275	360
DSRP	no	275	405
DSRP-b	yes	275	357
DSRP-b	no	275	402
DSRP-c	yes	275	362
DSRP-c	no	275	406

1.h. AIR-HX - DSRP

The AIR-HX heat exchanger utilizes the hot regenerator off gas (“ROG”) stream to raise the temperature of the high pressure air stream (“P-O₂-N₂”). Heating the air is required to achieve a sufficiently high temperature to initiate the regeneration reaction. Cooling the ROG reduces the heat removal required to keep the DSRP reactor at 600°C. The hot (above 800°C) ROG stream contains SO₂. The presence of hot SO₂ requires that the AIR-HX heat exchanger tubes be constructed from type 310 stainless steel (SS 310).

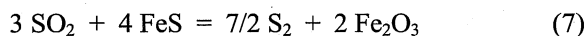
2. AHGP Equipment

The AHGP consists of a desulfurization transport reactor and a 3-stage bubbling bed regeneration reactor. The reactions that remove sulfur from coal gas (Reactions 5 and 6) proceed in the desulfurization reactor. In the regenerator the sorbent is regenerated with SO₂, to generate elemental sulfur (reaction 7), and is subsequently regenerated with O₂ to produce SO₂ (reactions 8 & 9). Forming elemental sulfur during regeneration eliminates the need for a third reactor, as the DSRP based process requires. Other major pieces of equipment in the AHGP include compressors, condensers, a demister, and heat exchangers.

2.a. Desulfurization and Regeneration Reactors - AHGP

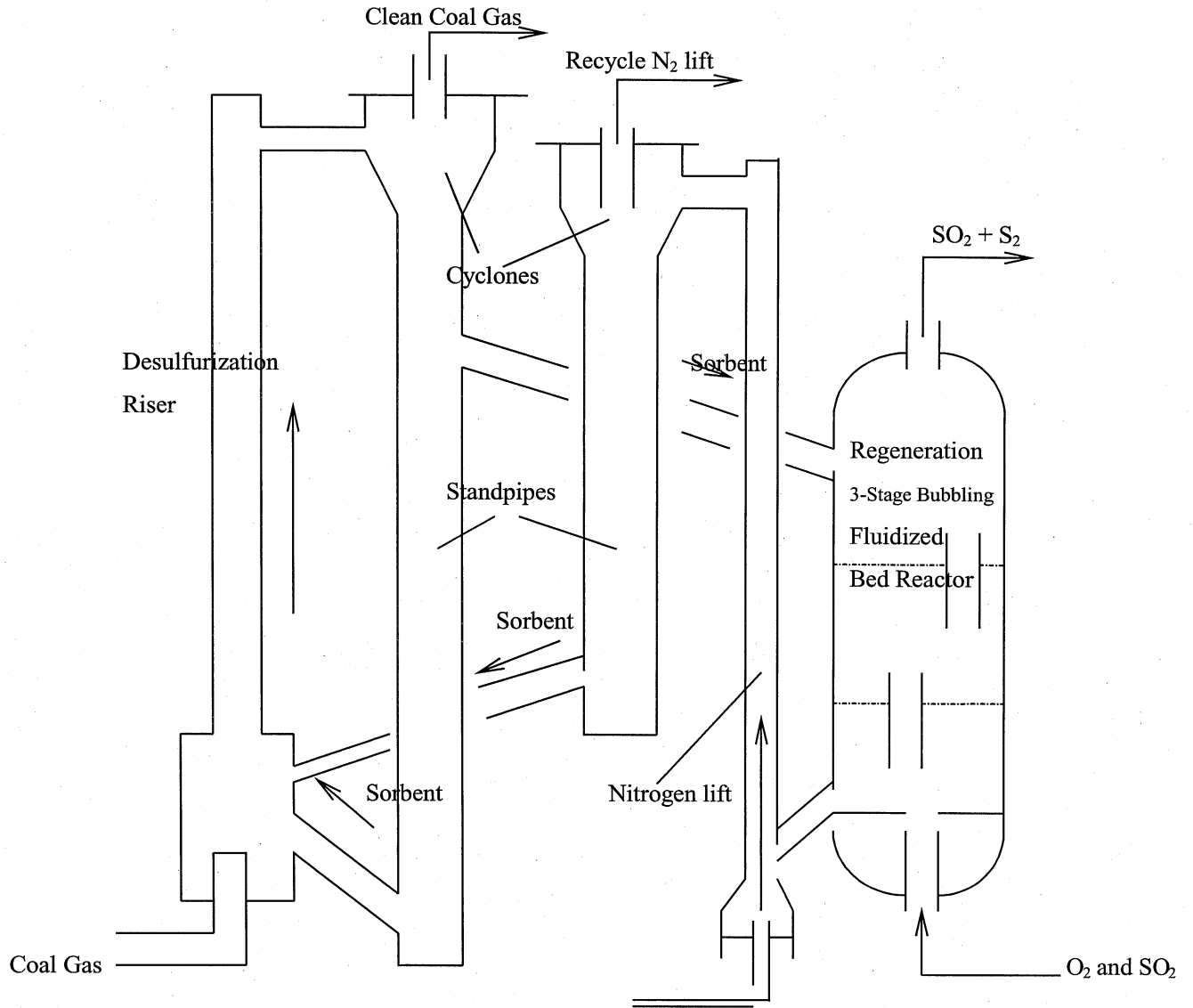
There are several differences between the AHGP desulfurization and regenerator reactor designs (Figure 6) and those envisioned for the DSRP -based process (Figure 5). For example, in the AHGP sorbent descends counter-currently against the rising SO₂ in the regeneration reactor. Sorbent descending through the regenerator makes it necessary to re-elevate sorbent into a standpipe located upstream of the desulfurization reactor. A heat exchanger in the standpipe enables cooling of the sorbent before it re-enters the desulfurization reactor.

The top stage of the regenerator (HX-STAGE, Figure 3) heats the entering sorbent by direct contact with the exiting SO₂ stream. The second stage of the regenerator is modeled with REGEN2 and S-REGEN2. REGEN2 models the following equilibrium reaction:



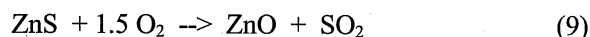
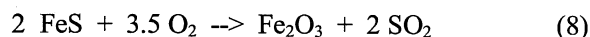
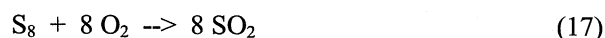
This equilibrium reaction is modeled with an RSTOICH block, assuming a 0.667 fractional conversion of FeS. An RSTOICH block is used due to the difficulty of balancing SO₂ consumption and generation. As discussed earlier in the report (Section II.4), assuming a 0.667

Figure 6: Schematic of AHGP Desulfurization and Regeneration Reactors



fractional conversion may be an optimistically high assumption. If so, more Fe will need to be circulated to make up for the discrepancy. The S-REGEN2 block establishes the equilibrium distribution of sulfur allotropes.

The bottom stage is modeled with the REGEN1 and S-REGEN1 blocks. Oxygen feed to REGEN1 oxidizes the sorbent. Although there is SO₂ present in large quantities in REGEN1, it is assumed not to oxidize any sorbent. Equilibrium conversion for SO₂ oxidation is assumed to be reached in the second stage. Any unreacted FeS present in the sorbent coming from the second stage is expected to react very quickly with oxygen present (reactions 17 & 18). The ZnS is expected to regenerate less rapidly than the iron compound. Uncondensed sulfur recycling back to REGEN1 will quickly oxidize. These reactions are modeled to occur in the following order:



The bottom stage is simulated to operate with all oxygen being consumed in REGEN1, and a small portion of ZnS remaining unoxidized.

More than one regeneration reactor maybe used in parallel for the AHGP. Sizing the reactor (Appendix I) revealed that to achieve the desired superficial velocity for removing the larger sulfur quantities requires undesirably large reactor diameters (25+ ft). The larger reactor diameters will require thicker reactor walls (4.5+ in) to contain the high pressures. Reactors in parallel reduce reactor diameter and the required wall thickness resulting in less steel required. A maximum reactor diameter of 13 feet was the guideline used during sizing. The 3-stage regenerator heights were set at 45 feet. It is expected that 5 ft will be needed for the heat exchanging stage, 10 ft for the middle stage, and 2.5 ft for the bottom stage. The rest of the reactor height will be used for phase separation.

The equations used for sizing and costing the AHGP desulfurization and regeneration transport reactor system are described in Appendix G-Calculation of Reactor Size. The actual calculations can be found in Appendix I-Sizing Reactors for the AHGP.

2.b. *LIFTCOMP - AHGP*

The AHGP desulfurization - regeneration transport reactor system requires a means of elevating the sorbent exiting the regeneration reactor. This will be accomplished using a nitrogen lift (Figure 3 and Figure 6). LIFTCOMP increases the pressure of the nitrogen recycle before it enters the nitrogen lift. A cyclone and filters placed upstream of LIFTCOMP and N2-COOLR will prevent sorbent from damaging the compressor.

2.c. *SO2-COMP - AHGP*

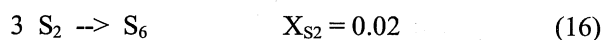
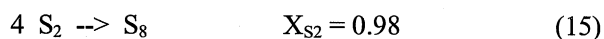
SO2-COMP recompresses the SO₂ loop. It is advantageous to recompress the SO₂ loop after the condenser because the lower gas temperature will increase the compressor efficiency and reduce wear on the compressor. The pressure increase required will be obtainable using a single stage centrifugal compressor.

2.d. *CON-COMP - AHGP*

The CON-COMP compressor is used to reintroduce the SO₂ that vaporizes when the sulfur stream is reduced to ambient pressures (LP-COND, Figure 3). The small flow rate means a single stage reciprocating compressor can be used to pressure the SO₂ stream. The pulsing flow of SO₂ coming from CON-COMP will not have a significant effect on the large SO₂ loop.

2.e. COND-EQ - AHGP

The condenser, COND-EQ, cools down the SO₂ loop so that sulfur can be condensed out. The stream temperature is reduced to 140°C, and sulfur distribution is established in COND-EQ. It was initially intended that sulfur equilibrium would be calculated using a REQUIL block; however, this caused convergence problems. Using the RSTOIC block eliminates the convergence problem and does not compromise the validity of the results. The sulfur equilibrium distribution was determined in a separate simulation.



The large vapor stream containing a small volume of molten sulfur will make a demister necessary to isolate the small liquid flow.

2.f. DEMISTR - AHGP

The large gas stream of SO₂ will suspend the relatively small flow of condensed sulfur. The demister (DEMISTR) will be necessary for collecting the sulfur. The liquid sulfur accounts for 8 wt% of the stream (“IN-COND”), but only 0.1 vol% of the SO₂ - sulfur flow.

2.g. LP-COND - AHGP

Sulfur leaving the demister needs to be brought to ambient pressure for storage. This can be accomplished in a flash tank (LP-COND, Figure 3). The pressure drop vaporizes much of the SO₂ that co-condenses with the sulfur. The temperature drop caused by SO₂ vaporization is not enough to freeze the sulfur. Vaporizing off the SO₂ decreases the sulfur stream temperature to 127°C, well above the melting temperature of sulfur (114°C). The volumetric flow of SO₂ vaporized is 47 times larger than the condensed sulfur flow. The tank should contain a demister pad or some other separation device to prevent sulfur from being entrained with the SO₂ vaporized.

2.h. HEATX - AHGP

The HEATX heat exchanger transfers heat from the warm regenerator effluent (SO₂ and sulfur) to preheat the cool regenerator feed stream of recycled SO₂ and oxygen. Sulfur condensation in the heat exchanger should be avoided. If sulfur condenses, the system would have to handle two phase flow from HEATX to the condenser. Shutdown procedures would also require removing sulfur from the heat exchanger to prevent sulfur from freezing inside. Assuming the sulfur allotrope distribution is at equilibrium when condensation occurs, the SO₂ - sulfur stream's dew point is 310°C. Cooling the SO₂ - sulfur stream to no lower than 315°C should prevent condensation from occurring.

2.i. N2-COOLR - AHGP

The N2-COOLR cools the nitrogen stream prior to its recompression in LIFTCOMP. Cooling the stream decreases the power required for recompression and reduces the possibility of damaging the compressor. The cool nitrogen stream contributes to reducing the temperature of sorbent feed to the desulfurization reactor. Sorbent entering the compressor would cause damage. Therefore, filters should be installed upstream of the compressor. The filters will also be placed upstream of the heat exchanger (N2-COOLR) to prevent build up of sorbent in the heat exchanger.

2.j. RCYHEATR - AHGP

The RCYHEATR was incorporated to ensure that the SO₂ - oxygen feed to the regenerator would be hot enough to initiate the regeneration reactions. Superheated steam is used to raise the SO₂ - oxygen stream temperature, as the separate steam generation process flow sheets show (Appendix F). RCYHEATR works with the HEATX heat exchanger to raise the SO₂ - oxygen stream temperature above 400°C. The RCYHEATR is needed because, HEATX heat transfer is limited to insure no condensation occurs upstream of the condenser.

V. PARAMETRIC STUDIES

Parametric studies were performed to determine how HGD requirements were affected by various coal gas feeds. Inlet H₂S concentrations were varied to simulate variation in sulfur content with different types of coal. Therefore, H₂S concentrations will vary between plants using different coal sources. The effect of power generation capacity was also simulated. Finally, different oxygen sources (air vs. pure oxygen) were investigated. Flow sheets and stream summaries for variations of both processes can be found in appendix H.

1. H₂S Inlet Concentration

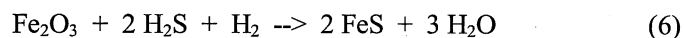
DSRP and AHGP simulations were performed using a base case coal gas feed containing 0.85 mol% H₂S and a base case power production of 260 megawatts, after sulfur removal. Additional simulations were performed to determine the effect of H₂S inlet concentration on the amount of coal gas that had to be produced. Table 7 shows how varying H₂S inlet concentration requires increasing the gasification of coal to maintain 260 MW generation.

Table 7: Coal Gas Fed to and Consumed by HGD for Various H₂S Concentrations

Simulation	H ₂ S inlet conc. (mol%)	Coal Gas Fed (lb/hr)	Consumed H ₂ (lb/hr)	Consumed CO (lb/hr)
DSRP	0.85	460,000	320	6,000
DSRP-b	2.50	501,000	1,000	19,000
DSRP-c	0.25	447,000	90	1,700
AHGP	0.85	450,000	160	0
AHGP-b	2.50	468,000	470	0
AHGP-c	0.25	444,000	46	0

The sulfur concentration has a profound effect on DSRP flow requirements because of the coal gas slipstream used in the DSRP reactor. The coal gas slipstream increases as the amount of sulfur converted in the DSRP reactor increases.

The small increase in required coal gas for the AHGP can be attributed to the consumption of H₂ in the desulfurization reaction:



The higher sulfur concentrations also require more sorbent circulation to dissipate the heat evolved during reactions. Increased sulfur concentrations require larger reactors. Increasing sulfur also increases the heat removal requirements.

2. Power Generation

Parametric studies were performed to determine the influence of power plant capacity; power generation is 260 MW in the base case. Inlet flows were altered to generate 110 MW and 540 MW. The power level adjustments resulted in flow rates and energy transfer that both scale directly with the change in power generation. The effect of the varying coal gas feed rate was similar to the effect of changing H₂S feed concentrations. An economic comparison shows that the process costs depend on the total sulfur removal requirements. Variations in the flow rates of the other coal gas components do not have a significant effect on the HGD.

3. Pure Oxygen vs. Air Oxidation

Sulfur is removed from the coal gas stream by the reaction of H₂S with the active components of the sorbent to form metal sulfides. Regenerating the sorbent allows it to be reused for removing more sulfur. Sorbent regeneration occurs by exposing the sulfurized sorbent to an oxidizing environment. Pure oxygen and air are both capable of performing the oxidation. Implications of using oxygen and air follow.

3.a. DSRP

Pure oxygen is an impractical oxidizing medium for sorbent regeneration. In the DSRP - based process, regenerating with pure oxygen would result in such high temperatures that the sorbent would sinter. By comparison, the nitrogen present in air dilutes the oxygen and serves as

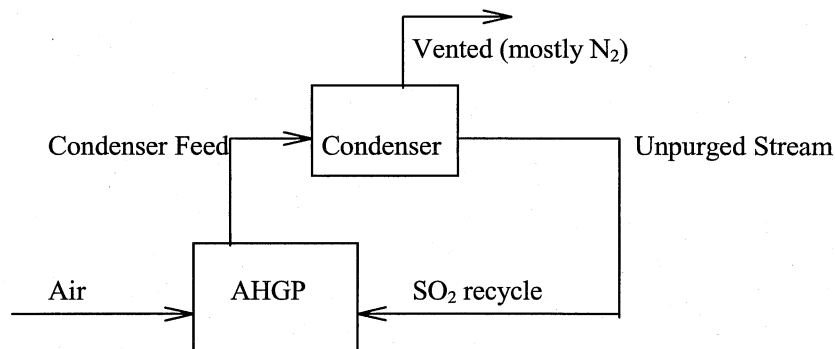
a heat sink for the highly exothermic regeneration reactions. What is not intuitively obvious is that it is more expensive to supply air to the system than to supply oxygen. For DSRP - based process conditions it is more expensive to compress air than to separate oxygen and then compress only the oxygen (Hvizdos).

3.b. AHGP

Air is not a viable oxidizing medium for use in the Advanced Hot Gas Desulfurization Process. The use of air would require separating nitrogen from sulfur dioxide. The AHGP process has a large SO₂ stream that circulates through the regeneration reactor and the sulfur condenser. In the AHGP, oxygen enters the SO₂ loop as a pure oxygen feed and leaves with the sorbent. Sulfur enters the SO₂ loop on the sorbent and leaves as condensed sulfur. Feeding air instead of oxygen would provide a steady flow of nitrogen into the SO₂ loop. Maintaining steady state would require removing nitrogen at the rate it is introduced.

The concept of adding a condenser to the SO₂ loop was investigated for separating nitrogen from SO₂ (Figure 7). ASPEN simulations were performed to determine the condenser conditions necessary for removing nitrogen at the rate it enters the system. The idea was to condense the SO₂ in the loop and vent only nitrogen. Table 8 shows that this concept is impractical. When the ratio of SO₂: N₂ is large the SO₂ is more prone to condense. This can be seen in table 8 where for the same temperature and pressure, uncondensed SO₂ (SO₂ vented) decreases as the mass fraction of SO₂ increases. Therefore, the most efficient condenser will have the minimum amount of N₂ feed to it. The minimum N₂ fed to the condenser will be equal to the rate at which nitrogen enters the system via the air stream. The minimum corresponds to a case where no N₂ condenses (N₂ unpurged). Table 8 shows that even with the very low N₂ concentration there is an unreasonable amount of SO₂ vented.

Figure 7: Condenser for Removal of Nitrogen



The simulations assumed that the total SO₂ loop flow would be 260,000 lbs/hr and 13,500 lbs N₂/hr would need to be removed.

Table 8: N₂ Removal at Various N₂ Concentrations, Condenser Temperatures and Pressures

Condenser Fed: SO ₂ mass fraction	Condenser Pressure (psia)	Condenser Temperature (°C)	N ₂ unpurged (lbs/hr)	SO ₂ vented (lbs/hr)	N ₂ vented (lbs/hr)
0.100	275	50	0	26,000	234,000
0.900	275	50	418	58,200	25,600
0.946	275	50	511	30,800	13,500
0.946	400	50	1,010	16,800	13,000
0.940	275	-20	716	1,540	14,900

Furthermore, nitrogen is not needed as a heat sink in the AHGP. The SO₂ stream is a sufficient gas phase heat sink to carry away the heat of the regeneration reaction. The economic analysis showed it is actually desirable to feed oxygen instead of air. The cost of compressing air is higher than the cost of separating out oxygen and then compressing only the oxygen.