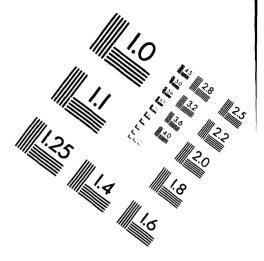


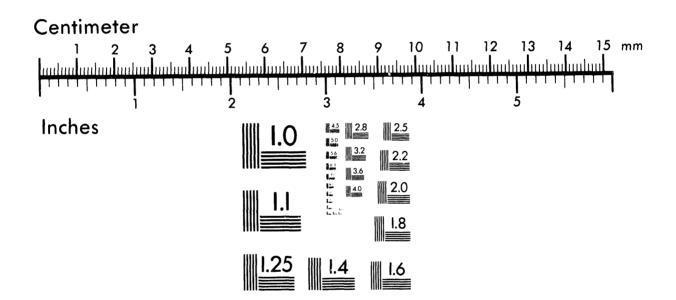


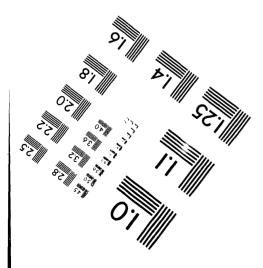


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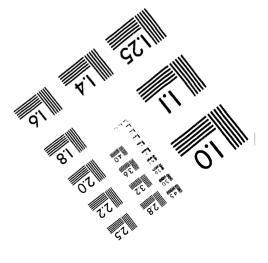
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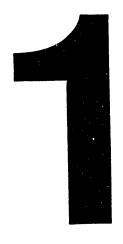






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Moving Granular-Bed Filter Development Program Option III -- Development of Moving Granular-Bed Filter Technology for Multi-Contaminant Control Task 14 -- Test Plan

Topical Report

J. C. Haas C. A. Olivo K. B. Wilson

April 1994

Work Performed Under Contract No.: DE-AC21-90MC27423

For U.S. Department of Energy Office of Fossil Energy Morgantown Energy Technology Center Morgantown, West Virginia

By Combustion Power Company Oakland, California



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> By Combustion Power Company 2101 Webster Street, No. 1700 Oakland, California 94612

> > April 1994

ABSTRACT

An experimental test plan has been prepared for DOE/METC review and approval to develop a filter media suitable for multi-contaminant control in granular-bed filter (GBF) applications. The plan includes identification, development, and demonstration of methods for enhanced media morphology, chemical reactivity, and mechanical strength. The test plan includes media preparation methods, physical and chemical characterization methods for fresh and reacted media, media evaluation criteria, details of test and analytical equipment, and test matrix of the proposed media testing.

A filter media composed of agglomerated limestone and clay was determined to be the best candidate for multi-contaminate control in GBF operation. The combined limestone/clay agglomerate has the potential to remove sulfur and alkali species, in addition to particulate, and possibly halogens and trace heavy metals from coal process streams.

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SECTION 1

INTRODUCTION

1.1 **OBJECTIVE**

The objective of this phase of the contract is to develop a chemically reactive filter media suitable for granular-bed filter (GBF) operation that is capable of removing a combination of pollutants in high temperature and high pressure (HTHP) gas streams from processes being developed for advanced coal utilization. The Department of Energy identified control of the following contaminants to be of interest: sulfur compounds, nitrogen compounds, alkali compounds, halogen ated compounds and tars. The primary emphasis of this test program will be the development of a GBF media composed of limestone and clay for the control of sulfur and alkali species in coal gas streams.

The developed media would also have the potential for the control of halogenated compounds, trace metals and tars. Except for the sorption of chlorine which will be investigated as part of the program which is directed at determining the effect of HCI on the sorption of alkali, these areas are not pursued in the proposed bench scale tests in order to concentrate efforts in the areas of sulfur and alkali control which appear to have the greatest chance of success. The developed media will be checked for reactivity with respect to halogenated compounds and trace metals as part of the pilot scale evaluation of the sorbent. Preliminary investigations on the control of nitrogen compounds suggested the use of a fixed bed of catalyst. If such catalysts are developed and are sufficiently rugged, it may be possible to incorporate them in a GBF. The test plan does not propose pursuing the control of nitrogen compounds at this time.

1.2 CONCEPTUAL DESIGN OF GRANULAR-BED FILTERS FOR MULTH CONTAMINANT CONTROL

The many possible approaches for the incorporation of a multi-contaminant control media in a GBF have been narrowed down to the following two concepts. In the preferred concept, the media used in the GBF would be composed of chemically reactive spheres of the same 6 mm size as that used for particulate control. In the second concept, the filter media is composed of two distinct size distributions. Larger, 6 mm diameter spheres would be the same inert media used for particulate control. In addition to this inert media, a smaller 2 mm diameter, chemically reactive media would be used. Both concepts use chemically reactive media with finite life. The frequency of removal and replacement of the chemically reactive media would depend on its reactivity and the extent of conversion in a single pass through the filter.

The first concept, of a filter with 6 mm diameter, chemically reactive spheres, is the preferred approach because it is similar to filter operation for only particulate control. The separation of different media sizes would not be required. The large size media would

1

maintain the high gas flow through the filter at a low pressure drop. In the case where the chemically active media is mainly limestone, the limestone media would circulate through the filter an average of 12.6 times before being discharged from the filter and replaced with fresh reactive media.

A 6 mm chemically reactive media will need sufficient attrition resistance and mechanical strength for multiple passes through the filter. We believe that such a media can be produced. Failing to produce 6 mm spherical media with acceptable chemical reactivity and mechanical strength would necessitate the second concept of a dual filter media approach. The filter bed would be composed of large inert media mixed with smaller chemically reactive media. A smaller 2 mm diameter, chemically reactive media. The larger inert media would be the main component of the filter bed fulfilling the requirement of a circulating media enabling a high gas flow through the filter with only a slight increase in the pressure drop. The smaller chemically reactive media, after a single pass through the filter, would be separated pneumatically from the larger media in the lift pipe or removed by gradual attrition in the pneumatic conveying system.

There are many possible materials which could be incorporated into a chemically reactive media. We have narrowed the field to three types of media: a reactive media composed of limestone and clay which could be used for control of sulfur, alkali, halogens, and some trace metals in either coal gasification or combustion processes at temperatures of 1550°F to 1800°F; a reactive media composed of nahcolite (NaHCO₃) which could be used for the removal of chlorides and fluorides in coal gasification processes at temperatures of 1100°F; or a reactive media of zinc titanate for the removal of H₂S. The limestone/clay media and the nahcolite media would be a non-regenerable sorbent. The zinc titanate media would require regeneration in a reactor separate from the GBF. Of the three types of media, the one believed to be the best candidate for success in GBF operation for a HTHP application is a reactive media of limestone and clay. The proposed test program will be concerned with the development of a limestone/clay media and an evaluation of the mechanical properties of the regenerable zinc titanate sorbent.

1.3 BACKGROUND INFORMATION

Previous work at New York University demonstrated that the GBF is effective and can meet New Source Performance Standards for HTHP particulate removal (Wilson and Haas, 1989). Besides removing particulate, the GBF has the potential of removing other pollutants in the gas streams. The GBF is an excellent gas/solids contactor. It has gas residence times in the order of several seconds, solids residence times in the order of several hours, uniform gas flow across the media, and the counter-current flow of gas and media for maximum driving potential.

Besides particulate, the contaminants of major concern in the advanced coal utilization processes are sulfur compounds, nitrogen compounds, alkali compounds, halogenated compounds, tars, and trace metals such as cadmium and mercury (Bossart et al., 1990). A GBF which is able to capture particulate and one or more of these additional contaminants would have significant benefits over just a particulate removal system. GBF operation for particulate removal by impact on filter media is very efficient and may be extended to include multi-contaminant control with the proper selection of filter media. The filter media would act as a sorbent for individual or combined removal of contaminants.

1.3.1 Limestone for Sulfur Control

The control of sulfur emissions has historically been the major thrust of pollution control systems and still remains a primary focus of innovative technology. In combustion systems, the need is for the removal of SO_2 and for gasification, the need is for the removal of H_2S . Of the many potential sorbents which may be suitable as a filter media for the control of sulfur emissions, limestone is the most commonly used sorbent in combustion and gasification processes due to its basic nature, its widespread availability, and it being a relatively inexpensive sorbent. For these three reasons, limestone was chosen as the best approach for sulfur removal in a GBF application.

Limestone, though widely used, has its shortcomings as a sulfur sorbent. In its natural form, calcined limestone has relatively poor chemical reactivity (sulfur absorption rate and total sulfur capacity) (Shen and Albanese, 1978; Voss, 1983; Spitsbergen et al., 1988). This low reactivity results in large consumptions of limestone (and large quantities of waste) for effective sulfur control in once-through processes. Calcined limestone has poor attrition characteristics so that particulates are carried over into the process gases (Yoo and Steinberg, 1983). This high attrition loss also results in large consumptions of limestone. To become a more effective sulfur sorbent, the reactivity and mechanical strength of calcined limestone have to be enhanced.

Previous investigators have found that agglomerating finely powdered limestone improved its chemical reactivity and the temperature range of its reactivity, and that addition of binders during agglomeration could improve mechanical strength. Shen and Albanese (1978), Voss (1983), and Spitsbergen et al. (1988) all demonstrated that calcined agglomerates of powdered limestone have considerably higher reactivity than calcined, similar-sized particles of the naturally occurring stone and may have increased mechanical strength. Zhang et al. (1989) demonstrated that not only is the chemical reactivity of calcined limestone improved by agglomeration, but also the temperature range for chemical reactivity.

The 0.85 to 1 mm size pellets of agglomerated fine limestone powder with colloidal silica binder prepared at Brookhaven National Laboratory were more accessible, reactive to SO_2 and attrition resistant than the raw limestone particles (Shen and Albanese, 1978).

Sulfation conversion was 55% for the calcined pellets versus 35% for calcined limestone particles. The rates of sulfation for the pellets were about 1.5 to 2 times greater than that of the limestone particles. Attrition loss for the calcined limestone particles was about 3 times higher than that of the calcined pellets. Higher sulfation conversions of 20 to 46% for agglomerates and 8 to 22% for natural limestones, greater SO₂ absorption capacity before breakthrough, and greater sulfation rates for the 0.5 to 1.2 mm diameter, calcined agglomerated pellets over the calcined natural limestones were reported at Engelhard Corporation (Voss, 1983). The effectiveness of the agglomerated pellets was attributed to the increase in porosity or pore volume during agglomeration. It was estimated that the agglomeration of limestone increased its reactivity by at least two-fold and maybe up to six times as much. Binder additions of clay and inorganic materials gave the calcined pellets attrition resistance comparable to the calcined natural limestones.

The calcined agglomerates made from ground limestone tested at the University of Twente had an internal pore volume which was 50% greater and a mean pore radius 20 to 40 times those of the calcined natural limestones (Spitsbergen et al., 1988). These 0.85 to 1 mm diameter calcined pellets had good attrition resistance compared to the calcined, hard natural limestones and far superior resistance compared to the calcined, soft natural limestones. Increased sulfidation conversion of 90% and sulfation conversion of 60% for these agglomerates were observed compared to 60% and 20 to 30%, respectively, for the natural limestones. The high conversion rates resulted from the porosity created by the macro pores formed during pellet agglomeration.

Limestone pellet work at Tsinghua University and Huazhong University of Science and Technology tested sulfation conversion to elevated temperatures of 2000° F (Zhang et al., 1989). Calcined, 2 mm size pellets, composed of crushed limestone and unspecified combustible additives, had sulfation conversions over 50% for temperatures between 1650 and 1950°F. The maximum sulfation conversion occurred at a temperature of about 1800°F. This was a drastic improvement over the 11 to 18% noted for calcined natural limestones at temperatures of 1600°F. The high temperature sulfation success of the pellets was credited to an improved microstructure over natural limestone. The limestone pellets had an increased pore volume of 0.9 cm³/g with pores evenly distributed within suitable pore diameters of around 10³ to 10⁴ A (angstrom). Natural limestone, on the other hand, had a pore volume of 0.4 cm³/g with pore diameters concentrated in the ranges smaller than 10³ A or larger than 10⁴ A.

The work of these investigators is encouraging in that they suggest that filter media composed of agglomerated limestone of 2 mm diameter can be readily made which could have the high reactivity and mechanical strength for GBF operation in either combustion or gasification processes. The potential also exists for the successful agglomeration of limestone to 6 mm diameter size possessing the reactivity and mechanical strength required.

1.3.1.1 Limestone for the Control of Hydrogen Sulfide

Background Limestone can react directly with H₂S by the reaction route shown in equation 1. If the temperature is high enough, the limestone first calcines to calcium oxide and reacts by the route shown in equations 2 and 3.

$$CaCO_3 + H_2S = CaS + CO_2 + H_2O$$
⁽¹⁾

$$CaCO_3 = CaO + CO_2$$
(2)

$$CaO + H_2S = CaS + H_2O$$
(3)

$$CaO + COS = CaS + CO_2 \tag{4}$$

$$CO + H_2O = CO_2 + H_2 \tag{5}$$

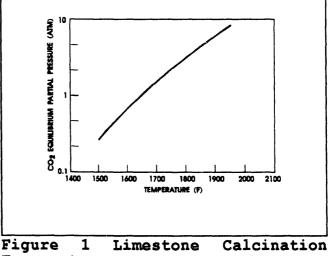
Carbonyl sulfide also reacts with calcium oxide as shown in equation 4. The extent of the above reactions are limited by the equilibrium concentrations.

The calcination of calcium carbonate is determined by the temperature and partial pressure of the carbon dioxide. Equation 6 gives an expression for the relationship between the carbon dioxide partial pressure and the calcination temperature of calcium Since most gasification processes operate at elevated pressures, the carbonate. calcination temperature is greater than that at atmospheric conditions. Figure 1 shows the relationship between calcination temperature and CO₂ partial pressure as given by equation 6.

$$\log K_2 = \log (P_{co2}) = -8799.7/T_k + 7.521$$
(6)

where K_2 is the equilibrium constant for equation 2 (atm), P_{co2} is the equilibrium partial pressure of CO, (atm), and T_k is the temperature (K) (Byran, 1988).

The equilibrium constants for equations 1, 3 (Byran, 1988) and 4 (Prudy, 1984) are respectively:



Temperature

 $\log K_{1} = \log (\{H2O\}\{CO2\}\{P\}/\{H2S\}) = 7.253-5280.5/T_{k}$ (7) $\log K_{3} = \log (\{H2O\}/\{H2S\}\}=3519.2/-T_{k} - 0.268$ (8) $\log K_{4} = \ln(\{CO2\}\{H2S\}/\{H2O\}/\{COS\})=-1.352+(4378.7)/T_{k}$ (9)

where K_1 is the equilibrium constant for equation 1, K_3 is the equilibrium constant for equation 3, K_4 is the equilibrium constant for equation 4, P is the gasifier pressure, {H2O} is the mole fraction of water vapor in the fuel gas, {CO2} is the mole fraction of carbon dioxide, {H2S} is the mole fraction of hydrogen sulfide, {COS} is the mole fraction of carbonyl sulfide, and T_k is the temperature (K) of the fuel gas. The concentration of carbon dioxide, carbon monoxide, water vapor, and hydrogen are assumed to be in equilibrium via the water gas shift reaction, equation 5, and are determined from a general equilibrium computer program. Equations 7, 8, and 9 can be used to determine the equilibrium concentrations of the hydrogen sulfide and carbonyl sulfide.

Reactions 1 and 2 are both endothermic reactions which need to be accounted for in a heat balance on a GBF which uses limestone to react with H_2S . The heat of reaction for reaction 1 at 1700°F is 560 Btu/lb of CaCO₃ and for reaction 2, the heat of reaction is 745 Btu/lb CaCO₃.

KRW Gasifier Table 1 shows the fuel gas constituents entering the gas turbine. The fuel gas prior to the gas turbine is quenched with steam to lower its temperature from 1900° F. The ratio of steam to fuel gas is 0.21 lb steam/lb product gas. Knowing the amount of steam dilution, the composition of the gas leaving the gasifier can be calculated. It is assumed that the methane is frozen and the water gas shift reaction is in equilibrium. The gas composition can be calculated as a function of temperature and the equilibrium concentration of hydrogen sulfide and carbonyl sulfide determined.

Gas	Turbine Inlet	GBF Inlet	GBF Outlet
со	7.77	25.5	25.6
	20.63	13.3	13.8
H₂ CO₂ CH₄	14.39	4.7	5.7
СН	0.64	0.9	0.9
N₂ Ar	38.67	50.1	49.2
Ar	0.45	0.6	0.6
H₂O H₂S	19.44	4.4	4.2
H,S	0.00	0.4413	0.0106
cos	not available	not available	0.0013

Table 1 KRW Gasifier Gas Composition (Vol. %)

Figure 2 shows the results of these calculations. The equilibrium H_2S concentration decreases with temperature until a minimum value of 90 ppmv is reached at the calcination temperature of calcium carbonate, 1692°F. After the calcium carbonate calcines to calcium oxide, the equilibrium concentration of H_2S increases with temperature.

As indicated by equation 9, the equilibrium concentration of COS depends on the concentration of H_2S . The minimum equilibrium COS concentration is 11 ppmv and it also occurs at 1692°F.

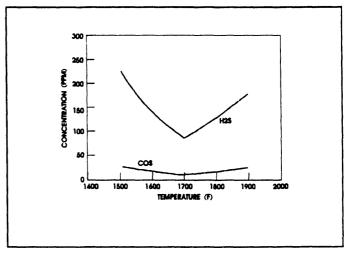


Figure 2 Equilibrium Concentrations of H_2S and COS for KRW Gas

Pilot plant tests conducted at IGT (Goyal, 1988) showed that in their gasifier, it is possible to achieve 85% or more approach to the equilibrium concentration of H_2S . Assuming an 85% approach to the equilibrium concentration of H_2S , the H_2S concentration at the outlet of the scrubber would be 106 ppmv. If the COS has the same approach to its equilibrium concentration, its concentration would be 13 ppmv. The combined concentration of H_2S and COS would be 119 ppmv which corresponds to 97.3% sulfur removal for the 2.68% sulfur coal used in the Wansley study (Southern Company Services, 1991).

Process Flow Sheet for GBF A GBF using limestone media should be able to remove H_2S and COS to within 85% of their equilibrium concentrations (Goyal, 1988). Figure 3 shows the process flow sheet for a MCC GBF for the removal of H_2S , COS, and particulate. The KRW gasifier outlet temperature is about 1900°F. The optimum temperature for sulfur removal from the KRW fuel gas is about 1700°F. The fuel gas from the gasifier needs to be cooled to 1800°F before entering the GBF. The fuel gas stream should be cooled by indirect heat exchange instead of steam injection. An increase in the water content of the fuel gas stream, increases the equilibrium concentration of H_2S . As the gas passes through the filter, it is cooled to 1700°F due to the heating of the limestone media which enters at ambient conditions, due to endothermic reactions 1 and 2, and due to ambient heat losses. The heat load is fairly evenly split between the three duties.

The media circulation rate is determined by the ash loading to the filter such that 2.5% of the ash/media mixture is ash. The amount of limestone required for sulfur suppression is considerably lower than the media circulation rate. As a consequence, the limestone media circulates through the filter an average of 12.6 times before it is discharged from the system. The limestone residence time in one pass through the filter is 0.93 hours so that the average residence before discharge from the filter is 11.7 hours. It is likely that the limestone will be almost completely utilized after one pass through the filter and completely reacted by the time it discharges from the filter. In calculating the rate of limestone utilization, a conservative calcium to sulfur ratio of 1.5 was used.

The process is very similar to that of a GBF used only for particulate control. The major differences are that limestone media is added to the seal leg entering the top of the filter, spent sorbent is removed from the bottom of the disengager, the filter operates at a somewhat higher inlet gas temperature, and there is a larger temperature drop through the filter. The limestone addition rate is 2.2 tons per hour. The particulate capture and cleaning of the media are the same as in a standard GBF designed for particulate control.

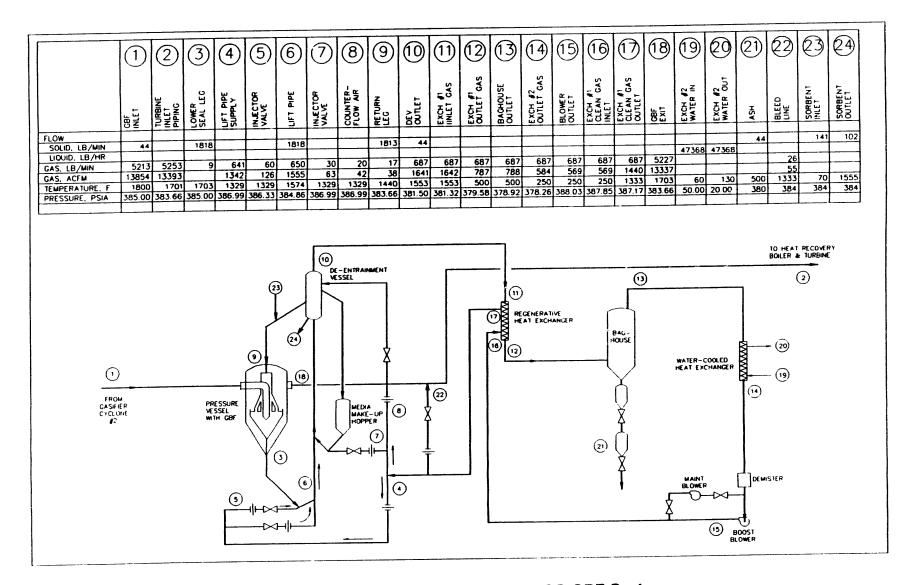


Figure 3 Process Flow Sheet for MCC GBF System

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1.3.1.2 Limestone for the Control of Sulfur Dioxide

Unlike the control of hydrogen sulfide with limestone, the control of sulfur dioxide is not thermodynamically limited in a pressurized fluidized-bed combustor operating at 10 atmosphere pressure at temperatures below 1050°C (Newby et al., 1989). Assuming that the PFBC has a limestone bed, a GBF with limestone media would be used as a polishing sulfur dioxide absorber and as a particulate filter. In such an application, the limestone/clay media would circulate through the GBF many times since the inlet concentration of sulfur dioxide would be low. The media would have to have a high attrition resistance to be able to circulate many times through the filter.

1.3.2 Limestone for Halogen Control

Chlorine and fluorine are present in coal as trace elements, and as such, are found in coal gasification and combustion streams in concentrations ranging from 50 to several thousand parts per million by volume (ppmv). These elements form acidic compounds which can cause acidic corrosion in downstream equipment such as gas turbine components and heat exchangers, and cause poisoning of molten carbonate fuel cell electrodes (TRW, 1981). They also represent the release of acidic compounds to the environment. For these reasons, it would be desirable to remove halogen contamination from coal process streams.

Besides the control of sulfur, a GBF with a limestone sorbent has the potential to control contaminants such as halogens. Work performed at Twente University (Akse et al., 1991) found that calcined pellets of limestone were effective in absorbing HCl. The CaO reacts with HCl to form CaCl₂. At 600°C, a 70% conversion was obtained after a 25 minute exposure and 80% conversion was obtained after 66 minutes. These limestone pellets had good attrition characteristics after calcining. Similar studies on calcined limestone pellets at 500°C by Peukert and Loffler (1993) achieved conversions over 90% for the sorption of HCl.

In coal combustion studies, Chughtai (1988) reported that lime (CaO) reacts with HCl and HF to produce $CaCl_2$ and CaF_2 , respectively, but no values for removal efficiencies were given. Work by Colclough and Carr (1990) found that limestone addition to the furnace increased the chlorine concentration in the bottom ash and fines. Chlorine concentrations of 0.01% or less were increased to 0.2% in the bottom ash and up to 5.6% in the fines trapped by the filtration system. Dolomite addition to the combustor can increase the halogens retained in the ash just as limestone. Dale and Williams (1988) reported a 28% or higher increase in the retention of chlorine, fluorine, and bromine in the combustor fly ash and the furnace ash with only 5.5% dolomite addition.

Munzner and Schilling (1985) found the in-bed retention of fluorine by finely powdered, calcined limestone to be much higher than that of chlorine at temperatures of 750 to 950°C. Fluorine retention was about 95% compared to about 5% for chlorine at 850°C. The low chlorine retention isn't surprising as the melting point for CaCl₂ is around 782°C while that of CaF₂ is around 1360°C.

Liang et al. (1991) predicted the distribution of the halogens in fluidized-bed combustors with limestone addition. In the temperature range of 700 to 950°C, the study predicts that bromine and iodine always remain in the gas phase which can explain the non-existent capture of either by the calcined limestone. For chlorine and fluorine, as the temperature was increased from 700 to 950°C, the amount of each in the gas phase was found to increase. Chlorine capture by the calcined limestone was low at 15 to 30%. Equilibrium calculations predicted that fluorine was the only halogen which might be effectively retained by calcined limestone under FBC conditions and the temperature range of 700 to 950°C.

The work of previous researchers shows that CaO is capable of reacting with halogens, particularly chlorine and fluorine as HCI and HF, in coal process streams. Calcium oxide or limestone as calcined, pelletized material could be used as the reactive media in a granular-bed filter for halogen control. Though halogen capture will not be pursued in this test program, the resultant sorbent media developed in this program may be suitable for halogen control in coal process streams at lower temperatures in the range of 1100 to 1200°F.

1.3.3 Clay for Alkali Control

The presence of alkali species in PFBC or IGCC gas streams is of concern because of the potential corrosion which alkali species can cause in a gas turbine. Also, alkali species are associated with low melting compounds which can provide the "glue" for forming deposits on turbine and heat exchanger surfaces. For these reasons, turbine manufacturers have placed restrictions on the amount of alkali (sodium and potassium) that can enter a gas turbine. The acceptable levels of alkali in the fuel gas stream entering the turbine combustor ranges from 50 to 200 ppbw depending on the gas temperature and the turbine manufacturer (Tamhankar and Wen, 1981). More recent studies are more stringent giving the permissible inlet concentration to the turbine itself as 24 ppbw (Bossart et al., 1990; Lee and Myles, 1987). These levels are below the expected alkali levels in coal process streams (Zakkay et al., 1985; Ciliberti and Lippert, 1986; Krishnan et al., 1990) so alkali concentration must be controlled.

Several investigators have reported successful alkali removal from high temperature gas streams with sorbents of activated bauxite, attapulgus clay, calcium montmorillonite clay, diatomaceous earth, kaolin clay, and emathlite clay. Activated bauxite and diatomaceous earth have been reported to effectively capture NaCl, KCl, and K_2SO_4 (Lee and Johnson, 1980). Sorbent screening experiments found diatomaceous earth, attapulgus clay, and activated bauxite to be the most effective for removal of alkali (Jain and Young, 1985). Results showed that either diatomaceous earth or activated bauxite could be used for 99% removal of alkalies using 0.6 to 1.0 mm diameter sorbent with contact times greater than 0.2 seconds.

Emathlite, a type of fullers earth, was found to be a leading getter of alkali (Bachovchin et al., 1986). The clay had a high capacity for sodium and binds the sodium irreversibly. At extreme conversions, the clay was found to become sticky. This could be a problem for GBF operation but is unlikely to occur as these extreme conversions are not realistically obtained and the anticipated fraction of clay within the agglomerated pellet is small. Kaolin, bauxite, and emathlite were all found to be capable of removing alkali from coal conversion streams (Uberoi et al., 1990). Kaolin and emathlite sorption of alkali was an irreversible process. The maximum sorption capacity of the kaolin was about 25% while that of bauxite and emathlite was about 15%. During screening of alkali sorbents, calcium montmorillonite clay was found to be superior and was chosen for further investigation (McLaughlin, 1990).

All of these sorbents are capable of alkali removal but only a few can be considered within the scope of this program. Of these alkali sorbents tested, bauxite was reported to be fractionally irreversible with alkali removal being 10% chemical sorption and 90% physisorption (physically absorbed as water soluble alkali) (Lee and Johnson, 1980) while only kaolin and emathlite were reported to react irreversibly with alkali (Bachovchin et al., 1986; Uberoi et al., 1990). Bauxite is also a relatively expensive sorbent which would not be suitable as a non-regenerable sorbent. Work on limestone agglomeration found

attapulgus clay to be an effective binding agent (Voss, 1983). With these points in mind, an alkali sorbent of kaolin, attapulgus or emathlite clay in conjunction with limestone will be investigated.

The reaction of alkali with clay is thought to proceed by the reactions 10, 11, and 12.

 $2 \operatorname{NaCl} + H_2 O + \operatorname{SiO}_2 = \operatorname{Na}_2 \operatorname{SiO}_3 + 2 \operatorname{HCl}$ (10)

$$2 \text{ NaCl} + H_2 O + A I_2 O_3 + O_2 = 2 \text{ NaAl} O_2 + 2 \text{ HCl}$$
(11)

$$2 \text{ NaCl} + 3 \text{ H}_2\text{O} + \text{B}_2\text{O}_3 + \text{O}_2 = 2 \text{ NaBO}_3 \text{ H}_2\text{O} + 2 \text{ HCl}$$
(12)

Bachovchin (Bachovchin et al., 1986) developed a model of a fixed bed reactor using cylindrical pellets of emathlite, a calcium montmorillonite clay mined in Florida, for the removal of alkali from coal gasification streams. We adapted the model to a spherical pellet geometry and to a circulating bed as used in a GBF. The predicted sorbent life would be 7400 hours for a 20 ft deep bed. The sorbent would contain 17.3% Na at the end of its life. The inlet sodium concentration used in the model is 10 ppmv and the outlet is 20 ppbv. A lower bed depth corresponds to a shorter sorbent life and lower sorbent utilization. A fixed bed reactor having a similar bed depth would have a life of 8400 hours and an average Na pick up of 19.7%. Details of the model used to predict alkali capture in a GBF with a clay sorbent are given in Appendix A.

1.3.4 Clay for Trace Metals Control

Besides the control of sulfur and alkali, a GBF has the potential to control other contaminants such as tars and trace metals. In a gasification environment, activated carbon may be suitable for the capture of heavy metals and possibly the cracking of tars. The 1100-1200°F temperature used in the zinc ferrite process for the absorption of H_2S would be the upper temperature limit for the use of activated carbon. This limiting temperature of 1200°F is significantly below the optimum temperature for sulfur removal with limestone.

Recent work at the University of Arizona indicates the potential of porous solids such as bauxite, kaolin or activated alumina for the absorption of heavy metals such as lead or cadmium (Uberoi and Shadman, 1991a). Results have shown that bauxite was considerably more effective than kaolinite for the sorption of cadmium vapors (Uberoi and Shadman, 1991b). The lower effectiveness of kaolinite was explained during examination of the particle which showed an almost completely reacted surface with an unreacted interior. This surface reaction is also typical of dense, natural limestones reactions with sulfur. Therefore, the use of kaolinite in an agglomerated pellet with large micro-pores may allow higher utilization just as it does for the sorption of sulfur species by limestone agglomerates. The kaolinite had a lower water soluble fraction of sorbed cadmium than

the bauxite which is desirable from the point of view of ultimate disposal. Also studied was the sorption of lead vapors by various sorbents and kaolinite was found to be the most effective (Uberoi, 1990).

Limestone and dolomite were found to be effective for the removal of zinc and lead vapors from simulated flue gases (Mojtahedi et al., 1989). Dolomite, with its more open pore structure, removed 82% of the lead vapors and 19% of the zinc vapors. Limestone removed 41% of the lead vapors and 81% of the zinc vapors. The sorption of lead vapors may possibly be improved by the agglomeration of limestone to give a more open pore structure similar to dolomite.

From the work of these investigators, a high temperature sorbent composed of kaolinite, bauxite, limestone or dolomite could be capable of heavy metals removal from coal process streams. These same materials have proven to be effective for the capture of alkalies and sulfur species.

1.3.5 Limestone/Clay Media for Combined Sulfur, Alkali, Halogen, and Trace Metals Control

As discussed in the previous sections, numerous studies have been performed to find sorbents for the individual removal of sulfur, alkali, halogen, and heavy metals from coal process streams. For sulfur removal, agglomerated limestone was chosen as the favored sorbent. Either kaolin, attapulgus or emathlite clay may be effective for alkali removal. Agglomerated limestone may be effective for halogen removal. For heavy metals removal, the same materials for sulfur and alkali removal, except attapulgus and emathlite clay, were found to be effective at high temperatures. Therefore, an agglomerated sorbent of limestone and clay composition may possibly perform the multi-function of sulfur, alkali, halogen, and heavy metals removal from flue gases making it much more attractive than just a single contaminant sorbent. It is our intent to find a suitable GBF filter media composed of limestone and clay which is effective for the removal of sulfur and alkali, and possibly halogens and trace heavy metals.

SECTION 2

FILTER MEDIA PREPARATION, CHARACTERIZATION, AND EVALUATION

2.1 MANUFACTURING PARAMETERS

The sorbents to be considered suitable as filter media have to possess acceptable chemical reactivity and mechanical strength for the circulating conditions present in granular-bed filter (GBF) systems. The important parameters in the manufacturing process of sorbents identified as possibly enhancing mechanical strength are:

- Pellet size
- Pellet shape
- Chemical composition
- Particle size
- Binder type
- Binder content
- Cure temperature
- Cure duration
- Pelletization equipment

Testing for all these parameters as variables would be a very large test matrix, beyond a feasible (economic and test duration) scope of this program. To maximize test efforts, the nine variables are narrowed down to those which have been demonstrated to have a major impact on mechanical strength and chemical reactivity, and to those which do not affect the conceptual design of the GBF.

The four selected test variables are:

- 1. Particle size
- 2. Binder type
- 3. Binder content
- 4. Pelletization equipment

The other parameters will be held constant for the sorbent testing at the following values.

- Pellet size: 6 mm (2 mm if not mechanically stable)
- Pellet shape: spherical
- Chemical composition: limestone with 5% by weight dry clay
- Cure temperature: 230°F
- Cure duration: 24 hours

The chemical composition of the sorbents to be tested is a mixture of limestone and clay. Longview is the design limestone to be used at DOE's Power System Development Facility, located at Southern Company Services' Wilsonville facility and as such, is the limestone which will be used in the test program. The clay will be either kaolin, bauxitic kaolin, attapulgus, or emathlite clay. The clay selected will be the one superior for alkali sorption as determined by TGA (thermogravimetric analysis). The mixture of 5% by weight clay addition was chosen as this content should be more than sufficient for alkali control of coal process gases. A lower clay addition may be possible, but the optimization of the sorbent's clay content is not addressed in this phase of the program.

2.1.1 Particle Size

Agglomeration creates a pellet with an open pore structure which increases its chemical reactivity, but conversely, tends to decrease its mechanical strength (Ayala, 1991). Besides high pellet reactivity, mechanical strength is an important parameter for GBF operation as the sorbent must be circulated many times before it is discarded. Numerous investigators using agglomerated material have shown that increasingly finer particles and wider particle size distributions give agglomerated pellets with better strength properties (Sastry et al., 1977; Ball et al., 1973). The finer and widely distributed particles tend to pack into denser pellets decreasing its volume of void space or porosity. This reduction in porosity gives a stronger pellet but with pellet strength may come a reduction in pellet reactivity.

Agglomerate work by Akse et al. (1991) used two types of limestone fines with one having particles less than 75 microns and the other having particles less than 150 microns. He mixed the two types of fines, with 75% by weight being the less than 75 micron fraction, and found that 0.5 to 1.0 mm diameter limestone agglomerates could be made which typically had calcined and uncalcined attrition losses of 2% by weight or less. Voss (1983) made agglomerates from limestone powder containing about 75% by weight finer than 44 micron particles. Agglomerates of 0.5 to 1.0 mm diameter could be made having calcined and uncalcined attrition losses of 5% by weight or less.

Zhang et al. (1989) made agglomerates from pulverized limestone having less than 90 micron particles. He found that the smaller, 2 mm calcined agglomerates had higher calcium utilization (higher conversion of CaO to CaSO₄) than calcined agglomerates of 6 mm size and larger. Testing for the effect of particle size, agglomerates were made from limestone of 154-180 microns and from limestone of less than 45 microns. Particle size was found to have no strong effect on the calcium utilization for the 2 to 6 mm calcined agglomerates. But in general, the smaller particle size, the higher the calcium utilization for agglomerates 4 mm and smaller. However, for the 6 mm agglomerates, the calcium utilization was 6% higher for the agglomerates made from the 154-180 micron limestone than the agglomerates made from 45 micron limestone.

For a 2 mm, agglomerated limestone pellet, work by Peukert and Loffler (1993) showed that particle size had a major impact on the calcined pellet chemical reactivity. They found that the smaller the particle size of the sulfated pellets, the higher the conversion was of CaO to $CaSO_4$. Particles sizes of 60, 9.8, and 1.8 microns were used to make the agglomerates. For a GBF system, utilizing particle sizes of 10 micron and smaller greatly adds to the cost of sorbent production (refer to Appendix B).

From the work of the previous investigators and the economic considerations, the agglomerated pellets in this test program will be made with the following two particle sizes and size distributions:

- 1. Limestone of 80% less than 149 microns
- 2. Limestone of 80% less than 44 microns

In all cases, the particle size of the clay will be held constant at a minimum of 80% less than 44 microns.

2.1.2 Binder Type

Though the particle size of the agglomerates has a great impact on the mechanical strength of the pellet, this particle size may not be sufficient to make a chemically reactive pellet that has the required mechanical strength. Binders are used to improve pellet strength. As with particle size, the goal is to find a binder which improves the pellet mechanical strength without greatly reducing its chemical reactivity.

Binders have been successfully used to improve the mechanical strength of agglomerates. Binders such as corn starch, Shur Bond, and lignon sulfonate have been used for pelletizing fine coal (Conkle et al., 1992; Mehrotra and Sastry, 1981). Bentonite (mostly clay mineral montmorillonite) and peridur (a cellulose derivative) have been successful binders for iron ore (Sastry et al., 1985). Ayala (1991) using zinc ferrite sorbent found a combination of bentonite and calcium sulfate binders to be superior in

improving pellet mechanical durability while maintaining high sulfidation reactivity. In itself, agglomerated portland cement (PC III) has been demonstrated to be a reactive and mechanically strong pellet (Yoo et al., 1982; Yoo et al., 1983).

For limestone agglomerates, Akse et al. (1991) found that their calcined and uncalcined attrition resistance improved with silicate or clay addition. Starch additive was superior to the silicate and clay additives for the uncalcined agglomerates, but was slightly inferior for the calcined agglomerates. Work by Voss (1983) demonstrated that binders such as attapulgite clay, attapulgite clay with boric acid, and sodium silicate gave the limestone agglomerates comparable, if not superior, mechanical strength to the natural limestones in both the calcined and uncalcined states. These calcined agglomerates had sulfation reactivities (Ca to CaSO₄ conversion) which were over four times higher than the calcined natural limestones except for the sodium silicate binder which gave only a two-fold increase in the sulfation reactivity.

With the previous work in mind for metal oxide sorbents (limestone and zinc ferrite), the binders to be tested are:

- 1. attapulgus clay and boric acid
- 2. sodium silicate
- 3. corn starch
- 4. sodium bentonite and calcium sulfate
- 5. sodium bentonite (high swelling)
- 6. calcium montmorillonite (low swelling bentonite)
- 7. calcium sulfate hemihydrate (plaster of paris)
- 8. portland cement (PC III)
- 9. Fluidized-Bed Combustor (FBC) bed ash

2.1.3 Binder Content

As stated in Section 2.1.2, eight inorganic and one organic binder will be tested as they have been demonstrated to be effective in improving the mechanical strength of agglomerated pellets. These binders have been used in concentrations ranging from 2% to up to 15% by weight dry solids (neglecting PC III pellets which were 100% cement solids). Binders add to the cost of the sorbent so minimizing their addition will keep

sorbent raw material costs at a minimum. Large additions of binder not only increase sorbent cost, but also reduce the amount of limestone in the sorbent available for sulfur control and possibly trace metals control.

Akse et al. (1991) found limestone agglomerates with 3% silicate addition, or 2% clay or starch addition to be the best performers. Concentrations of 15% attapulgite clay, of 15% attapulgite clay with 2% boric acid and of 4% by weight sodium silicate were also found to be effective for limestone agglomerates (Voss, 1983).

Work with zinc ferrite sorbent demonstrated that binder concentrations of 2% bentonite and 10% calcium sulfate to be the superior formulation (Ayala, 1991). The addition of portland cement and FBC bed ash as binders will be limited to 15% by weight dry solids.

A concentration of 4% by weight corn starch was superior in improving the mechanical strength of pelletized fine coal (Conkle et al., 1992). Similarly in previous work, the mechanical strength of the coal pellets was increased with increasing corn starch concentration where a maximum concentration of 1.5% by weight corn starch was tested (Mehrotra and Sastry, 1981).

It should also be noted that the clay alone in the chemical composition of the sorbent formulation may perform the dual function of alkali removal as well as the mechanical binding of the agglomerated pellet. For the attapulgus clay with boric acid binder, the 5% clay for chemical composition will not be added.

Of the binders selected, the concentrations (% by weight) to be tested are:

- 1. 15% attapulgus clay with 2% boric acid
- 2. 2% and 4% sodium silicate
- 3. 2% and 4% corn starch
- 4. 2% sodium bentonite with 10% calcium sulfate
- 5. 2% and 5% sodium bentonite
- 6. 2% and 5% calcium montmorillonite
- 7. 5% and 10% calcium sulfate hemihydrate
- 8. 10% and 15% portland cement
- 9. 10% and 15% FBC bed ash

For all water insoluble binders, the particle size will be held constant at a minimum of 80% less than 44 microns.

2.1.4 Pelletization Equipment

Besides the particle size, binder type and binder content of the agglomerates, the equipment used for agglomerating the pellets has a significant effect on the mechanical strength of the resultant pellets. There are four general types of agglomeration equipment available for pellet formation. The first is a disc pelletizer which is the easiest to operate and utilizes gravitational forces to produce balls or pellets. The second is a type of mixer or blender such as a TurbulatorTM which is a more intense pelletizer than the disc and often used for hard-to-pelletize material applications. A third type is an extruder that forces a semi-solid through a die opening. And a fourth is a briquetter which uses extreme compactive forces to form pellets or briquettes.

Of these four types of pelletization equipment, the most likely to yield acceptable pellets for GBF operation is the disc pelletizer. The disc pelletizer has been widely used to produce variously sized spherical pellets. Mixer/blending is limited to producing pellets of about 3 mm diameter maximum size. Extrusion typically produces cylindrical pellets which can be rounded into spherical or elliptical pellets in a disc pelletizer. The briquetting process virtually eliminates the voidage within the pellet giving it superior strength but minimal chemical reactivity.

For the production of 6 mm pellets, the disc pelletizer and the extruder with disc pelletizer may be utilized. Production of acceptable sorbent pellets will first be attempted with a disc pelletizer and later with an extruder and rounding if unsuccessful with the disc pelletizer. If an acceptable 6 mm or 2 mm sorbent pellet is not found with the disc pelletizer, than 6 mm extruded and rounded sorbent will be evaluated.

2.1.5 Test Matrix of Sorbent Formulations

The four selected test variables of particle size, binder type, binder content, and pelletization equipment have been broken down into the conditions which are to be tested in Sections 2.1.1 through 2.1.4. Compiling these conditions gives a matrix of sorbent formulations as shown in Table 2. This matrix has 68 possible formulations and natural limestone. The goal is to find a formulation that possesses mechanical strength suitable for the GBF.

As stated in Section 2.1.4, the production of an acceptable 6 mm diameter sorbent pellet will first be attempted with the disc pelletizer. These formulations will have the suffix "A". Starting with the disc pelletizer, the 68 formulations in Table 2.1 are reduced to 34. If the disc pelletizer does not produce acceptable 6 mm pellets, pellets will be produced with an extruder followed by rounding in the disc pelletizer. These formulations will have the

suffix "B". Only 5 formulations will be tested from the possible 34 formulations. These will be the 5 best formulations possessing the superior mechanical strength and chemical reactivity from the screening performed on pellets produced with the disc pelletizer.

	Particle Size	Binder		Form.	Produ	ction
Pellet Form	of Limestone	Туре	Conc.	No.	Disc	Extrude
Natural	6 mm			1	****	
			0%	2	A	
		Attapulgus Clay	15%			
		w/ Boric Acid	2%	3	<u>A</u>	
		Sodium	2%	4	A	
		Silicate	4%	5	A	1
		Corn	2%	6	A	1
			4%	7	<u>A</u>	4
		Bentonite w/	2%			
		Calcium Sulfate	10%	8	<u>A</u>	-
	80% less	Sodium	2%	9	A	-
	thth	Bentonite	5%	10	A	_
	149 microns	Calcium	2%	11	A	_
		Montmorillonite	5%	12	A	_
		Calcium Sulfate	2%	13	A	_
		Hemihydrate	5%	14	A	
		Portland	10%	15	A	Best 5 of Form.s 2A thru 35A
		Cement	15%	16	A	
		FBC Spent	10%	17	A	
Limestone/Clay		Bed Ash	15%	18	A	
Aggiomerate (1)			0%	19	A	
		Attapulgus Clay	15%			
		w/ Boric Acid	2%	20	A	
		Sodium	2%	21		
		Silicate	4%	22	A	
		Corn	2%	23	A	
		Starch	4%	24	A	
		Bentonite w/	2%			
		Calcium Sulfate	10%	25	A	
	80% less	Sodium	2%	26	A	
	than	Bentonite	5%	27	A	
	44 microns	Calcium	2%	28	A	
		Montmorillonite	5%	29	Ā	
		Calcium Sulfate	2%	30	A	
		Hemihydrate	5%	31	A	
		Portland	10%	32	A	
		Cement	15%	33	A	-
		FBC Spent	10%	34	A	
		Bed Ash	15%	35	A	

(1) The agglomerate with binder of attapulgus clay will not have the 5% clay addition for alkali control.

2.2 EXPERIMENTAL TEST PLAN

2.2.1 Sorbent Preparation

A. Pellet Preparation for Initial Screening Tests

Screening tests will be performed on the 34 sorbent formulations given in Table 2 for pellet production utilizing the disc pelletizer. In preparation for the pelletization of the formulations, 400 lbs of 1/4 inch nominal limestone will be pulverized into 200 lb batches of 80% less than 149 microns and 80% less than 44 microns. The batches of pulverized limestone should be well mixed and stored until use. A screen analysis on a representative sample for each particle size will be run to determine the size distribution.

A disk pelletizer will be used to prepare the initial formulations. The dry mixture of limestone, clay, and binder are wetted with water to get 10% by weight initial moisture content. This initial wetting allows the mixture to tumble versus slide in the disc pelletizer. Water soluble binders will be dissolved into solution to give the required binder concentration on a dry basis assuming 10% by weight initial moisture content of the solids mixture.

The wetted mixture will be agglomerated at varying water spray rates to form pellets with maximum green strength. The drop test described in Section 2.2.2 will be used to measure pellet green strength. At the optimum water content giving maximum pellet green strength, a 0.5 lb batch of 2 mm and a 0.5 lb batch of 6 mm pellets will be generated.

The screened pellets are cured by drying in an oven at 230°F for 24 hours. Pellets are then allowed to cool to room temperature of about 70°F. Pellets are stored in a moisture-free environment. Pellets having PC III or calcium sulfate binders will be stored in a moist environment at 100°F for 48 hours. The cementing properties of these binders involve hydraulic reactions requiring the presence of water.

Should the disk pelletizer fail to produce 6 mm pellets with adequate strength properties, limited testing would be conducted with a extruder followed by a spheronizer to produce round 6 mm pellets. Extrusion followed by spheronization has been used to produced highly attrition resistant zinc titinate pellets. The most promising 5 formulations prepared on the disk pelletizer would be pelletized using a bench extruder. These pellets would then be tested for crush strength, attrition resistance, and chemical reactivity. If it is not possible to make a 6 mm pellet with adequate properties, the characteristics of 2 mm pellets produced with the disk pelletizer will be evaluated.

B. Pellet Preparation for Batch Testing

Based on the results of the initial screening tests, 5 formulations will be chosen for further evaluation. A five pound batch of 6 mm pellets for each formulation at its optimum water content will be prepared, cured, and stored until testing.

C. Pellet Preparation for Pneumatic Lift Pipe/Moving Bed Attrition Test and Alkali Sorption Tests

A 75 lb batch of 6 mm pellets of what is deemed to be the best sorbent formulation will be prepared and cured.

2.2.2 Physical Characterization of Sorbents

The physical properties of the pellets will be evaluated in terms of the particle morphology of pellet size, shape, pore volume, and moisture content. The mechanical strength of the pellets will be determined in terms of drop strength, crush strength, and attrition resistance. Pellets which exhibit superior strength characteristics will be evaluated further for their chemical reactivity.

A. Description of Mechanical Strength Tests

The mechanical strength of the sorbents will be demonstrated in four tests. The four tests are drop test, crush strength test, attrition resistance test, and a specialized pneumatic lift pipe/moving bed attrition test.

- The drop test is a test for pellet handling strength. Individual pellets of a sorbent formulation are dropped from a height of 18 inches onto a stainless steel pan. Pellets are dropped until they break or shatter into pieces. The number of drops before breakage is recorded for each pellet. The number of drops are averaged over a minimum of 15 pellets for each sorbent formulation.
- Crush strength test is a test for pellet loading (deadweight load) strength. Pellet crush strength is measured by a compression tester which subjects a single pellet to an increasing load until breakage occurs. The load or force measured at breakage is averaged over a minimum of 20 pellets.
- Attrition resistance test will measure pellet durability. Attrition resistance is determined according to and following ASTM D 4058-92 procedure, "Standard Test Method for Attrition and Abrasion of Catalysts and Catalyst Carriers". Approximately 100 grams of sample pellets are weighed and

transferred to a clean cylindrical drum. The cylindrical drum has an inside diameter of 10 inches and inside length of 6 inches with a single radial baffle, 2 inches high, extending its full length. The lid is secured to provide a dust-tight enclosure. The drum is placed on a device (such as a ball mill roller) to rotate it for 1800 revolutions at a rate of 60 ± 5 rpm. After approximately 30 minutes, the contents of the drum are hand-sieved with a U.S. No. 20 sieve. Fines passing through the sieve are collected and weighed. The percent attrition loss is calculated as follows:

Loss on = <u>wt of pellet sample - wt of fines</u> x 100 Attrition, % wt of pellet sample

A specialized mechanical strength test is performed in a pneumatic lift pipe/moving bed attrition apparatus as shown in Figure 4. The apparatus simulates the pneumatic transport and recycle that pellets would see in GBF operation. Approximately 20 lbs of pellets are used to fill the moving bed section of the apparatus. Ten psig air is supplied to the test apparatus. Air flow to the L-valve at the bottom seal leg controls the media circulation rate. A second stream of air to the bottom of the lift pipe conveys the circulating media to a dis-engagement vessel at the top of the lift pipe. The lift pipe air is discharged through a bag filter which catches any material attrited from the media in the lift pipe. A third stream of air purges the moving bed test section of any fines generated in this region. The purge gas from the moving bed test section passes through a separate filter before being discharged. No solids should be picked up by the moving bed purge gas since this gas simulates the flow of coal gas through the filter. Any solids in this stream would be carried over into the turbine. Up to a 15% attrition rate in the lift pipe gas would be acceptable since this gas would also contain the particulate removed from the coal stream. The percent attrition loss is calculated in the same manner as ASTM procedure D 4058-92 given previously.

Mechanical Strength Testing

- Drop tests will be performed on the 34 initial screening test formulations. Each formulation will require about 3 sets of drop tests to determine the optimum water content which corresponds to maximum green pellet strength.
- Crush strength tests will be performed on the 34 initial screening formulations which are able to meet the minimum green strength criteria of surviving 6 drops. A maximum of 34 crush strength tests will be performed on these calcined pellets during the initial screening. Crush strength will be determined for the 5 sulfided and the 5 sulfated pellet formulations

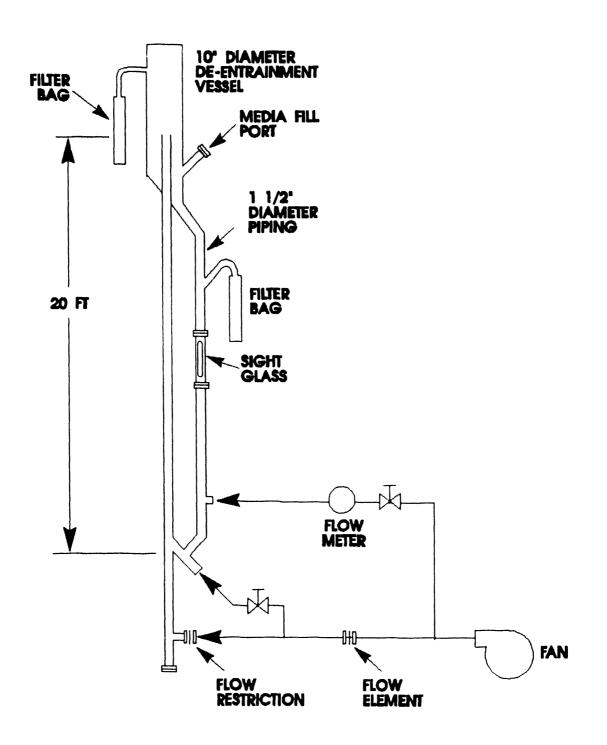
produced during batch testing and 5 pellet formulations which are reacted with alkali. The crush strength will also be determined for calcined, sulfided, and sulfated 6 mm natural limestone granules. Pellets and limestone will be calcined at a temperature of 1550°F and one (1) atmosphere pressure. The total possible number of crush strength tests is 52.

- ASTM attrition resistance tests will be performed on the same formulations which are tested for crush strength. The total possible number of ASTM attrition resistance tests is also 52.
- The specialized lift pipe/moving bed attrition test will be run on the most promising sorbent formulation after it is sulfided in the fixed bed reactor described in Section 2.2.3. In addition, specialized attrition tests will be run on sulfided natural limestone granules, inert GBF media, and regenerated zinc titanate pellets. The apparatus, shown in Figure 4, will operate 40 hours for each test for a total of 4 tests.

C. Physical Morphology of the 5 Most Promising Sorbents and Natural Limestone

The 5 most promising sorbents and natural limestone are to be physically characterized by pellet size, shape, particle size, surface area, bulk density, pore volume, median pore diameter, moisture content, and microstructure.

 Pellet shape is held constant as spheres to be consistent with past GBF media. Pelletization with a disc pelletizer yields pellets in the shape of balls. Approximately 2 to 3 each of calcined pellets and calcined natural limestone granules will be randomly selected and viewed under a laboratory microscope to check for pellet roundness.





Pneumatic lift pipe/ moving bed attrition apparatus

- Particle size of the raw ingredients used in pellet production is determined by screening the ground powders of limestone, clay, and binder. A sieve shaker utilizing a stack of U.S. sieves will determine the particle size distribution. A maximum of 10 particle size distributions will be performed.
- The bulk density of calcined pellets and calcined natural limestone granules is measured following procedures of ASTM D 4164-88, "Standard Test Method for Mechanically Tapped Packing Density of Formed Catalyst and Catalyst Carriers". A maximum of 6 bulk density measurements will be performed.
- Pore volume and median pore diameter of pellets and natural limestone granules in calcined, sulfided, sulfated, and alkalized forms are measured by mercury porosimetry. A maximum of 24 measurements will be performed.
- The moisture content of the green pellets at the optimum water content will be determined by low temperature oven drying. The equilibrium moisture content of the cured pellets will also be determined. Not more than 10 moisture contents will be measured.
- The microstructure of various pellets and natural limestone granules in cured, calcined, and reacted forms will be observed utilizing scanning electron microscopy (SEM). A maximum of 20 samples will be examined.

2.2.3 Chemical Reactivity

Sorbent chemical reactivity will be determined by thermogravimetric analysis (TGA) by measuring single-pellet capacity for sulfur and for alkali. Larger scale reactivity tests will also be conducted in fixed bed reactors.

A. Sulfidation Tests

The initial screening tests for chemical reactivity will use TGA to determine the rate of reaction and extent of reaction of the pelletized sorbents. Fifteen (15) sorbent formulations of 6 mm pellet size which exhibit the suitable calcined mechanical strength will be evaluated. TGA testing will be run at a temperature of 1700°F at one (1) atmosphere pressure. Gas composition into the TGA apparatus will be 94% CO₂, 5% H₂, and 1% H₂S which will equilibrate to 89.2% CO₂, 4.8% CO, 4.8% H₂O, and 1% H₂S. Under these conditions, the limestone calcines at 1609°F so that the TGA tests will be on a calcined pellet. In addition to the pelletized sorbents, a TGA will be run on a 6 mm natural limestone granule for comparison purposes.

- Additional screening tests will use TGA to measure the reactivity of 3 sorbent formulations of 2 mm pellet size based on the results of the 6 mm pellet screening tests. Test conditions will be the same as for the 6 mm pellet.
- The above initial screening tests should allow the determination of the 5 best potential sorbent formulations. These 5 formulations as well as 6 mm natural limestone will be sulfided in a batch reactor containing 150 g of material. The batch reactor will operate at 1700°F, one (1) atmosphere pressure, and the same gas composition used with the TGA. The crush strength and attrition resistance of the sulfided materials will be measured.
- The above screening tests should allow us to determine the most likely sorbent formulation for use in a GBF for hydrogen sulfide control. Further tests will be performed to more completely evaluate this sorbent formulation.
- Detailed kinetic data on the preferred sorbent formulation will be obtained from additional TGA testing. An additional 16 tests would be run in which gas composition (4 levels) and gas temperature (4 levels) would be varied. A total of not more than 36 atmospheric TGA tests will be run.
- Tests on natural limestones (Newby et al., 1987) showed that the reaction rate is proportional to the square root of the absolute pressure. Five (5) TGA tests will be run at 10 to 16 atmospheres on the preferred sorbent formulation to determine the effects of pressure on reaction rates. In these tests, the partial pressure of the CO_2 will be remain constant at 0.94 atmospheres. The TGA temperature will be 1700°F.
- Two fixed bed sulfidation tests will be used to verify the kinetics determined by TGA and to prepare sulfided material for the lift pipe/moving bed attrition tests. The fixed bed tests will be run on the natural limestone aggregate and on the most promising pellet formulation. A 4 inch diameter packed bed, 2 ft high operated at atmospheric pressure will be used. Each test will be terminated when the outlet concentration of hydrogen sulfide starts to increase with time. The bed will be sectioned to determine the concentration profile of calcium sulfide in the bed. The measured profile will be compared with that predicted on the basis of the TGA kinetics. The reacted bed material will be used in the lift pipe/moving bed attrition tests. A third of a cubic foot of each material will be produced for the attrition tests.

• The calcium sulfide reaction products need to be converted to calcium sulfate before disposal. It has been shown that sulfided dolomite has a much higher conversion to the sulfate form than limestones due to the larger pore structure of dolomite (Abbasian et al., 1992). It is believed that sulfided limestone pellets will have high conversion to sulfate because of the induced pore structure formed during pelletization. TGA will be used to obtain kinetic data on the conversion of sulfide to sulfate. The oxidation of calcium sulfide to calcium sulfate tests will be run on the natural limestone aggregate and on the most promising pellet formulation. Ten (10) tests at atmospheric pressure are planned in which gas concentration and temperature will be varied.

B. Sulfation Tests

The majority of the evaluation tests will be on the use of a sulfur control sorbent in a gasification environment. The pelletized limestone sorbent can also be used to remove sulfur dioxide from combustion gases.

The 5 best sorbent formulations for hydrogen sulfide control and 6 mm natural limestone will also be evaluated for control of sulfur dioxide. Twelve (12) TGA tests will be run using the test matrix shown in Table 3. The first 8 tests are at a high CO₂ pressure such that the limestone will not calcine and the sulfur dioxide reacts directly with the calcium carbonate. In most PFBC applications this is expected to be the case. The last four tests are at a lower CO₂ partial pressure so that the limestone calcines to CaO before reacting with sulfur dioxide.

Test No.	Pellet Type	SO₂ Concentration ppmv	CO₂ Concentration mole %
1	Candidate 1	300	70
2	Candidate 2	300	70
3	Candidate 3	300	70
4	Candidate 4	300	70
5	Candidate 5	300	70
6	Natural Limestone	300	70
7	Best of 5	150	70
8	Best of 5	75	70
9	Natural Limestone	300	50
10	Candidate 1	300	50
11	Candidate 2	300	50
12	Candidate 3	300	50

Table 3 Test Matrix for Sulfation ExperimentsT=1600° F, P=14.7 psia

• The 5 best formulations and natural limestone will be sulfated in 150 g batches so that the material can be evaluated by attrition resistance and crush strength tests.

C. Alkali Absorption Tests

Besides the removal of sulfur products, the pelletized sorbent will have the capability of removing alkali vapors from the coal process stream. The following 5 clays will be evaluated as potential alkali sorbents as part of a limestone pellet.

- 1. Kaolin clay
- 2. Bauxitic kaolin clay
- 3. Emathlite clay (Calcium montmorillonite)
- 4. Attapulgite clay
- 5. Bentonite clay
- Screening Tests: McLaughlin (1990) developed a simple screening test for the evaluation of possible alkali sorbents. The procedure will be modified to include limestone with the alkali sorbent. TGA/DTA will be run on mixtures containing 10% NaCl, 45% clay sorbent, and 45% calcined limestone, and on mixtures containing only clay and alkali. As the sample is heated, the alkali will vaporize except for the alkali which reacts with the sorbent. The sample with the least weight loss contains the sorbent with the highest sorption capacity. A total of 10 sorption tests will be run. The carrier gas for these experiments will contain 95% CO₂ and 5% H₂. The TGA apparatus will heat the samples to 1800°F.
- Fixed-Bed Alkali Absorption Tests: The purpose of these tests is to obtain kinetic data on the reactivity of the prepared sorbents with respect to the absorption of alkali and sulfur compounds. A heated sample holder whose change in weight is monitored with a micro balance heats salt crystals which vaporize into a carrier stream. The rate of evaporation is controlled by the temperature of the sample holder. The alkali vapors are mixed with either a gas stream containing H₂S or one containing SO₂ and are carried into the packed bed of sorbent. The packed bed section will be 3 inch diameter by 12 inch long, in a tube of alumina which is inert with respect to the alkali vapors. There will be a total of 18 packed bed tests. The first 12 tests are defined in Table 4. The test durations are estimates which will be refined on the basis of data from the first tests. The first 10 tests use a carrier gas containing N₂, 5% H₂O, and additives of H₂S and HCI. In tests 11 and 12, the carrier gas contains 95% CO₂ and 5% H₂O with additives of SO₂ and HCI. The first five tests use a shallow bed which will be analyzed for the average alkali and sulfur sorption. After the first five tests, the bed will be sectioned into ninths and analyzed for alkali and sulfur content as a function of the position in the bed. In some of the tests, the carrier gas will contain HCI which is know to inhibit the sorption of alkali.

Test No.	Pellet type	Alkali conc. ppmv	HCI conc. ppmv	Test hours	H₂S conc. ppmv	SO₂ conc. ppmv	Bed depth inch	Tempe- rature ° F
1	1	40	0	24	1000	0	1	1700
2	2	40	0	24	1000	0	1	1700
3	3	40	0	24	1000	0	1	1700
4	4	40	0	24	1000	0	1	1700
5	5	40	0	24	1000	0	1	1700
6	best	40	0	48	0	0	9	1700
7	best	40	50	48	0	0	9	1700
8	best	40	0	48	1000	0	9	1700
9	best	10	50	48	1000	0	9	1700
10	best	40	50	100	1000	0	9	1700
11	best	40	0	48	0	300	9	1575
12	best	40	50	48	0	300	9	1575

Table 4 Test Matrix for Fixed Alkali Tests

2.2.4 Chemical Analyses

Various chemical analyses will be performed on single pellets as well as groups of like pellets to collect data which will describe or characterize the mechanisms and events occurring during TGA and bench-scale fixed bed reactor testing. The planned analyses are:

- Elemental ash analysis on the raw ingredients used to make the sorbents. The limestone, clay, and binders will be analyzed. A maximum of 9 elemental ash analyses will be performed.
- Total sulfur analysis on the reacted sorbents. The 5 most promising sorbents as well as the 6 mm natural limestone that were sulfided and sulfated in the batch reactor will be analyzed. A total of 12 analyses will be performed.
- Sulfur forms on the reacted sorbents. The 10 oxidation tests for conversion of calcium sulfide to calcium sulfate will each have a determination of the sulfide, sulfite, and sulfate content. A total of 30 sulfur forms will be determined.

- Total sulfur and alkali analyses on the reacted sorbents. Sorbent samples from fixed-bed alkali absorption testing will be analyzed. Thirteen (13) absorption tests will each have the total sulfur and alkali determined in pellets from 9 sections of the bed. In the first five tests, the bed will be analyzed as a single layer. There will be a total of 122 determinations of total sulfur and alkali.
- Chloride analysis on the reacted sorbents. This analysis will determine if the calcined limestone in the pellets has any capability to remove chlorine (halogen) at elevated temperatures in the range of 1700°F. Sorbent samples from fixed-bed alkali absorption testing will be analyzed. The 18 absorption tests may each have the chloride determined in pellets from sections of the bed. There may be a maximum of 61 chloride determinations.
- EDAX (Energy Dispersive Analysis X-ray) on the reacted sorbents. EDAX will give the sulfur and alkali profile (mapping) within the sorbent pellet. Various pellets of the 5 most promising sorbents and natural limestone in sulfided, sulfated, and alkalized forms will be observed. A maximum of 20 samples will be examined.

2.2.5 Modeling of Sorbent Reactivity

The kinetic data collected on sorbent reactivity will be used to create a model of the sorbent's chemical reactivity in a GBF. The model will take into account the sorbent reactivity with respect to sulfur species and alkali. The model will provide information on the required bed depth of the GBF, the expected outlet concentration of sulfur and alkali species and the extent of reaction of the sorbent. The model given in Appendix A for just alkali sorption is illustrative of the type of model which will be developed.

2.3 PERFORMANCE EVALUATION

2.3.1 Performance Criteria

For a sorbent to be suitable as filter media, it must possess acceptable morphology, chemical reactivity, and mechanical strength for the conditions dictated in GBF operation. The sorbent must be spherical with high porosity (pore volume and diameter), have high chemical reactivity to be completely reacted in a minimal of filter passes (preferably a single pass), and have good mechanical strength to withstand the continuous, circulating pneumatic transport of the GBF system. In order to find the superior sorbents, the formulations in Table 2 will be screened and evaluated based on meeting selected performance criteria. Formulations which do not meet the minimum criterion will not be investigated further.

Six criteria will be used as guidelines to assess sorbent performance. The performance criteria are:

Criterion 1 for Green Pellets:

- Be of 6 mm diameter and spherical shape.
- Drop strength of at least 6 drops.

Criterion 2 for Calcined Pellets:

- Crush strength greater than 15 lb/pellet.
- Attrition loss less than 10% per ASTM D 4058-92 procedure.

Criterion 3 for Sulfided Pellets:

- Single-pellet chemical reactivity
 - TGA for sulfidation conversion in 2 hours (based on limestone available in formulation) greater than natural limestone.
 - TGA for total sulfur loading capacity by sulfidation (based on limestone available in formulation) greater than natural limestone.
- Mechanical strength
 - Batch reacted sulfided pellet crush strength greater than 15 lb/pellet.
 - Batch reacted sulfided pellet attrition loss less than 10% per ASTM D 4058-92 procedure.

Criterion 4 for Sulfated Pellets:

- Single-pellet chemical reactivity
 - TGA for sulfation conversion in 2 hours (based on limestone available in formulation) greater than natural limestone.
 - TGA for total sulfur loading capacity by sulfation (based on limestone available in formulation) greater than natural limestone.

- Mechanical strength
 - Batch reacted sulfated pellet crush strength greater than 15 lb/pellet.
 - Batch reacted sulfated pellet attrition loss less than 10% per ASTM D 4058-92 procedure.

Criterion 5 for Pellets Exposed to Alkali:

- Single-pellet chemical reactivity
 - TGA for alkali sorption in 24 hours
 - Total alkali capture capacity

Criterion 6 for Lift Pipe/Moving Bed Attrition Test:

• Sulfided pellet attrition loss less than 15% from the lift pipe section of the apparatus and less than 0.06% from the moving bed section.

Criterion 1 will be applied to freshly prepared green pellets to determine the optimum water spray rate during agglomeration. The water spray rate will be varied until the pellets formed meet Criterion 1.

Green pellets meeting Criterion 1 will be cured, calcined, and subjected to Criterion 2 requirements. Calcined pellet mechanical strength will be measured by crush strength and attrition resistance testing.

If more than 15 sorbent formulations exist after Criterion 2 screening, the best 15 formulations will be selected for single-pellet chemical reactivity testing. Criterion 3 will be applied to find the best sorbent formulations for sulfur removal in gasification processes. Fifteen (15) formulations will be subjected to TGA for sulfidation with the best 5 formulations being selected for batch sulfidation in a fixed-bed reactor and for sulfation TGA.

Criterion 4 will be applied to the 5 sorbent formulations to determine the sulfation reactivity and the mechanical strength of the sulfated pellets.

Criterion 5 will be testing to find the formulations most likely to perform the combined duty of sulfur and alkali removal. The best formulation will be subjected to Criterion 6 testing to determine the mechanical durability of the sorbent in simulated GBF operation. This formulation, if successful, will be more completely evaluated to obtain kinetic data for sulfidation and conversion of sulfide to sulfate.

Throughout the screening process, the "best" formulations were selected for further testing. The best will be those possessing high strength characteristics and good chemical reactivity. Formulas for weighted evaluations of strength and reactivity will be developed for the Criteria based on the range of data values obtained for mechanical strength for sulfided and sulfated pellets, and for chemical reactivity during sulfidation, sulfation, and alkali removal to find the superior formulations.

If during the screening and evaluation process all sorbent formulations fail to meet a given criterion, the testing for a 6 mm diameter sorbent pellet produced by disc pelletizer will be aborted. Testing will commence for screening a 6 mm diameter sorbent pellet produced by extrusion and disc pelletizer rounding based upon the results of the disc pelletizer work. The best 5 sorbent formulations from disc pelletizer work will be used. If these 5 formulations fail to meet the given criteria, all testing will be re-directed to finding a 2 mm diameter sorbent formulation suitable for GBF filter media.

SECTION 3

PILOT PLANT TESTING

3.1 INTRODUCTION

In Section 2, bench scale tests are used to develop and evaluate multi-contaminant control media. The developed media is evaluated in terms of its chemical and physical properties in a bench scale environment. The next phase of evaluation will be at the pilot plant scale. Combustion Power Co. is participating in the DOE sponsored tests at a Power Systems Development Facility (PSDF) to be installed in a Southern Company Services Facility in Wilsonville, AL. The first year of testing at the PSDF will be dedicated to the evaluation of the GBF for particulate control. For these tests, the GBF is connected to M.W. Kellogg's transport reactor which can be operated in either a gasification or combustion mode. After the evaluation of a GBF for particulate control, the opportunity may exist to evaluate the GBF with a reactive media for the control of sulfur and alkali compounds. This portion of the test plan assumes that the PSDF will be available for evaluating the GBF using a chemically reactive media for combined particulate control and the removal of sulfur and alkali contaminants.

3.2 DESIGN OF MODIFICATIONS TO THE GBF AT THE PSDF

In order to use the GBF at the PSDF with a reactive media, modifications to the GBF will be required. Lock hoppers will be installed for feeding reactive media into the media circulation loop and for removal of spent media from the filter. We are assuming that 6 mm reactive media will be used and that there will be no need for the separation of reactive media from an inert media. If the reactive media is 2 mm in diameter and requires separation from a larger inert media, the dis-engagement vessel at the top of the lift pipe would also have to be redesigned. The process flow sheets and the P&ID's will be revised for the incorporation of reactive media. Specifications will be prepared for the lock hoppers and the feed and spent sorbent hoppers to fit into the existing structure. A detailed test plan for the test to be conducted at the PSDF will be prepared in conjunction with SCS and Kellogg.

3.3 PREPARATION OF REACTIVE MEDIA FOR TEST PROGRAM

The bench scale testing will determine the composition of sorbent to be used in the pilot plant testing. It is proposed to have 9 tons of the media manufactured for testing in the GBF at the PSDF. Assuming that the sulfur capture in the transport reactor is reduced to 50% and the remaining sulfur is captured in the GBF, 9 tons of the limestone media would provide about 80 hours of testing. The preparation of the media would be

subcontracted to a vendor of pelletizing equipment or to the laboratory which prepared the pellets for the bench scale testing. During the pelletization process, close attention will be paid to quality control to insure the production of pellets with properties similar to those produced in the bench scale process. We have received cost estimates for pelletizing the large quantity of material needed for the pilot plant. These cost estimates will be updated and other possible vendors will be contacted to provide firm cost proposals for the production of 9 tons of the pelletized limestone/clay mixture.

3.4 MODIFICATION OF GBF AT THE PSDF

The GBF at the PSDF will be modified to include: sorbent feed hopper, lock hopper, spent sorbent lock hopper and spent sorbent hopper. The installation of this new equipment will be monitored by Combustion Power. The equipment will be installed by Southern Company Services under subcontract to Combustion Power.

3.5 TESTING AT THE PSDF

About 80 hours of testing will occur in a 4 week period. The objective the testing will be to demonstrate the use of reactive media for the control of sulfur and alkali species. Given the limited amount of sorbent, it is likely that the test will be conducted only in the gasification mode of operation. The independent test variables are shown in Table 5 along with their value for the test period. The results of the test will be evaluated in terms of media attrition, particulate capture, H_2S removal, approach to H_2S equilibrium concentration, calcium sulfur ratio, alkali removal, extent of reaction with alkali, and trace metal sorption. Table 6 shows the dependent variables which will be measured either during or after the test. After the completion of the test, an interim test report will be prepared.

The following procedure will be followed for testing the MCC sorbent in the GBF at the PSDF.

- 1.0 The transport reactor will be operated in the gasification mode. The GBF will be initially filled with particulate control medium. Both the transport reactor and the GBF will be brought to operating conditions in the same manner as used for the particulate control testing.
- 2.0 After steady operating conditions are reached, MCC sorbent will be fed to the GBF and excess filter medium will be removed. The residence time of the filter medium in the filter is about 4 hours. After 4 hours of operation, the GBF will have MCC sorbent dispersed through the entire filter.

- 3.0 The limestone rate to the transport reactor will then be gradually reduced to 50% of its normal feed rate over a 2 hour period. As a result of the reduced feed rate of limestone to the transport reactor, the H_2S concentration to the GBF will gradually increase. Eventually a point in time will be reached in which the feed rate of MCC sorbent will need to be modulated to control the outlet concentration of H_2S .
- 4.0 Because of the relative limited supply of MCC sorbent, the concentration of MCC sorbent in the GBF will be changing over the entire test period. Kinetic data on the reaction of the MCC sorbent with H₂S and alkali will be determined in the bench scale development of the MCC sorbent. We expect the data to show that the limestone will be nearly completely reacted with the H₂S on its first pass through the filter. The MCC sorbent re-circulated back to the GBF will be nearly inert with respect to further H₂S removal. For sulfur control, once the sorbent has passed through the filter there will be little difference between the spent MCC sorbent and the inert filter medium. The fact that the concentration of MCC sorbent in the filter is changing with time will have a small effect on the evaluation of the sorbent for sulfur removal. The reaction of the MCC sorbent with alkali is expected to continue as the MCC sorbent is recirculated. The amount of clay in the sorbent is considerably greater that the amount needed to remove the alkali encountered in a single pass through the filter. As the concentration of MCC sorbent increases in the filter, the removal of alkali may also increase.
- 5.0 The MCC sorbent will be tested at one steady state operating condition. The operating conditions corresponds to the transport reactor operating in the gasification mode. For the limestone to be reactive with the H₂S, the filter must operate above the calcination temperature of the limestone. The calcination temperate of the limestone depends on the CO₂ partial pressure. For the gasifier operating at 285 psia and with a gas containing 8.1 mol percent CO₂, the calcination temperature is 1702°F. In order to have the temperature of the sorbent greater than 1702°F, the temperature of the inlet gas will have to be at least 1850°F. It is anticipated that the granular bed filter will be capable of operating at this temperature for the test period.
- 6.0 The filter will be run at constant operating conditions as shown in Table 5 for the duration of the tests. The dependent variables shown in Table 6 will be measured during the test period. After the test, the MCC sorbent remaining in the filter will be analyzed for its Ca:S ratio, Alkali, halogens and trace metals sorption, and attrition loss.

Table 5	Independent Tes	t Variables for MCC	Evaluation at the PS	DF
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Independent Variable	Value
Gas Inlet Temperature	1850°F
Filter Inlet Pressure	285 psia
Gas Flow Rate	18080 lb/hr
Particulate Inlet Concentration	4000 ppmw or less
H ₂ S Inlet Concentration	2061 ppmv
H ₂ S Outlet Concentration	200 ppmv
Test Duration	Approximately 80 hours

Table 6 Dependent Test Variables for MCC Evaluation at the PSDF

Dependent Variable	Expected Value
Particulate Outlet Concentration	less than 20 ppmw
MCC Flow Rate	175 to 250 lb/hr
Alkali Inlet Concentration	0.1 to 20 ppm
Alkali Outlet Concentration	less than 24 ppb
Media Circulation Rate	2000 to 4000 lb/hr
Calcium:Sulfur Ratio	1.0 to 2.0
MCC Sorbent Attrition	less than 10%
Trace Metals Sorption	unknown
Halogenated Compound Sorption	unknown

4.0 Cost Estimate

Table 7 shows the estimated cost of developing and testing a limestone/clay sorbent from the bench scale through pilot plant testing. The details of the cost estimate are contained in a separate document: Option III, Development of Moving Granular-Bed Technology for Multi-Contaminant Control, Updated Cost Proposal.

Work Step	Estimated Cost, \$
Bench scale tests for sorbent development Design of modifications to the GBF at the PSDF Preparation of MCC sorbent for PSDF test Modification of GBF at the PSDF Testing at the PSDF	553,613 121,287 78,868 241,481 103,612
Total Cost	1,098,861

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APPENDIX A

MODEL OF ALKALI CAPTURE IN A GBF USING A CLAY SORBENT

MODEL DEVELOPMENT

For a single pellet, the rate of reaction at a given position in the pellet is proportional to the solid phase alkali in the pellet at that position (Bachovchin et al., 1986) and for spherical geometry is given by:

$$\frac{dm}{dt} = 4 \pi r D_s \frac{dc'}{dr}$$
(1)
where: $m = moles alkali per peliet$
 $t = time, hr$
 $r = radial position, m$
 $D_s = diffusivity of alkali through glass, m^2/hr$
 $C'= solid phase alkali concentration, mol/m^3.$

At any time the relationship between the amount of alkali absorbed and pellet conversion is:

$$m = \frac{4}{3} \pi (R^3 - r^3) F$$
 (2)

where:

R = outside pellet radius, m r = inside radius of reacted zone, m F = moles of alkali/m³ of pellet at complete reaction.

A mass balance yields the rate of diffusion through the reacted layer equals the diffusion of alkali through the gas phase or:

$$\frac{dm}{dt} = 4 \pi R^2 k_g (C - C_s)$$
(3)

where:

 C_s = concentration of alkali in gas at pellet surface, mol/m³.

Equation 1 can be integrated, from C_s' (concentration of alkali in solid at pellet surface, r=R) to 0 (concentration in solid at r, where it is assumed that the surface solid-phase concentration is proportional to the surface gas-phase concentration:

$$C_{s}' = ZC_{s}$$
(4)

where Z = adsorption equilibrium constant.

Equations 2, 3, and 4 are used to eliminate r, C_s ', and C_s to give an expression for the single pellet kinetics in spherical geometry.

$$\frac{dm}{dt} = \frac{R4\Pi DC}{1 - \frac{D}{Rk_g} - \sqrt{\frac{R^3 - \frac{3m}{4\Pi}}{R}}}$$
(5)

where $D=ZD_s$, lumping together the unknowns Z and D_s . The rest of the derivation of the model is similar to that given by Bachovchin et al. (1986). The mass transfer coefficient, k_g , is obtained from a correlation of Carberry (1976). A numerical solution is used in which the reactor is divided into small increments of time, Δt , and small intervals of distance, Δh . Equation 5 shows that the reaction rate decreases as solid-phase alkali concentration, m, increases. For small bed depth and time increments, m will be approximately constant so that equation 5 may be approximated by:

$$\frac{\mathrm{dm}}{\mathrm{dt}} = \mathrm{KC} \tag{6}$$

where K is a rate constant (m³/hr/pellet).

An expression by Levenspiel (1972) is used for the first-order conversion of a gaseous reactant in a plug flow reactor.

$$C_{out} = \frac{4 \text{ a } C_{in} \exp(\text{Pe}/2)}{(1+a)^2 \exp(a \text{ Pe}/2) - (1-a)^2 \exp(-a \text{ Pe}/2)}$$
(7)
where $a^2 = 1 + 4 \text{ kN } \Delta h / (U \text{ Pe})$ (8)

C _{out} =	gas-phase concentration of alkali leaving
	section, mol/m ³
Ν	= number of pellets per m ³ of bed
Ре	= Peclet number U∆h/D _e
D,	= axial dispersion coefficient
U	= gas velocity past the pellet.

The Peclet number for the bed section may be derived from the particle Peclet number:

$$Pe = Pe_{p} \Delta h/d_{p}$$
(9)

Correlations for particle Peclet number may be found in several sources. In most cases it will be about 2.0 (Reynolds number >10).

Within a small Δh , the solid-phase concentration is assumed to be independent of axial position and varies with time. During the short time interval, the gas-phase concentration is assumed to vary with axial position but not with time. These assumptions lead to the following mass balance:

$$m_n = m_o + (C_{in} - C_{out}) (U\Delta t/N \Delta h)$$
(10)

where $m_n = mol$ alkali per pellet in section at end of Δt $m_o = mol$ alkali per pellet in section at start of Δt .

Unlike the fixed reactor model of Bachovchin et al. (1986), in the moving bed model, the pellet concentration changes as the pellets move through the reactor in plug flow. This is accounted for in the numerical solution routine.

The following numerical procedure is used:

- 1. The bed depth, H, is divided into increments of depth , Δh .
- 2. The bed life is divided into increments such that the time increment, Δt , is the time required for the solids to move a distance equal to Δh . Then steps 3 through 8 are followed for all time increments.
- 3. For each bed depth increment, steps 4 through 8 are followed for each increment, inlet to outlet.
- 4. The inlet gas-phase concentration, C_{in} , (outlet of the previous bed slice) and the initial solid-phase concentration, m_{o} , of the current bed slice are noted.

- 5. The mean solid-phase alkali concentration, m is guessed for the current time and position increment. It is used to determine K as defined by equations 5 and 6.
- 6. The outlet concentration is determined using equation 7.
- 7. The new value of m is calculated form Equation 10.
- 8. The mean value of m is determined based on the initial value (step 4) and the final value (step 7). This new mean value is compared to the value estimated in step 5. If it is different a new mean is guessed and the calculation is repeated from step 5.
- 9. After the solid-phase concentration is determined for each slice, the bed solids move into the next slice increment such that the solid-phase concentration of the nth slice becomes the concentration of the nth-1 slice. The time is incremented and steps 3 to 8 are repeated until the life of the bed is reached.

PARAMETER VALUES FOR MOVING BED MODEL

In order to be able to use the model, data is required on the pellet ultimate gettering capacity, F, and the rate constant. Bachovchin et al. (1986) determined values for these parameters for cylindrical pellets made by an extrusion process. Using a fixed bed reactor, the ultimate gettering capacity for the commercial pellets is 14,100 gmol/m³ for sodium absorption and the rate constant is 0.004 m²/hr. For lack of better data, these parameters were used with the model for spherical pellets. Table 1 shows the input for the model which are entered into a file which is accessed during execution of the Basic program. During the execution of the program, the life of the sorbent is entered so that the model can be run for different sorbent life to determine by trial and error the sorbent life which corresponds to the desired outlet concentration of alkali. Figure 1 shows a listing of the Basic program and Figure 2 shows the listing of the output file. The first line of the output file is the input data, the second line are calculated parameters used in the model and the rest of the output shows the calculated results for the last time step for each slice of the reactor.

MODEL RESULTS

The model was used to predict bed life for the KRW gasifier for various bed depths. The results of these calculations are shown in Figures 3 and 4. The entering alkali concentration was assumed to be 10 ppmv and the exiting alkali concentration was 20 ppbv. The sorbent properties used in the model are for 1/4 inch diameter spheres of emathlite clay. Unlike a fixed bed reactor, a circulating bed has a nearly uniform alkali concentration throughout the bed. For a plant with an availability of 65%, a 17 ft deep

bed would be required for a plant which changed sorbent on a yearly basis. The alkali concentration in the sorbent at the time of change of sorbent would be 15.4%. Longer bed life and higher alkali concentrations are possible with deeper bed depths but there are diminishing returns as the sorbent becomes saturated.

The model can also be used to compare a circulating bed with a fixed bed absorber. Figure 3 shows the output of the fixed bed model. The sorbent is 6 mm diameter spheres as used in the moving bed model. A fixed bed reactor has longer sorbent life than a circulating moving bed reactor, 8425 hours for a 20 feet deep fixed bed reactor compared with 7450 for 20 ft deep circulating moving bed reactor. Sorbent utilization was higher with the fixed bed reactor, 19.7% vs. 17.3% sodium for the moving bed reactor.

TABLE 1

INPUT PARAMETERS FOR MOVING BED REACTOR MODEL USING SPHERICAL PARTICLES FOR THE KRW GASIFIER

Input <u>Parameter</u>	Definition	Units	Value
н	Bed depth	m	6.06
NH%	Number of increments into which H will be divided (recommended: 10)		10.0
т	Bed life	hr	7450
VS	Velocity of Solids	m/hr	2.38
R	Pellet Radius	m	0.003
RHOP	Pellet dry density (1450 for commercial pellets)	kg/m³	1450
VOID	Bed void fraction		0.49
F	Pellet ultimate gettering capacity, (14100 for commercial pellets)	gmol Na/m³	14100
U	Superficial gas velocity	m/hr	1630
PRG	Abs. pressure	kPa	2645
TMG	Temperature	к	1144
MW	Gas molecular weight		23.2
PPMIN	Inlet NaCI concentration	ppmv	10.0
DS	Rate constant (recommend: 0.004)	m²/hr	.004
DSN	Convergence parameter (recommended: 0.001)		.001

10 REM This program performs circulating bed getter reaction calculations. 20 REM it assumes spherical poliets 30 OPTION BASE 1: DIM M(100): PRINT "THIS IS CYLINDRICAL SPHERICAL MODEL" 40 INPUT "FILE WITH INPUT DATA";F\$: OPEN F\$ FOR INPUT AS #1 50 INPUT "FILE FOR OUTPUT DATA"; FOS: IF FOS -> " THEN OPEN FOS FOR OUTPUT AS #2 60 INPUT #1,H,NH%,T,VS,R,RHOP,VOID,F,U,PRG,TMG,MW,PPMIN,DS,DSN 65 INPUT "TIME":T 70 PRINT H;NH%;T;VS;R;L;RHOP;VOID;F;U;PRG;TMG;MW;PPMIN;DS;DSN;FO\$ 80 IF FO\$<>** THEN PRINT #2,H;NH%;T;VS;R;L;RHOP;VOID;F;U;PRG;TMG;MW;PPMIN;DS;DSN 85 NT%=T/H*NH%*VS 90 RHOG=MW*PRG/TMG*.1204: VISC=.00526*TMG*1.5/(TMG+110): D12=43.8/PRG 100 SC=VISC/RHOG/D12: VOL=3.14*R^3*4/3: DP=(VOL*6/3.14)^(1/3) 110 RE=DP*U*RHOG/VISC/VOID: KG=U/VOID*1.15*SC^(-2/3)*RE^(-1/2) 120 DEF FNM(X)=6.28*2*DS*(R)/(1-(R*3-3*X/4/3.14/F)*(1/3)/R+(DS/KG/R)) 130 CIN=PPMIN*RHOG/MW/1000: N=(1-VOID)/VOL: MMAX=VOL*F 140 DELH=H/NH%: DELT=T/NT% 150 PE=2*DELH/DP: PRINT RHOG;VISC;D12;SC;VOL;DP:RE;KG;CIN;N;MMAX;PE 160 IF FO\$<>** THEN PRINT #2,RHOG;VISC;D12;SC;VOL;DP;RE;KG;CIN;N;MMAX;PE 170 PRINT TIME LENGTH TIME, LENGTH, PELLET, GAS OUT," 180 PRINT * STEP STEP I 181 PRINT #2,* TIME LENGTH 182 PRINT #2,* STEP STEP WT % Na PPMV ' HR M TIME, LENGTH, PELLET, GAS OUT," HR WT % Na PPMV * M 190 FOR IH%=1 TO NH%: M(IH%)=0: NEXT IH% 200 FOR IT%=1 TO NT%: C=CIN: TN=IT%/NT%*T: FOR IH%=1 TO NH%: HN=IH%/NH%*H 210 IF M(IH%)<MMAX THEN SMAXO=FNM(M(IH%)) ELSE SMAXO=0 220 SMAX=SMAXO: MNEW=M(IH%)+SMAX*DELT*C 230 IF MNEW>MMAX THEN SMAX=(MMAX-M(IH%))/DELT/C 240 CNEW=C*EXP(SMAX*DELH/U*N) 250 BETA=SQR(1+4*SMAX/PE*DELH*N/U): CNEW=C*4*BETA/((1+BETA)^2*EXP(-(1-BETA)/2*PE)-(1-BETA)^2*EXP(-(1+BETA)/2*PE)) 260 IF M(IH%)<MMAX THEN S1=FNM(M(IH%)): ELSE S1=0 270 IF M(IH%)<MMAX*.9999 GOTO 290 280 MNEW=MMAX: CNEW=C-(MMAX-M(IH%))/DELT*DELH*N/U: GOTO 400 290 DELS=SMAX0: DEL=SMAX/2: S=DEL 300 BETA=SQR(1+4*S/PE*DELH*N/U) 301 CNEW=C*4*BETA/((1+BETA)^2*EXP(-(1-BETA)/2*PE)-(1-BETA)^2*EXP(-(1+BETA)/2*PE)) 302 MNEW=M(IH%)+(C-CNEW)*U*DELT/N/DELH 310 IF CNEW<0 THEN CNEW=0 320 IF MNEW>=MMAX THEN MNEW=MMAX: SN=0: GOTO 350 330 S2=FNM(MNEW): IF S2<0 THEN SN=0: GOTO 350 340 IF ABS(S1-S2)<.001*S1 THEN SN=(S1+S2)/2: ELSE SN=(S1-S2)/LOG(S1/S2) 350 IF ABS(SN-S)<DSN*S OR S=SL GOTO 400 360 CMIN=.0000001*RHOG/MW: IF C<CMIN AND CNEW<CMIN GOTO 400 370 DELSO=DELS: DELS=SN-S: IF DELSO*DELS<0 THEN DEL=-DEL/2 380 SL=S: S=S+DEL: IF S>SMAX THEN S=SMAX 390 GOTO 300 400 C=CNEW: M(IH%)=MNEW: PPM=C/RHOG*MW*1000: WP=MNEW/VOL/RHOP*2.3 424 K=NH%-1: LAST=M(1) 425 NEXT IH%: FOR II=1 TO (NH%-1): M(II)=M(II+1): NEXT II: M(NH%)=LAST

431 NEXT IT%: END

Figure 1 Basic Program for Model of a Moving Bed Alkali Sorbent

6.06 10						.004 .001				
6.458239	.162303	3 1.655955E-02	1.517626	1.1304B-07 5.	.9999998-03 794.1995	102.7893	2.783724E-03	4511677	1.593864E-03	202
TIME	LENGTH	TIME,	LENGTH,	PELLET.	GAS OUT.					
STEP	STEP	HR	м	WT Na	PPMV					
29259	1	7450.000	0.606	17.347	5.369					
29259	2	7450.000	1.212	17.344	2.882					
29259	3	7450.000	1.818	17.345	5 1.547					
29259	4	7450.000	2.424	17.346	5 0,931					
29259	5	7450.000	3.030	17.346	5 9.446					
29259	6	7450.000	3.636	17.347	0.239					
29259	7	7450.000	4.242	17.347	0.129					
29259	8	7450.000	4.848	17.347	0.069					
29259	9	7450.000	5.454	17.347	7 0.037					
29259	10	7450.000	6.060	17.34	0.020					

Figure	2	Output F	ile fo	r Input	Data	Shown	in	Table 1

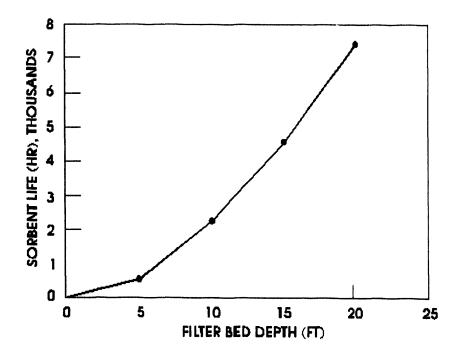


Figure 3 Sorbent Life as a Function of Bed Depth for 1/4 Inch Diameter Spheres for a GBF Applied to the KRW Gasifier

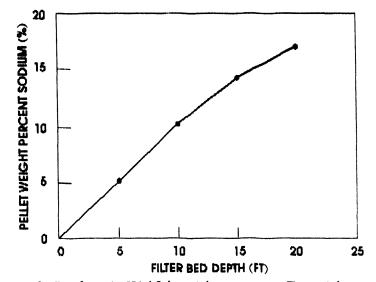


Figure 4 Sorbent Utilization as a Function of Bed Depth for 1/4 Inch Diameter Spheres for a GBF Applied to the KRW Gasifier

6.06 10 7450 10 .003 .004 1450 .49 14100 1630 2645 1144 23.2 10 .004 .001 6.458239 .1623033 1.655955E-02 1.517626 1.1304E-07 5.999999E-03 794.1995 102.7893 2.783724E-03 4511677 1.593864E-03 202

TIME	LENGTH	TIME,	LENGTH,	PELLET,	GAS OUT,
STEP	STEP	HR	M	WT 🕯 Na	PPMV
10	1	8425.000	0.606	22.366	10.000
10	2	8425.000	1.212	22.366	10.000
10	3	8425.000	1.818	22.366	10.000
10	4	8425.000	2.424	22.366	10.000
10	5	8425.000	3.030	22.366	10.000
10	6	8425.000	3.636	22.365	9.992
10	7	8425.000	4.242	22.328	9.394
10	8	8425.000	4.848	20.658	6.643
10	9	8425.000	5.454	14.348	2.317
10	10	8425.000	6.060	4.635	0.019

Figure	5	Model	Results	for	Fixed	Bed	Reactor	Usina	Input	from	Figure /	A.1	ļ
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APPENDIX B

COST ESTIMATE FOR THE PRODUCTION OF GBF MEDIA

SUMMARY

Plant scale processes have been developed to estimate the capital and operating costs to produce a GBF media of limestone and clay at three different production rates. The production rates chosen were 5,000 ton/yr, 50,000 ton/yr, and 500,000 ton/yr. For a 5,000,000 ton/yr media production rate, the 500,000 ton/yr process would be built tenfold.

To develop the plant processes and cost estimates for the three production rates, assumptions had to be made concerning the media composition, i.e. the sorbent formulation. Of the 68 possible formulations, a single formulation was chosen as the base case. This formulation is 6 mm pellets of 80% less than 149 micron limestone with 5% montmorillonite clay and 10% dry binder addition of portland cement (PC III). The pellets would be formed by disc pelletization requiring 20% pellet moisture and moist environment curing for 72 hours.

As a comparison to the base case sorbent formulation chosen, lower and upper limits of the capital and operating costs were also developed using the remaining formulations. The only assumption made was that the pellets were of 6 mm size. The lower limit formulation is pellets of 80% less than 149 micron limestone with 5% kaolin clay requiring no binder addition. These pellets would be formed by disc pelletization requiring 20% pellet moisture and no curing. For the upper limit, there are two formulations. The highest capital cost is for pellets of 80% less than 44 micron limestone with 5% attapulgite clay, and 2% bentonite and 10% These pellets would be formed by calcium sulfate binders. extrusion requiring 20% pellet moisture followed by spheronization and moist environment curing for 72 hours. The highest operating cost is for pellets of 80% less than 44 micron limestone with 5% attapulgite clay and 4% sodium silicate binder. These pellets would be formed by extrusion requiring 20% pellet moisture followed by spheronization and drying to 5% pellet moisture.

Table 1 gives the results of the cost estimate.

Productic Rate ton/yr		pital Cost M\$	Operating Cost \$/ton			
	Base	Range	Base	Range		
5,000 50,000 500,000	2.5 4.38 15.29	2.14 - 2.82 3.67 - 5.11 12.29 - 16.96	152.01 39.72 26.90	137.83 - 200.31 31.12 - 86.10 19.17 - 71.93		

Table 1 Cost Estimate for GBF Media Production

The cost estimates are accurate to -20% and +40%. At production rates less than 5,000 ton/yr, it is likely that a toll manufacturer could be found to produce the filter media at a cost comparable, if not less than, that of a dedicated plant.

The following sections contain the supporting information for the development of the cost estimate.

PLANT PROCESS

1. Process Description

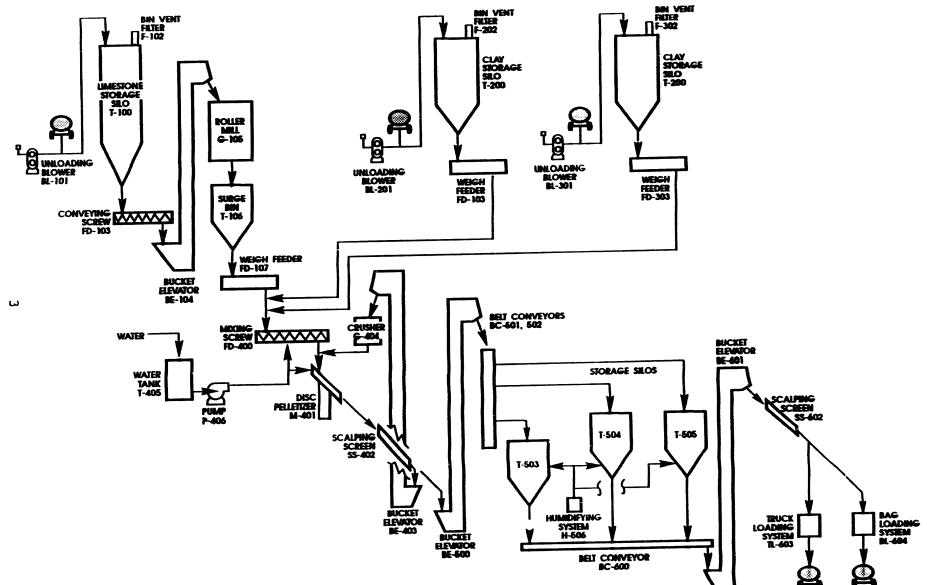
The process description for the base case sorbent formulation, 6 mm pellets of 80% less than 149 micron limestone with 5% montmorillonite clay and 10% portland cement binder, is similar for all production rates. The only differences are the quantity, capacity, and throughput of each piece of equipment, and an additional conveyor when needed to minimize plant elevation. Refer to Figure 1, Process Flow Schematic for GBF Media Production, for a schematic of the process being described.

a. Limestone Unloading and Storage

Limestone is received in truck or railcar quantities and is unloaded pneumatically into the storage silo (T-100). A blower (BL-101) provides the conveying air for the limestone. A bin vent filter (F-102) is mounted on the silo to control dust from pneumatic unloading.

b. Limestone Preparation

Limestone from the storage silo gravity flows to a conveying screw (FD-103) which feeds the bucket elevator (BE-104). The elevator lifts the limestone to the roller



Process Flow Schematic for GBF Media Production Figure 1

mill (G-105). The roller mill pulverizes the material to the required particle size. Pulverized limestone gravity flows to the surge bin (T-106).

c. Limestone Transfer to Process

From the surge bin, limestone gravity flows to the weigh feeder (FD-107) which meters the limestone to the mixing system.

For the 50,000 and 500,000 ton/yr production rates, an additional bucket elevator (BE-108) is required to lift the limestone, clay, and binder to the mixing screw elevation.

d. Clay Unloading and Storage

Clay is received in truck or railcar quantities and is unloaded pneumatically into the storage silo (T-200). A blower (BL-201) provides the conveying air for the clay. A bin vent filter (F-202) is mounted on the silo to control dust from pneumatic unloading.

e. Clay Transfer to Process

From the storage silo, clay gravity flows to the weigh feeder (FD-203) which meters the clay to the mixing system.

f. Binder Unloading and Storage

Dry binder is received in truck or railcar quantities and is unloaded pneumatically into the storage silo (T-300). A blower (BL-301) provides the conveying air. A bin vent filter (F-302) is mounted on the silo.

g. Binder Transfer to Process

Binder gravity flows to the weigh feeder (FD-303) from the storage silo. The feeder meters and discharges the binder to the mixing system.

The limestone, clay, and binder weigh belt feeders have variable speed controls to adjust the addition rate to process demand.

h. Mixing System

Limestone, clay, and binder are mixed and pre-wetted in a mixing screw (FD-400). Near the inlet of the screw, the dry materials are mixed. Within the last half of the screw length, nozzles spray water to initially wet the mixture providing a consistency which will tumble instead of slide in the disc pelletizer.

The mixing screw controls the feed rate to the disc pelletizer (M-401). The screw has variable speed controls to adjust the feed rate to the pelletizer.

i. Agglomerating System

The wetted mixture from the mixing screw is agglomerated on the disc pelletizer to form pellets of approximately 6 mm diameter. The pellets discharge from the pelletizer to scalping screens (SS-402) which obtain the required size pellets. Oversized and undersized pellets are discharged to the bucket elevator (BE-403) which takes the material to the inlet of the crusher (G-404). The crusher crushes the material and discharges to the feed chute of the pelletizer. The 6 mm diameter pellets gravity flow to a bucket elevator (BE-500) which feeds the curing and storage system.

A water hold tank (T-405) stores spray water. The water gravity flows to the pump (P-406) which boosts the water pressure for delivery to the mixing screw and pelletizer spray nozzles.

j. Curing and Storage System

Sized pellets are conveyed to the storage silos with belt conveyors (BC-501 and BC-502) which take the discharge from the bucket elevator (BE-500). The belt conveyors fill each of the three storage silos (T-503, T-504, and T-505). The storage silos hold and cure the pellets. A humidifying system (H-506) provides moisture to the silos for the hydraulic binder reactions. The pellets are stored (cured) in the silos for 72 hours.

k. Product Packaging System

After the pellets are cured, they are unloaded to trucks or packaged in mini-ton bags (27 cu.ft.). Pellets from the storage silos are discharged to a belt conveyor (BC-600) that feeds a bucket elevator (BE-601). The bucket elevator takes the pellets to the scalping screen (SS-602) to remove the broken pellets and fines, and then feeds the truck loading system (TL-603) or the bag loading system (BL-604). The truck loading system includes an elevated, retractable spout with dust suppression equipment and bulk load scale. The bag loading system is complete to load and weigh mini-ton bags for shipment.

1. Miscellaneous

An air compressor (C-700) is required to supply the compressed air to the plant to operate equipment and instrumentation.

Likewise, the lower and upper limit formulations have similar process descriptions for all production rates. The process description for the lower limit formulation of 6 mm pellets of 80% less than 149 micron limestone with 5% kaolinite clay and no binder addition is simpler than the base case formulation description. The process would not require the binder unloading, storage, and feed system (300 series equipment), the storage belt conveyors (BC-501 and BC-502) except BC-501 needed for the largest production rate, two of the storage silos (T-504 and T-505), and the humidifying system (H-506).

For the highest capital cost of 6 mm pellets of 80% less than 44 micron limestone with 5% attapulgite clay and 2% bentonite and 10% calcium sulfate binders, the process description is more extensive than the base case. An additional binder addition system is required which includes the storage silo, unloading blower, vent filter, and weigh feeder (similar to 300 series). The finer ground limestone requires a larger roller mill system (G-105). An extrusion mill (M-407) is required to extrude cylindrical pellets and the pelletizer (M-401) is used for spheronization. For binders other than portland cement and calcium sulfate products, the highest capital cost process would require a drying system to reduce pellet moisture from 20% to 5%.

2. Equipment List

An equipment list has been developed for the base case sorbent formulation at the three production rates. Included in the list are major process equipment, tanks, bins, conveyors, raw material unloading and storage equipment, limestone processing equipment, and product storage and packaging systems. Table 2 gives a listing of the equipment classified into the three production rates.

Also included in Tables 3 and 4 are listings of the alternate equipment required for the lower and upper limit formulations.

Table 2 Equipment List

Base Case Formulation

<u>Description</u>

Item No.	Name	5,000 tpy	50,000 tpy	500,000 tpy
T-100	Limestone	1700 cu.ft.,	8000 cu.ft.,	35000 cu.ft.,
	Storage Silo	C.S.	C.S.	C.S., 2 req.
BL-101	Limestone	P.D., 2100	P.D., 2100	P.D., 2800 cfm
	Unloading	cfm @ 13	cfm @ 13	@ 15 psig, 300
	Blower	psig, 200 hp	psig, 200 hp	hp, 4 req.
F-102	Limestone	445 sq.ft.,	445 sq.ft.,	1346 sq.ft.,
	Vent Filter	C.S.	C.S.	C.S., 2 req.
FD-103	Limestone Conveying Screw	4 in. dia.x 11 ft. long, C.S., 1/2 hp	9 in. dia. x 17 ft. long, C.S., 3 hp	12 in. dia. x 25 ft. long, C.S., 10 hp, 2 req.
BE-104	Limestone	76 ft.,	81 ft.,	110 ft.,
	Bucket	C.S.,	C.S.,	C.S., 15 hp,
	Elevator	3 hp	5 hp	2 req.
G - 105	Limestone	0.7 tph,	7 tph,	35 tph, 1050
	Roller Mill	28 hp	236 hp	hp, 2 req.
T-106	Limestone	200 cu.ft.,	2000 cu.ft.,	10000 cu.ft.,
	Surge Bin	C.S.	C.S.	C.S., 2 req.
FD-107	Limestone	0.7 tph, 11	7 tph, 16	35 tph, 22 ft
	Weigh	ft. long,	ft. long,	long, 1 1/2
	Feeder	1 1/4 hp	l hp	hp, 2 req.
BE-108	Mixer Bucket Elevator	N/R	53 ft., 3 hp	68 ft., 7 1/2 hp, 2 req.
T-200	Clay	900 cu.ft.,	900 cu.ft.,	8000 cu.ft.,
	Storage Silo	C.S.	C.S.	C.S.
BL-201	Clay	P.D., 900	P.D., 900	P.D., 900
	Unloading	cfm @ 12	cfm @ 12	cfm @ 12
	Blower	psig, 75 hp	psig, 75 hp	psig, 75 hp
F-202	Clay Vent	254 sq.ft.,	254 sq.ft.,	254 sq.ft.,
	Filter	C.S.	C.S.	C.S.
FD-203	Clay	140 pph, 15	0.7 tph, 22	3.5 tph, 27 ft.
	Weigh	ft. long,	ft. long,	long, 2 1/4
	Feeder	3/4 hp	1 1/2 hp	hp, 2 req.

Table 2 Equipment List (cont)

Base Case Formulation

<u>Description</u>

Item No.	Name	5,000 tpy	50,000 tpy	500,000 tpy
T-300	Binder	900 cu.ft.,	900 cu.ft.,	9000 cu.ft.,
	Storage Silo	C.S.	C.S.	C.S.
BL-301	Binder	P.D., 1700	P.D., 1700	P.D., 1700
	Unloading	cfm @ 12	cfm @ 12	cfm @ 12
	Blower	psig, 125 hp	psig, 125 hp	psig, 125 hp
F-302	Binder	339 sq.ft.,	339 sq.ft.,	339 sq.ft.,
	Vent Filter	C.S.	C.S.	C.S.
FD-303	Binder	160 pph, 17	0.8 tph, 30	4 tph, 22 ft.
	Weigh	ft. long,	ft. long,	long, 1 1/2
	Feeder	3/4 hp	1 3/4 hp	hp, 2 req.
FD-400	Mixing Screw	4 in. dia. x 18 ft. long, C.S., 1 hp	9 in. dia. x 24 ft. long, C.S., 5 hp	14 in. dia. x 27 ft. long, C.S., 10 hp, 2 req.
M-401	Disc Pelletizer	4 ft6 in. dia. pan, C.S., 4 hp	10 ft. dia. pan, C.S., 40 hp	20 ft. dia. pan, C.S., 140 hp, 2 req.
SS-402	Scalping Screens	2 ft.x 6 ft., C.S., 3 hp	3 ft.x 8 ft., C.S., 3 hp	4 ft.x 10 ft., C.S., 3 hp, 2 req.
BE-403	Recycle	59 ft.,	76 ft.,	108 ft.,
	Bucket	C.S.,	C.S.,	C.S.,
	Elevator	3 hp	3 hp	15 hp
G-404	Pellet	0.3 tph,	3 tph,	30 tph,
	Crusher	18 hp	109 hp	852 hp
T-405	Water	300 gal.,	3000 gal.,	30000 gal.,
	Tank	C.S.	C.S.	C.S.
P-406	Water	0.7 gpm @	6 gpm @	30 gpm @ 30
	Spray	30 psig,	30 psig,	psig, 1 1/2
	Pump	1/2 hp	3/4 hp	hp, 2 req.
BE-500	Storage	58 ft.,	84 ft.,	124 ft.,
	Bucket	C.S.,	C.S.,	C.S., 15
	Elevator	3 hp	5 hp	hp, 2 req.

Table 2 Equipment List (cont)

Base Case Formulation

<u>Description</u>

Item No.	Name	5,000 tpy	50,000 tpy	500,000 tpy
BC-501	Storage Belt	1 tph,	10 tph,	50 tph, 42
	Conveyor	12 ft.	20 ft.	ft., 2 req.
BC-502	Storage Belt	1 tph,	10 tph,	50 tph, 85
	Conveyor	32 ft.	50 ft.	ft., 2 req.
T-503	Storage	900 cu.ft.,	9000 cu.ft.,	45000 cu.ft.,
	Silo	C.S.	C.S.	C.S., 2 req.
T-504	Storage	900 cu.ft.,	9000 cu.ft.,	45000 cu.ft.,
	Silo	C.S.	C.S.	C.S., 2 req.
T-505	Storage	900 cu.ft.,	9000 cu.ft.,	45000 cu.ft.,
	Silo	C.S.	C.S.	C.S., 2 req.
H-506	Humidifying	40 pph unit,	120 pph unit,	300 pph unit,
	System	3 req.	3 req.	6 req.
BC-600	Unloading Belt Conveyor	25 tph, 40 ft.	25 tph, 64 ft.	50 tph, 101 ft., 2 req.
BE-601	Unloading	58 ft.,	63 ft.,	64 ft.,
	Bucket	C.S.,	C.S.,	C.S., 10
	Elevator	7 1/2 hp	7 1/2 hp	hp, 2 req.
SS-602	Scalping Screen	3 ft.x 8 ft., C.S., 3 hp	3 ft.x 8 ft., C.S., 3 hp	4 ft.x 10 ft., C.S., 3 hp, 2 req.
TL-603	Truck Loading System	25 tph, dust supp., retractable	25 tph, dust supp., retractable	50 tph, dust supp., retractable, 2 req.
BL-604	Bag Loading	6 bph, mini-	6 bph, mini-	6 bph, mini-ton
	System	ton bags	ton bags	bags, 2 req.
C-700	Compressed Air System	100 cfm @ 125 psig, 30 hp	200 scfm @ 125 psig, 50 hp	600 scfm @ 125 psig, 150 hp

Table 3 Equipment List

Lower Limit Formulation			Description		
Item No.	Name	5,000 tpy	50,000 tpy	500,000 tpy	
T-100	Limestone Storage Silo		9000 cu.ft., C.S.		
T-200	Clay Storage Silo			7000 cu.ft., C.S.	
BE-500	Storage Bucket Elevator	51 ft., C.S., 3 hp	79 ft., C.S., 5 hp	119 ft., C.S., 15 hp, 2 req.	
BC-600	Unloading Belt Conveyor	25 tph, 13 ft.	25 tph, 18 ft.	50 tph, 25 ft., 2 req.	
C-700	Compressed Air System		100 scfm @ 125 psig, 30 hp	200 scfm @ 125 psig, 50 hp	

Table 4 Equipment List

Upper Limit Formulation

<u>Description</u>

<u>Item No.</u>	Name	5,000 tpy	50,000 tpy	500,000 tpy
BE-104	Limestone	78 ft.,	85 ft.,	112 ft.,
	Bucket	C.S.,	C.S.,	C.S., 25 hp
	Elevator	3 hp	3 hp	2 req.
G-105	Limestone	0.7 tph,	7 tph,	35 tph, 1350
	Roller Mill	38 hp	337 hp	hp, 2 req.
FD-303	Binder Weigh Feeder	160 pph, 20 ft. long, 3/4 hp	0.8 tph, 26 ft. long, 1 3/4 hp	
T-304	Binder	900 cu.ft.,	900 cu.ft.,	3000 cu.ft.,
	Storage Silo	C.S.	C.S.	C.S.
BL-305	Binder	P.D., 900	P.D., 900	P.D., 900
	Unloading	cfm @ 12	cfm @ 12	cfm @ 12
	Blower	psig, 75 hp	psig, 75 hp	psig, 75 hp
F-306	Binder	254 sq.ft.,	254 sq.ft.,	254 sq.ft.,
	Vent Filter	C.S.	C.S.	C.S.
FD-307	Binder	35 pph, 19	350 pph, 34	0.85 tph, 34
	Weigh	ft. long,	ft. long,	ft. long, 1 1/2
	Feeder	3/4 hp	1 1/4 hp	hp, 2 req.
FD-400	Mixing Screw	4 in. dia. x 11 ft. long, C.S., 1 hp	9 in. dia. x 11 ft. long, C.S., 5 hp	14 in. dia. x 9 ft. long, C.S., 10 hp, 2 req.
M-401	Disc Pelletizer	4 ft6 in. dia. pan, C.S., 3 hp	10 ft. dia. pan, C.S., 30 hp	20 ft. dia. pan, C.S., 125 hp, 2 req.
M-407	Extrusion	1 tph,	10 tph,	25 tph, 125
	Mill	7 1/2 hp	60 hp	hp, 4 req.

3. Process Layout

The process equipment given in the equipment list has been arranged in a proposed plant layout for the base case formulation at the three production rates. Figure B.2 shows the proposed layout for the 5,000 ton/yr production rate. For 50,000 and 500,000 ton/yr production rates, the layouts are very similar to Figure 2. Gravity transfer has been utilized where possible and the plant is enclosed within a building structure.

At the 5,000 ton/yr production rate, the plant requires approximately 3,800 square feet of ground floor area, excluding truck access areas, with a maximum vertical ceiling height of 100 feet. There are four main bay areas required in the structure to support the equipment. These bays occur at approximately 15, 30, 50, and 65 feet above ground level. Intermediate platform levels are required to access all equipment.

For the 50,000 and 500,000 ton/yr production rates for the base case formulation, the plants require approximately 8,500 and 34,800 square feet of ground floor area with a maximum vertical ceiling height of 90 and 130 feet above ground level, respectively. There are three main bay areas required in the 50,000 tpy plant at 15, 40, and 65 feet above ground level with intermediate platform levels. There are four main bay areas required in the 500,000 tpy plant at 15, 50, 70, and 100 feet above ground level with intermediate platforming.

Space for utility equipment is not included in the plant layouts.

Descriptions of the plant layout for the lower and upper limit sorbent formulations are summarized below.

	Production Rate, ton/yr			
	5,000	50,000	500,000	
Lower Limit Formulation: Space, sq.ft. Roof Height, ft. No. of Main Bays	3,400 100 4	6,100 90 3	23,100 130 4	
Upper Limit Formulation: Space, sq.ft. Roof Height, ft. No. of Main Bays	4,200 100 4	12,300 90 3	37,600 130 4	

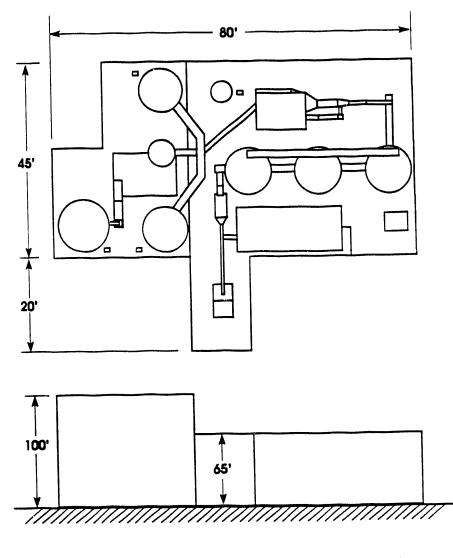


Figure 2 Process Layout for 5,000 tpy Production Rate

4. Utility Consumption

Preliminary utility usages for all of the sorbent formulations at the three production rates have been developed. Plant process on-stream times of approximately 90% have been assumed. The utility usages for the base case formulation and the range for all formulations are estimated as follows:

	Production Rate, ton/yr					
Utility	5,000		50,000		500,000	
	Base	Range	Base	Range	Base	Range
Electricity (kW)	52	46-68	289	271-437	2633	2519- 3710
Compressed Air (scfm @ 100 psig	30)	23-34	62	42-72	299	198- 338
Natural Gas (scfm)	0	0-10	0	0-94	0	0- 937

5. Raw Materials Usage

Preliminary raw material usages have been developed. A material loss of approximately 10% has been assumed for each process. Losses are due to fines production and material lost during handling (conveying, processing, etc.).

Overall raw material usages for production rates of 5,000, 50,000, and 500,000 ton/yr at the base case and remaining formulations are as follows:

Material	Usage, to	n/ton product
	Base	Range
Limestone Clay Binder Water	0.797 0.052 0.090 0.170	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

COST ESTIMATE

Order-of-magnitude cost estimates have been developed for the three sorbent formulations at the three production rates. These estimates are accurate to -20% to +40% and are shown in Tables 5, 6, and 7. They include all direct and indirect costs. The land for the plants is assumed to be available and is not part of the project cost.

The costs were developed as follows:

- 1. Direct Costs
 - a. Process Equipment

The equipment in the process description was sized as given in the equipment lists. Vendor verbal quotes were obtained and the costs are listed in Tables 8, 9, and 10.

b. Equipment Installation

Man-hours were estimated for removing the process equipment from a truck, setting it in place, bolting it down, and welding to adjacent components for multiple section equipment. A rate of \$40 per hour was used for labor.

c. Civil/Structural

The civil/structural work was estimated for land that is ready for plant installation requiring minor excavation and backfill. Work includes the substructures (concrete foundation and pedestals, grouting, anchor bolts, etc.), the superstructures (steelwork for equipment, platforms, stairways, etc.), and the building enclosure.

d. Piping and Ductwork

Piping and ductwork was assumed to be all carbon steel pipe and plate. Individual pipe and duct sizes were estimated based on flow rates and runs were estimated from the plant layouts. Costs were estimated based on the quantity of materials needed and the number of connections required. Labor cost was estimated at \$40 per hour. An additional allowance of 100% was added for valves, fittings, and installation difficulties.

e. Electrical

Electrical work was based on the installed motor horsepower for each motor and a factor of \$200 per horsepower. f. Instrumentation

Instrumentation devices were estimated from previous boiler processes and costed out based on previous purchases. The installation of the instrumentation was assumed to be equal to the instrument costs.

g. Painting and Insulation

Painting and insulation work was based on a factor of approximately 3.7% of the total direct cost.

h. Auxiliary Facilities

Plant services such as water, electricity, and natural gas was based on a factor of approximately 10% of the total direct cost.

i. Insurance, Taxes and Freight

The costs for insurance, taxes, and freight were based on a factor of approximately 3.5% of the total direct cost.

2. Indirect Costs

a. Home Office Expenses

This category includes costs for engineering, purchasing, and construction supervision. It was assumed to be 12% of the total project cost.

b. Field Expenses

This category includes costs for construction which include materials, tools and rentals, taxes, permits, insurance, and contractors fee. These costs were assumed to be 8% of the total project cost.

c. Contingency

A 10% contingency was used based on the total project cost.

Table 5 Cost Estimate, k\$

Base Case Formulation	duction Rat	ion Rate, ton/yr	
	5,000	50,000	500,000
Process Equipment Equipment Installation Civil/Structural Piping and Ductwork Electrical Instrumentation Painting and Insulation	888.7 103.7 140.5 89.2 96 120.8 63.9	1,569 180.5 327.9 157.1 166.3 120.8 112.2	5,461.9 560.7 1,059.1 546.6 965.8 204.4 390.3
Auxiliary Facilities Insurance, Taxes, Freight	183.3 61.7		1,126.5 378.9
Total Direct Cost	1,747.8	3,065.9	10,694.2
Home Office Expenses Field Expenses Contingency	299.6 199.1 249.4	526.2 352.6 437.4	1,830.1 1,235.5 1,525.7
Total Indirect Cost	748.1	1,316.2	4,591.3
TOTAL PROJECT COST	2,495.9	4,382.1	15,285.5

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Table 6 Cost Estimate, k\$

Lower Limit Formulation Production Rate, ton/yr

TOTAL PROJECT COST	2,142.3	3,672.6	12,291.8
Total Indirect Cost	642.1	1,100.7	3,686.3
Contingency	214.1		
Home Office Expenses Field Expenses	255.6 172.4		1,486.3 972.3
Total Direct Cost	1,500.2	2,571.9	8,605.5
Insurance, Taxes, Freight	52.4	90.8	304.3
Auxiliary Facilities	149.6		
Instrumentation Painting and Insulation	100.6 55.3		164.2 321.7
Electrical	70.6		
Piping and Ductwork	79.1		463.3
Equipment Installation Civil/Structural	84.5 130.2		460.8 736
Process Equipment	777.9	1,348.8	-
	5,000	50,000	500,000

Table 7 Cost Estimate, k\$

Upper Limit Formulation Production Rate, ton/yr

	5,000	50,000	500,000
Process Equipment	990.6	1,800.5	6,015.9
Equipment Installation	138.2	258.5	792.6
Civil/Structural	150.9	382.7	1,130.3
Piping and Ductwork	108.9	196.3	643.7
Electrical	112.5	191.6	1,029.6
Instrumentation	131.1	131.1	220.6
Painting and Insulation	72.8	132.8	438.9
Auxiliary Facilities	196.7	357.5	1,186.4
Insurance, Taxes, Freight	68.8	125.3	415.3
Total Direct Cost	1,970.5	3,576.3	11,873.3
Home Office Expenses	338.2	612	2,030.6
Field Expenses	225.3	408.6	1,356.6
Contingency	281.8	510.3	1,694.6
Total Indirect Cost	845.3	1,530.9	5,081.8
TOTAL PROJECT COST	2,815.8	5,107.2	16,955.1

Table 8 Equipment Cost, k\$

Base Case Formulation

Production Rate, ton/yr

Item No.	Name	5,000	50,000	500,000	Vendor
	Limestone				
T-100	Storage Silo	21.5	55.9	355.1	CPC
BL-101	Unloading Blower	36.8	36.8	260	Aerzen
F-102	Bin Vent Filter	8.2	8.2	28.3	Flex-Kleen
FD-103	Conveying Screw	1.7	5.3	18	Hutchinson
BE-104	Bucket Elevator	33.5	34.1	46.8	Rexnord
G-105	Roller Mill	160	375	1,200	Williams
T-106	Surge Bin	2.8	21.6	126.7	CPC
FD-107	Weigh Feeder	26.1	27	60	Thayer Scale
BE-108	Bucket Elevator	N/R	23	66.8	Rexnord
	<u>Clay</u>				
T-200	Storage Silo	12.9	12.9	55.9	CPC 4
BL-201	Unloading Blower	14.5	14.5	14.5	Aerzen
F-202	Bin Vent Filter	5.5	5.5	5.5	Flex-Kleen
FD-203	Weigh Feeder	26	26.9	56.8	Thayer Scale
10 205	Binder	20	2019	0010	inajer beare
T-300	Storage Silo	12.9	12.9	61.3	CPC
BL-301	Unloading Blower	23.5	23.5	23.5	Aerzen
F-302	Bin Vent Filter	6.1	6.1	6.1	Flex-Kleen
FD-303	Weigh Feeder	26.1	27.5	60	Thayer Scale
rD-202	Process	20.1	27.5	00	mayer scare
FD-400	Mixing Screw	2.8	7.4	25.4	Hutchinson
M-401	Disc Pelletizer	25	108	588.6	Ferro-Tech
SS-402	Scalping Screens	13.9	18.6	41.6	Tyler
BE-403	Bucket Elevator	29.3	33.2	46.6	Rexnord
G-404	Pellet Crusher	170	275	500	Williams
T-405	Water Tank	1.8	8.1	47	CPC
P-406	Water Spray Pump	0.5	0.5	1.3	Price Pump
1 100	Storage				_
BE-500	Bucket Elevator	28.8	34.1	99	Rexnord
BC-501	Belt Conveyor	1.8	3	10.6	FEI
BC-502	Belt Conveyor	3.1	5.5	17.8	FEI
T-503	Storage Tank	12.9	61.3	431.3	CPC
T-504	Storage Tank	12.9	61.3	431.3	CPC
T-505	Storage Tank	12.9	61.3	431.3	CPC
H-506	Humidifying System	7.5	9.8	30.4	Herrmidifier
	Unloading and Pack				
BC-600	Belt Conveyor	4.8	6.8	20.5	FEI
BE-601	Bucket Elevator	31.5	32.5	65.4	Rexnord
SS-602	Scalping Screen	16.8	16.8	37.4	Tyler
TL-603	Truck Loading	46.8	46.8	73.2	Hutchinson
BL-604	Bag Loading	30	30	60	Hutchinson
	Miscellaneous				
C-700	Compressed Air	17.4	27.3	57.9	Ingersoll-
	compressed ner	7 (• 4	21.5	57.5	Rand
	EQUIPMENT TOTAL	888.7	1,569	5,461.9	

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Table 9 Equipment Cost, k\$

Lower Limit Formulation

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Production Rate, ton/yr

Item No.	Name	5,000	50,000	500,000	Vendor
	<u>Limestone</u>				
T-100	Storage Silo		5.4		CPC
	<u>Clay</u>				
T-200	Storage Silo			(5.4)	CPC
	Binder				
T-300	Storage Silo	(12.9)	(12.9)	(61.3)	CPC
BL-301	Unloading Blower	(23.5)	(23.5)	(23.5)	Aerzen
F-302	Bin Vent Filter	(6.1)	(6.1)	(6.1)	Flex-Kleen
FD-303	Weigh Feeder	(26.1)	(27.5)	(60)	Thayer Scale
	Storage				
BE-500	Bucket Elevator	(1.7)	(0.9)	(1.0)	Rexnord
BC-501	Belt Conveyor	(1.8)	(3)		FEI
BC-502	Belt Conveyor	(3.1)	(5.5)	(17.8)	FEI
T-504	Storage Tank	(12.9)	(61.3)	(431.3)	CPC
T-505	Storage Tank	(12.9)	(61.3)	(431.3)	CPC
H-506	Humidifying System	(7.5)	(9.8)	(30.4)	Herrmidifier
	Unloading and Packa	ging			
BC-600	Belt Conveyor	(2.3)	(3.9)	(16.4)	FEI
	Miscellaneous				
C-700	Compressed Air		(9.9)	(30.6)	I-R
	DIFFERENCE TOTAL	(110.8)	(220.2)	(1,115.	1)
	BASE CASE EQUIPMENT	888.7	1,569	5,461.9	
	EQUIPMENT TOTAL	777.9	1,348.8	4,346.8	
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Table 10 Equipment Cost, k\$

Upper Limit Formulation

Production Rate, ton/yr

Name	5,000	50,000	500,000	Vendor
Limestone				
Bucket Elevator	0.5	0.8	0.4	Rexnord
Roller Mill	25	75	200	Williams
<u>Binder</u>				
	0.2	(0.2)		Thayer Scale
	12.9	12.9	29.4	CPC
Unloading Blower	14.5	14.5	14.5	Aerzen
Bin Vent Filter	5.5	5.5	5.5	Flex-Kleen
Weigh Feeder	26.3	27.5	57.6	Thayer Scale
Process				
	(0.5)	(1.5)	(3.4)	Hutchinson
Disc Pelletizer	(0.5)	(3)	(10)	Ferro-Tech
Extrusion Mill	18	100	260	Bonnot
DIFFERENCE TOTAL	101.9	231.5	554	
BASE CASE EQUIPMENT	888.7	1,569	5,461.9	
EQUIPMENT TOTAL	990.6	1,800.5	6,015.9	
	Limestone Bucket Elevator Roller Mill <u>Binder</u> Weigh Feeder Storage Silo Unloading Blower Bin Vent Filter Weigh Feeder <u>Process</u> Mixing Screw Disc Pelletizer Extrusion Mill DIFFERENCE TOTAL	LimestoneBucket Elevator0.5Roller Mill25Binder25Weigh Feeder0.2Storage Silo12.9Unloading Blower14.5Bin Vent Filter5.5Weigh Feeder26.3Process(0.5)Disc Pelletizer(0.5)Extrusion Mill18DIFFERENCE TOTAL101.9BASE CASE EQUIPMENT888.7	Limestone Bucket Elevator0.50.8Roller Mill2575Binder Weigh Feeder0.2(0.2)Storage Silo12.912.9Unloading Blower14.514.5Bin Vent Filter5.55.5Weigh Feeder26.327.5Process Mixing Screw(0.5)(1.5)Disc Pelletizer(0.5)(3)Extrusion Mill18100DIFFERENCE TOTAL101.9231.5BASE CASE EQUIPMENT888.71,569	Limestone Bucket Elevator0.50.80.4Roller Mill2575200Binder0.2(0.2)Weigh Feeder0.2(0.2)Storage Silo12.912.9Unloading Blower14.514.5Jin Vent Filter5.55.5Weigh Feeder26.327.5Weigh Feeder26.327.5ProcessMixing Screw(0.5)(1.5)Mixing Screw(0.5)(1.5)(3.4)Disc Pelletizer(0.5)(3)(10)Extrusion Mill18100260DIFFERENCE TOTAL101.9231.5554BASE CASE EQUIPMENT888.71,5695,461.9

OPERATING COST

Operating costs were developed for the three sorbent formulations at each of the three production rates. Tables 11, 12, and 13 show in detail the operating costs.

The operating costs were developed with the following basis:

Raw material usage was estimated assuming a material loss of approximately 10%.

The cost of the raw materials was provided by the chemical vendors. Limestone is Longview as provided by Dravo. Clays are kaolinite, montmorillonite, and attapulgite as provided by Albion Kaolin Company and Floridin. Binders are portland cement and boric acid as provided by National Cement and North American Chemicals.

Utility costs for water, electricity, and natural gas were estimated at \$0.0017 per gallon, \$0.08 per kWH, and \$0.009 per scf, respectively. Compressed air costs have been included with the electricity usage.

Packaging of the product was assumed to be by bulk truck or railcar.

Labor was based on three operators per shift at the 5,000 and 50,000 tpy rates. These operators would also perform quality control and product packaging. Four operators per shift are required at the 500,000 tpy rate. Operator yearly salary was estimated at \$60,000.

For the 500,000 tpy rate, quality control and product packaging would require two operators per shift. Operator yearly salary was estimated at \$50,000.

Maintenance was based on one mechanic full time at the 5,000 tpy rate, two mechanics full time at the 50,000 tpy rate, and three mechanics full time at the 500,000 tpy rate. Mechanic yearly salary was estimated at \$40,000.

Depreciation was based on an 11 year straight line rate for chemical plants.

Table 11 Operating Cost

Base Case Formulation

	Units	Usage, units/ton of Product	Cost, \$/unit	Cost, \$/ton of <u>Product</u>
Limestone	ton	0.797	10.00	7.97
Clay	ton	0.051	90.00	4.59
Binder	ton	0.090	72.00	6.48
Water	gal	69.6	0.0017	0.12
Electricity	кwн	93.4	0.08	7.47
Labor	yr		360,000	72.00
Maintenance	yr		40,000	8.00
Depreciation	yr		226,900	45.38
TOTAL OPERATING C	OST FOR	5,000 TPY P	RODUCTION	\$152.01/ton
Limestone	ton	0.797	10.00	7.97
Clay	ton	0.051	90.00	4.59
Binder	ton	0.090	72.00	6.48
Water	gal	52.1	0.0017	0.09
Electricity	кwн	47.7	0.08	3.82
Labor	yr		360,000	7.20
Maintenance	ŷr		80,000	1.60
Depreciation	yr		398,400	7.97
TOTAL OPERATING C	OST FOR	50,000 TPY	PRODUCTION	\$39.72/ton
		-		
Limestone	ton	0.797	10.00	7.97
Clay	ton	0.051	90.00	4.59
Binder	ton	0.090	72.00	6.48
Water	gal	46.5	0.0017	0.08
Electricity	kWH	42.5	0.08	3.40
Labor	yr		480,000	0.96
Quality Control	ÿr		200,000	0.40
Maintenance	ÿr		120,000	0.24
Depreciation	ÿr		1,389,600	2.78

TOTAL OPERATING COST FOR 500,000 TPY PRODUCTION \$26.90/ton

Table 12 Operating Cost

Lower Limit Formulation

Limestone Clay Binder Water Electricity Labor Quality Control	<u>Units</u> ton ton gal kWH yr yr	Usage, units/ton of Product 0.046 0 44.8 90.4	Cost, \$/unit 10.00 59.50 0.00 0.0017 0.08 360,000 40,000	Cost, \$/ton of <u>Product</u> 8.90 2.74 0.00 0.08 7.23 72.00 8.00
Depreciation	yr	5.000 TPY PR	194,800	38.96 \$137.83/ton
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Limestone Clay Binder Water Electricity	ton ton gal kWH	0.890 0.046 0 44.8 49.0	10.00 59.50 0.00 0.0017 0.08	8.90 2.74 0.00 0.08 3.92
Labor Maintenance Depreciation	yr yr yr		360,000 80,000 333,900	7.20 1.60 6.68
TOTAL OPERATING C	OST FOR	50,000 TPY F	RODUCTION	\$31.12/ton
Limestone Clay Binder Water Electricity	ton ton gal kWH	0.890 0.046 0 44.8 45.2	10.00 59.50 0.00 0.0017 0.08	8.90 2.74 0.00 0.08 3.62
Labor Quality Control Maintenance Depreciation	yr yr yr yr	:	480,000 200,000 120,000 1,117,400	0.96 0.40 0.24 2.23

TOTAL OPERATING COST FOR 500,000 TPY PRODUCTION \$19.17/ton

Table 13 Operating Cost

Upper Limit Formulation

Limestone Clay Binder Water Electricity Natural Gas	Units ton ton gal kWH scf	Usage, units/ton of Product 1.013 0.062 0.153 25.7 125.3 886.4	Cost, <u>\$/unit</u> 10.00 116.00 250.00 0.0017 0.08 0.009	Cost, \$/ton of Product 10.13 7.19 38.25 0.04 10.02 7.98
Labor Maintenance Depreciation	yr yr yr		360,000 40,000 233,500	72.00 8.00 46.70
TOTAL OPERATING CO	ST FOR	5,000 TPY PR	ODUCTION	\$200.31/ton
Limestone Clay Binder Water Electricity Natural Gas Labor Maintenance Depreciation	ton ton gal kWH scf yr yr yr yr yr	1.013 0.062 0.153 25.7 66.6 886.4	10.00 116.00 250.00 0.0017 0.08 0.009 360,000 80,000 419,000	10.13 7.19 38.25 0.04 5.33 7.98 7.20 1.60 8.38 \$86.10/ton
TOTAL OPERATING C	OST FOR	50,000 TPY 1	PRODUCTION	588.10/ CON
Limestone Clay Binder Water Electricity Natural Gas	ton ton gal kWH scf	1.013 0.062 0.153 25.7 49.5 886.4	10.00 116.00 250.00 0.0017 0.08 0.009	10.13 7.19 38.25 0.04 3.96 7.98
Labor Quality Control Maintenance Depreciation	yr yr yr yr		480,000 200,000 120,000 1,388,000	0.96 0.40 0.24 2.78

TOTAL OPERATING COST FOR 500,000 TPY PRODUCTION \$71.93/ton



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