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Characterization and Optimization of Sorbents Utilized for Emission Control During Coal Gasification

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Abstract

To overcome the shortage of components required for high temperature operation required by current IGCC and PFBC systems, researchers recently have decided that the power systems can be optimized within an operation temperature range of 343 to 538 degree C. The lower operation temperature range for new IGCC and PFBC system will facilitate its commercial applications in the near future.

The findings of this research work support the use of iron oxides as an efficient, disposable hot gas desulfurization sorbent candidate to meet the temperature range of 343 to 538 degree C to further optimize its application for hot gas desulfurization. The low cost of iron oxides, the availability of standard off shelf components for hot gas cleanup system design, the significant capital savings and the simplification for hot gas cleanup system fabrication, operation and maintenance of the use of iron oxides for hot gas desulfurization justify its use for the optimization of hot gas cleanup.

Advanced integrated gasification combined cycle and pressurized fluidized bed combustion power system requires both hot gas desulfurization and particulate filtration to improve system thermal efficiency and overall performance. To meet the environmental emission requirements and improve thermal efficiency, desulfurization sorbent is mainly utilized to cleanup the hydrogen sulfide from the hot gas stream to protect downstream heat exchanger and gas turbine components from being corroded. Several metal oxides were developed as sorbent candidates for hot gas desulfurization process by different research institutes.

To evaluate the design and performance of desulfurization sorbents, different long term testing programs were conducted. Zinc oxide, zinc ferrite and zinc titanate had been tested in fixed bed and fluidized bed reactor. Zinc titanate sorbent was elected as the most promising sorbent candidate as it can efficiently reduce hydrogen sulfide to a low ppm level with an outstanding attrition resistance. Zinc oxide and zinc ferrite sorbents were disqualified mainly because the zinc vaporization and their physical degradation under temperature more than 500 degree C reacted in a mild reducing coal gas. However, the high capital investment, required for desulfurization and regeneration cycle, as well as the high cost of zinc titanate sorbent and its weight loss for long term use still prevented it from economical commercial application.

On the contrary, the proposed use of iron oxide as a disposable metal oxide sorbent will alleviate the constraints imposed on a regenerable sorbent such as the degradation of its sulfur capacity and physical attrition required for long term use.

Disposable metal oxides can be injected into coal combustion or Gasification process in the upstream location to efficiently absorb corrosive hydrogen sulfide with proper selection of space velocity and residence time. The very low cost of waste iron oxides, the reduction of the capital investment on sorbent regeneration system and the low operation cost appears attractive to use waste iron oxides as an alternative to replace expensive, regenerable sorbent candidates.

A parametric study was performed to characterize the controlling parameters dominating the absorption process of hydrogen sulfide by waste iron oxide as a sorbent alternative with in a stringent environment with the use of simulated KRW reducing gas. The major parameters studied for hot gas desulfurization with the use of waste iron oxide; mixed in coal ash and reacted with hot sulfurized gas; in hot gas stream include 1) dust cake permeability during heavy

dust loading, 2) feasibility of dust cake removal with current back pulse cleaning technology, 3) the reaction temperature, 4) the space velocity of the gas stream. Desulfurization test data will be analyzed for the optimization of hot gas desulfurization operation with the use of waste iron oxides.

To ensure waste iron oxide is an adequate disposable sorbent alternative, the success of particulate filtration and the removal of the extra dust loading needs to be confirmed besides the capability of chemical capture of hydrogen sulfide by iron oxides. To evaluate the filtration performance on mixtures of coal ash and iron oxides, extra research work was conducted on the characterization on filtration and back pulse cleaning performance on dust cake, made of coal ash and iron oxide with different ratios required by different space velocities. The encouraging results of the test data concluded that current back pulse dust cake cleaning technology is capable to dislodge dust cake developed by various mixtures of coal ash and iron oxides. The use of iron oxides provided benefits of maintaining a low differential pressure across dust cake and helping the removal of dust cakes during filtration testing. Filtration test results strongly supported the use of waste iron oxides, because iron oxides will aid particulate filtration performance.

The results of studies on hot gas desulfurization and particulate filtration provide insights into key issues of using iron oxides as a hot gas desulfurization sorbent. The test data answered questions concerning the variations of dust cake permeability of various mixtures of coal ash and iron oxide ratios, efficiency of back pulse dust cake cleaning, design of space velocity optimization for hot gas desulfurization, design of operation temperature range, and the plenum of hot gas cleaning system design to optimize reaction residence time between iron oxide and hot hydrogen sulfide gas stream.

Based on the parametric testing performed on hot gas desulfurization and particulate filtration, the test results of this study indicate that the simultaneous operation of hot gas desulfurization and particulate filtration is feasible. The significant savings of capital investment, system operation and maintenance justify the use of iron oxides as an excellent candidate for hot gas cleanup.

The test results obtained from this study will serve as a guideline for future system design optimization on hot gas desulfurization operation with the use of the economical disposable iron oxide material, especially for the study of the temperature effect within the feasible operation temperature range of 343 to 538 degree C for IGCC and PFBC systems.

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Executive Summary

The development of hot gas desulfurization sorbents is one of the most critical issue for both IGCC and PFBC power systems. Zinc oxide, zinc ferrite and zinc titanate were the leading mixed metal oxides for hot gas desulfurization applications. These sorbents have high sulfur capacities and can remove hydrogen sulfide from coal gasifier gas down to less than 20 ppm. They can also be regenerated with inert-diluted air for multicycle operation.

Zinc oxide suffered from zinc vaporization and severe physical degradation problems under high temperature and mild reducing coal gas. Zinc ferrite sorbents prepared by granulation exhibited superior attrition resistance and long term chemical reactivity performance, but it is limited to a maximum temperature of about 550 degree C. Beyond that temperature, it tends to lose its mechanical strength due to excessive reduction and iron carbide formation.

Zinc titanate sorbents has shown higher durability than zinc ferrite and it can also withstand highly reducing fuel gas. In zinc titanate sorbent, zinc oxide is the only reactant agent, titanium oxide only help stabilize the sorbent performance. However, the high cost of zinc titanate sorbent and the capital investment of regeneration process makes the low cost, disposable iron oxides more attractive as hot gas desulfurization sorbent alternative.

Besides the economical benefit, the use of iron oxides material as a disposable sorbent alternative will increase the dust loading significantly. To ensure the normal operation of the particulate filtration system, the permeability of the dust cake made of coal ash and iron oxide mixture shall be remained unchanged or the same level as no iron oxides were added to the gas stream. The high dust loading of iron oxide additive also requires a higher frequency of dust cake dislodging. Parametric testing on dust cake removal is mandatory to study the feasibility of the use of waste iron oxide as a sorbent alternative to replace expensive sorbent candidates developed in last decade.

To overcome the shortage of components required for 1200 to 1600 degree F high temperature operation required by previous IGCC and PFBC systems, researchers recently have decided that the power systems can be optimized within an operation temperature range of 343 to 538 degree C.

The subject research was dedicated on parametric studies on both hot gas desulfurization and the aid of particulate removal. To characterize major parameters affecting hot gas cleanup, hot gas desulfurization and particulate filtration were independently evaluated.

For particulate filtration study, a very heavy dust loading of coal ash and iron oxide mixture was utilized to develop dust cake along the external surface of the candle filter for mixtures with coal ash to iron oxide ratio ranged from 1:0, 1:1, 1:2 and 1:3 during filtration process. According to the test results, each dust cake developed with different coal ash to iron oxide ratio can be successfully dislodged with the use of back pulse cleaning technique. The filtration results indicate that heavy mixed dust loading exceeding an iron oxide to coal ash ratio more than 3 can be successfully dislodged because iron oxides can aid the back pulse cleaning and it can help maintain a low differential pressure across the filtration system.

Parametric testing were performed to characterize hydrogen sulfide reaction with mixtures of coal ash and iron oxide with different ratios in a KRW reducing gas environment. Test data were converted to space velocity as a convenient and useful guideline for desulfurization system design.

The advantage of the use of iron oxides with various ratio to coal ash facilitate the design of space velocity and gas stream plenum design. For desulfurization process optimization it is flexible to adjust operation temperature and the chemical reaction rate between hydrogen sulfide and iron oxides. The benefit of using iron oxides as a disposable sorbent is the feasibility to load iron oxides in the upstream of coal processing to provide a longer residence time for iron oxides to react with hydrogen sulfide than the use of regenarable sorbents in either a fixed bed or a fluidized bed. Therefore, space velocity can be optimized as required with the use of iron oxides to make it more efficient for hot gas desulfurization.

For hot gas desulfurization testing, simulated KRW gas mixture was supplied from a pre-mixed gas bottle supplied from Scott Gas Supply Company. Stainless steel gas regulator was installed on the corrosive and flammable gas bottle. A mass flow controller with flow rate display were connected from the gas bottle to a mixing manifold. A water injection pump was also connected to the mixing manifold to wet the gas stream prior its entry to carry coal ash and iron oxide mixture into the gas stream preheater temperature chamber. After preheating, the gas stream flows into a 50 to 100 feet long 1/4-inch coil tubing installed in the 1000 degree F temperature oven for desulfurization reaction. As the hot gas exited from the reaction temperature oven, the hot gas stream was designed to be cooled by a heat exchanger before its entry to the post gas stream treatment chamber at low temperature. The post treated gas stream then goes into the filtration system.

After the testing of hot gas desulfurization at 1000 degree F, the integration testing of hot gas desulfurization and particulate was set up for operation. The integration testing of hot gas desulfurization and particulate filtration was performed for few times. However, the difficulty experienced from carrying the mixture of coal ash and iron oxide through a 1/4-inch O.D. tubing by sulfur contained gas stream prevented the pursue of the long term operation of continuous desulfurization and particulate filtration testing. Therefore, more testing were concentrated on hot gas desulfurization testing with a controlled test plan to characterize the reaction process between hydrogen sulfide and iron oxide in coal ash mixtures and the KRW reducing gas stream.

To further understand the temperature effect on the reaction rate between iron oxide and hydrogen sulfide, extra hydrogen sulfide absorption testing were performed at temperature levels between 343 to 538 degree C to optimize the selection of operation temperature range for new IGCC and PFBC system.

To evaluate hot gas desulfurization testing at different space velocities, the reaction time was controlled and repeated for each temperature during testing. According to the test results of hot gas desulfurization, the reaction time available and the space velocity of iron oxides doping in a KRW reducing gas play important roles for hot gas desulfurization. Iron oxide can absorb hydrogen sulfide efficiently if sufficient iron oxide is provided with sufficient reaction time in the gas stream. High temperature will improve the reaction rate between iron oxide and hydrogen sulfide. Heavy doping of iron oxides will improve the efficiency of hydrogen sulfide absorption if cost permitting.

After post test analysis on the test results of hot gas desulfurization and particulate filtration performance, it concludes in this research program that the use of waste iron oxide as a disposable sorbent alternative can be optimized in desulfurization system design. The savings in sorbent spent, capital investment reduction, operation and maintenance simplification make it very attractive to replace other expensive regeneration required sorbents. Based on the test data, it appears that the use of iron oxides for hot gas desulfurization is especially efficient within the operation temperature range of 343 to 538 degree C.

1.0 INTRODUCTION

1.1 Contract Objectives

After performing literature survey and parametric study on hot gas cleanup, a low capital investment and low operation cost oriented desulfurization system, to be realized with the use of disposable sorbent, was proposed as an optimized system for hot gas cleanup application. To demonstrate the feasibility of this innovative hot gas cleanup proposal, the subject research was concentrated on the study of the most economical sorbent alternative, waste iron oxide, for hot gas desulfurization.

To fulfill the requirements of sorbent optimization, the objectives of this work include the research work on 1) hot gas desulfurization performance evaluation with the use of iron oxides as a disposable sorbent alternative to replace other expensive sorbents developed in the last decade and 2) feasibility study on particulate filtration and dust cake removal with the extra dust loading of iron oxides into gas stream for desulfurization purpose. Compared with current regenerable hot gas cleanup system, the simplification of the innovative desulfurization system design, the low cost of waste iron oxide supply than other expensive sorbent candidates, and off shelf standard components for hot gas cleanup system, operating between 343 to 548 degree C, provides significant room for the design optimization on hot gas cleanup operation.

The scope of the research work include the following areas: 1) the characterization of hot gas desulfurization properties of iron oxides utilized for hot gas particulate cleanup on the effect of space velocity, residence time, reaction temperature on hot gas cleanup, 2) heavy dust loading filtration and dust cake removal on various mixtures of coal ash and iron oxides and 3) perform a cost saving analysis on the use of iron oxides as a disposable sorbent alternative than the use of regenerable sorbent for hot gas desulfurization.

1.2 Background

Electricity demand has been closely tied to economic growth. The need for electrical power is estimated to double for every twenty years. Advanced energy conversion systems, including the integrated gasification combined cycle (IGCC) and pressurized fluidized bed combustion (PFBC) are attractive for power generation, because it can improve the thermal efficiency of electricity generation with low capital and operating costs. However, IGCC and PFBC power system requires both hot gas desulfurization and particulate filtration to improve power system performance and to protect high temperature gas turbine system, heat exchange components from corrosion and damages caused by gasified particulate and hydrogen sulfide. Hot gas cleanup is indispensable to meet the clean air environmental protection measures. Hot gas cleanup is one of the most critical technologies required to ensure the success of low-cost methods of electric power generation.

However, the current IGCC and PFBC power systems were designed with a very high operating temperature, ranged from 537 to 871 degree C (1,000 to 1,600 degree F), to improve its thermal efficiency. The elevated system operating temperature created a barrier to use off shelf valves, fittings, heat exchanger equipment and related parts to have hot gas cleanup system built. The lack of very high temperature equipment demands significant time to have it developed, and the operating and maintenance expenses will be higher than those of the lower temperature operating system.

To overcome the shortage of components required for high temperature operation required by current IGCC and PFBC systems, researchers recently have decided that the power systems can still be optimized within an operation temperature range of 343 to 538 degree C (667 to 1,000 degree C). The lower operation temperature range for new IGCC and PFBC system will definitely facilitate its commercial applications in the near future with big savings.

The proposed application is based upon the principle of the dual use of waste iron oxide as a disposable sorbent and the aid additives in hot dusty gas stream to optimize hot gas cleanup. This innovative operation could help desulfurization process, maintaining high dust cake permeability and enhanced particle removal efficiency at elevated temperatures.

However, the current filtration test setup at PV A&M University is limited for cold flow study, the part of filtration work was performed at room temperature only. High temperature filtration research work can be applied in the near future at PV A&MU. Even though the filtration work was concentrated at cold flow study, but the encouraging results derived from this research work could be served as a guideline for hot gas cleanup study in the future.

Current hot gas desulfurization research has demonstrated a few regenerable sorbents are good candidates for desulfurization purpose. ZnO was found to be most suitable as it could reduce hydrogen sulfide in coal gas to a level of a few ppm depending on the temperature and steam content of coal gas. However under a mild reducing environment, a significant decrease in crush strength and bulk density of ZnO pellets was reported. The deterioration of ZnO sorbent structure was derived from reduction of zinc oxide to zinc followed by vaporization of zinc. This limit set a threshold for the use of ZnO as sorbent for hot gas desulfurization at temperature lower than 500 degree C.

Iron oxide was investigated as a hot gas desulfurization sorbent since 1970s, and it has a high sulfur capacity and possesses high reactivity. However, iron oxide sorbent was not recommended for hot gas desulfurization application in U.S. due to the excessive reduction and iron carbide formation under highly reducing conditions. In Japan, iron oxide was once tested as a hot gas desulfurization sorbent material using raw iron ore. This research work will perform further study on the use of iron oxides as a disposable sorbent candidate, because the reduction of iron oxide and its physical attrition are not issues any more if it is treated as a disposable sorbent candidate. To illustrate the feasibility of using iron oxide as a disposable sorbent, hot gas desulfurization testing was performed in a relative strong reducing KRW gas in this study.

Zinc ferrite, an equimolar mixture of zinc oxide and iron oxide calcined at 800 to 850 degree C, was tested to remove hydrogen sulfide to a level less than 20 parts per million by volume (ppmv) over multiple desulfurization and regeneration cycles in a fixed bed reactor. Zinc ferrite also experienced excessive sorbent loss during desulfurization cycle even under moderately reducing coal gas.

Researchers then developed zinc titanate sorbent to resolve thermal stable and attrition difficulties experienced by other sorbent candidates. In zinc titanate sorbent, only zinc oxide is the reactive component of the sorbent, while titanium oxide provided stability to the sorbent by preventing zinc vaporization. But the high cost and problems of physical degradation and sintering at high temperature prevents it from commercial application for multiple desulfurization and regeneration cycles as planned.

According to the findings of the literature survey, it is imperative that the power systems need be optimized within an operation temperature range of 343 to 538 degree C. The release of high operational temperature requirement makes it beneficial to use current standard equipment from the shelf to minimize the difficulty in realizing the application of high thermal efficiency power systems with less cost and ease. The sulfur capacity of iron oxide, operating in the temperature range of 343 to 548 degree C, needs to be verified to justify the innovative use of low cost waste metal oxides as a sorbent alternative for an optimized hot gas desulfurization and hot particulate removal system for future applications. Therefore, the subject research work performed on hot gas desulfurization study was concentrated within the temperature range of 343 - 538 degree C (650 - 1000 degree F).

To characterize temperature effect on hot gas desulfurization for waste iron oxides, desulfurization testing had been conducted at four temperatures, 625, 750, 875 and 1,000 degree F. The relief of physical attrition and the reduction imposed on disposable sorbent provides excellent opportunity for iron oxides operating in strong reducing gas, in which iron oxides was previously prevented from being used as a regenerable sorbent due to reducing issue.

Besides hot gas desulfurization, it is important to evaluate if iron oxide can help maintain a high permeability throughout the dust cake for particulate filtration and whether it can be used as an aid additive for dust cake removal during back pulse cleaning. The benefits gained on assisting dust cake removal and maintaining high dust permeability in dust cake would ensure that the add of iron oxides into coal ash will not have filters plugged. Successful particulate filtration for the increase of dust loading due to continuous feeding of iron oxide is mandatory hot gas cleanup. Therefore, parametric testing on particulate filtration was first performed to ensure the particulate cleaning can be managed by current filtration system on various mixtures of coal ash and iron oxide.

During particulate filtration investigation, the differential pressure across within the filter chamber and the filtrated gas stream plenum was constantly measured; because it can be used as a reference on judging if iron oxide can help maintain a high permeability through the dust cake, developed by mixed coal ash and iron oxide. Back pulse cleaning technology was evaluated on its efficiency for dust cake removal as iron oxide was added into gas stream.

Based on the test data of particulate cleaning, it appears that the current back pulse cleaning technology is capable to satisfy the filtration and dust cake removal requirements even for heavy dust loading via a 3:1 ratio of iron oxide to coal ash. The high iron oxide to coal ash ratio assures that a low space velocity can be utilized for hot gas desulfurization, if required.

To demonstrate the feasibility of using iron oxides in a reducing environment, iron oxide hot gas desulfurization research work had been conducted in a severe, simulated KRW reducing gas stream with a reducing power of 2.58. After hot gas desulfurization testing, pictures were taken on mixture of coal ash to show the color change of mixture before and after the reaction testing to visualize desulfurization reaction.

To simulate a continuous operation of hot gas desulfurization and particulate cleaning, an integrated operation system for desulfurization and particulate filtration setup was prepared. As soon as the independent hot gas desulfurization testing was conducted, the integrated hot gas desulfurization and particulate filtration testing was performed.

After a few iterations, however, it was decided that it was very difficult to have wet gas stream carrying particulate of mixed coal ash and waste iron oxides through the 1/4-inch O.D., 0.150-inch I.D. stainless tubing to have the integration testing conducted. Many efforts were provided to feed the particulate through the stainless steel tubing, but it did not succeed. Significant efforts were exercised to feed dry particulate with dry gas stream into preheated stainless tubing with positive upstream pressure and downstream vacuum pull at either end of a 50 feet long coil tubing, but particulate still failed to pass through the tubing.

To characterize the mechanism of hot gas desulfurization of iron oxide, parametric hot gas desulfurization testing were performed to characterize temperature, space velocity and residence time for desulfurization optimization design.

A cost saving analysis was performed on the use of iron oxides as a disposable sorbent vs the use of regenerable sorbent for hot gas desulfurization. The cost analysis was based on a small scale bench test setup, but the savings on a commercial scale application will be much more outstanding due to the savings in big system fabrication, more components utilized, and the lower operation and maintenance expenses needed.

2.0 RESULTS AND DISCUSSION

2.1 Characterization of filtration process on mixtures of iron oxide and coal ash

2.1.1 Summary of particulate filtration process

To study particulate filtration phenomena, a particulate filtration test chamber was built to characterize particulate filtration process. To facilitate the testing and observation of extra particulate loading of iron oxides into coal ash and the process of particulate deposition on candle filter; a cold flow research on particulate filtration was investigated within a transparent filtration chamber. Test data, required to characterize the process of filtration and dust cake removal of iron oxide and coal ash mixtures, were acquired through a simulated cold flow study.

To facilitate the measurement of the variation of the pressure field within the filter chamber, small size and fast response pressure silicon micro-machined pressure sensors were utilized. An advanced data acquisition programming was developed with the use of the data acquisition hardware, procured from National Instruments, to interface with various instruments via RS 232, RS 485 and IEEE 488 to perform data acquisition task.

A hand held fast response pressure calibrator was also utilized to measure the differential pressure across within the filter chamber and the filtrated gas stream. The variation of differential pressure vs different loading of iron oxide and coal ash is served as an indication of the change of the permeability throughout the dust cake of various mixtures during filtration process. According to filtration test data, it appeared that iron oxides can help the dust cake maintain a high permeability even for a very heavy dust loading during the filtration process. It was also noted that iron oxides can aid the removal of dust cake with the use of back pulse cleaning technology. The success of filtration operation for heavy dust loadings assures that the use of waste iron oxide material for sorbent alternative is promising, and the innovative hot gas cleaning design can be optimized with an efficient back pulse cleaning system in the near future.

2.1.2 Discussion on particulate filtration testing

The ceramic filter used for particulate filtration testing was supplied by IF&P, with the dimensions of 100.00 cm long, 3.81 cm I.D. and an O.D. of 6.35 cm. The first study was filter permeability variations on the dust cake of the mixtures of iron oxide and coal ash. Each mixture has different percentage of iron oxide vs coal ash. Filter permeability was also measured before and after every filtration test cycle with the use of back pulse cleaning to evaluate the efficiency and repeatability of back pulse cleaning technique.

Literature survey, selection of filter samples and filter characterization test plan were conducted prior to the design of the filtration chamber. Extensive literature survey was performed on particulate filtration research work conducted by academic and industrial researchers. A transparent filter chamber was designed and built for heavy dust loaded particulate filtration study. Significant effort was provided to develop an automatic data acquisition system via the use of LabVIEW graphical programming procured from National Instruments. The test software and instrumentation interfacing programming was installed in a personal computer (PC) controlled by Window. The PC based data acquisition system helped collect pressure sensor outputs automatically and was also interfaced with Excel spreadsheet for test data post processing.

To characterize particulate filtration process of iron oxide and coal ash mixture, iron oxides was mixed with coal ash at 0:1,1:1, 2:1, and 3:1 ratios prior to its injection into the filtration chamber. The wide range ratio of iron oxide to coal ash mixture provides a significant room to adjust the space velocity for hot gas desulfurization. Dust cake developed by coal ash alone and mixtures of coal ash and iron oxides were dislodged with the use of back pulse cleaning technology.

The differential pressure (Delta P), measured across from within the filtration chamber and the filtrated gas plenum, was normally measured as the lump-sum filter flow resistance. The measured Delta P is an averaged value of filter resistance to the filtrated gas stream. Delta P is very informative on identifying the plugged condition of the filter via the increase of its value as dust cake deposits on filter surface during the filtration process. Pressure sensors were utilized with the data acquisition system to investigate the pressure field within the filtration chamber as the gas stream flew through the filtration system. Silicon pressure transducers, with 1.0 inch O.D. and 1/2-20 threaded pressure port, were mounted along one side of the filtration chamber, equally spaced along the axis of the chamber, to monitor vessel pressure during filtration process.

Based on test data acquired from back pulse cleaning testing, the reduction of filter permeability did make the dust dislodging less efficient than the use of a high permeable filter. Less porous filter was difficult to be cleaned than that of a unplugged filter with the back pulse even though the cleaning setup remained unchanged as that for unused filter. The reduction of back pulse cleaning efficiency enhanced the dust patch deposition on the less porous filter surface areas. As particulate filtration operation proceeds, the dust patches left on the filter surface were easier to grow, and ash bridging could be developed if environment for sintering process is created in the filter vessel. The build up of dust patches could reduce the efficiency of particulate filtration and the back pulse cleaning more difficult. These vicious circulation of particulate cleaning process converted the filtration process difficult to control, and system failure might happen as the filtration process proceeds.

After research on particulate filtration, the test results acquired indicated that the success of the particulate filtration and dust cake removal operation for heavy dust loading confirmed that iron oxides can be utilized as a disposable hot gas desulfurization sorbent. Particulate filtration can be well managed even when the rate of dust loading increased to three times of normal coal ash loading as shown in a dust cake removal for a mixture of 3:1 iron oxide to coal ash ratio. Success of particulate cleanup for mixtures with high ratio of iron oxide to coal ash established a solid foundation for hot gas desulfurization application.

2.1.3 Description of particulate filtration test facility

The filtration test facility consists of a transparent filter test chamber, an automatic data acquisition system, a set of micro-machined silicon pressure sensors, a set of pressure source supply, a back pulse cleaning pressure reservoir and instruments for pressure control and back pulse dislodging.

To facilitate the testing, this test chamber vessel was made from a transparent plastic pipe with a 15.24 cm I.D. (6.00 inches), 198.12 cm (78 inches) long and 0.71 cm (0.28 inches) wall thickness. This filtration vessel passed a 10.2 bars (150.0 psig) static pressure testing, compatible with Tidd APF pressure level, prior to particulate filtration testing. Ten 1/2 - 20 threaded holes are evenly spaced along the chamber axis to mount fast response pressure transducers and also serve as the provisions for Delta P sensor port installation. The sensors were interfaced with the data acquisition system and an advanced pressure calibrator during testing.

The output of the pressure sensors, acquired by the PC based data acquisition system were post processed by a program developed at PV A&M University. Data acquired by the advanced pressure calibrator were displayed on its LCD screen. The pressure calibrator has two ports for two different sensing modules, and its output display can be configured with different units for ease of operation and data management. The pressure sensor outputs can be monitored real time with the use of the advanced pressure calibrator; therefore, the pressure calibrator was utilized when the real time pressure reading was required.

A filter sealing plug base of 15.33 cm (6.03 inches) diameter by 8.90 cm (3.50 inches) thick and a pressure inlet plug with the same exterior dimensions were installed: one at the top and one at the bottom end of the test chamber respectively. All the machined parts of the test chamber were fabricated with a tight tolerance control of +/- 0.002 inches to ensure air tight sealing was secured throughout the filtration testing.

The ceramic candle filter was installed in a multiple pressure sealed assembly to ensure the hermetic sealing was held between the machined parts and the filter chamber, between the filter and the machined parts and between the filter and the filtrated gas stream plenum assembly. Silicone sealing grease was applied between all the machined parts and the interfaced filter sealing areas to enhance the hermeticity sealing and the capture the unfiltered particulate, if any, throughout the filtration testing. This design assembly was filtration tested with maximum testing pressure to perform leakage proof testing. Particulate filtration test results confirmed that no particulate could be carried by the filtrated gas stream outside the filter as long as the sealing components were properly installed properly.

The candle filter was located at the center of the pressure sealing assembly. The alignment of the filter axis and that of the filter testing chamber converted the test system into a configuration with cylindrical symmetry. To reduce shock impact and mechanical stress on the filter flange during filter installation process and particulate filtration testing, specially designed elastomer pads were installed within and between the filter and the sealing plug assembly to absorb various mechanical load and impact load during testing.

Fast response solenoid valves, with a quick close and opening response time less than 700 milliseconds, were utilized for dust cake dislodging testing. A high speed pressure jet pulse was released from within a back pulse pressure reservoir into the filter chamber through filter internal cavity as soon as a normally closed fast response solenoid valve opened. The very high speed jet pulse penetrating through the filter wall dislodged dust cake from filter surface. The schematic of the test setup is shown in Figure A.

2.1.4 Parametric study on particulate filtration process

2.1.4.1 Description of back pulse cleaning setup

According to METC test report of dust cake filtration (DOE/METC-91/4105), the blow-back system reservoir tank provided a volume of 2.3 cubic feet, with the pressure regulated to 225 psig from a 600 psig nitrogen source for the purge of a 6 inches I.D., and 70 inches long single filter test chamber. The METC back pulse cleaning setup was equipped with a solenoid connected to the reservoir tank by 59 inches of 0.5-inch stainless steel tubing with a wall thickness of 0.035 inches. And the final connection from inside the filter vessel to a 0.375-inch tube on top of the hold down flange.

At PV A&MU, the filtration chamber was fabricated with the use of a six (6) inches I.D. transparent plastic pipe with a 72-inch overall length. The filter chamber was equipped with a 60 inches (5-foot) long cavity, and a single filter was installed at the center of the chamber. The filter chamber at PV A&MU has the same configuration as the one built at METC. The close match of the filter chamber between PV A&MU and METC eliminated issue on difference of test setup for the investigation of particulate cleanup.

Back pulse cleaning design depends on the discharge of a high momentum gas jet from a pressure reservoir into the filter cavity. The momentum of the jet is transformed into a pressure increase inside the filter cavity. Based on literature research on filtration testing and the filtration test data acquired at PV A&MU, it appeared that the energy transformation from pressure to high momentum of the cleaning jet can be acquired either with a combination of either a large pipe diameter and a low pressure or with a small pipe diameter and high pulse pressure. The pulse jet generated from either design configuration was powerful enough to dislodge the dust cake deposited on filter surface. The amount of the momentum conversion within the filter cavity depends on the design configuration of the back pulse cleaning setup. Back pulse cleaning system design shall be optimized to ensure the success of filtration process, especially for heavy dust loading.

In the parametric study of particulate filtration, a 1.2-cubic foot gas reservoir was designed for the pulse cleaning testing. This gas mass needed to be fed into the filter chamber instantaneously with the use of a fast response normally closed solenoid valve, with a response time of 700 milli-seconds or less, to provide the high mass flow rate for dust cake dislodging work.

To perform the pulse cleaning study economically, a large pulse stream plenum and a large I.D. blow-tube combination was selected to use a lower pressure gas reservoir for cost saving on dust cake dislodging. To further minimize the frictional loss for the gas stream, only one normally closed solenoid valve was installed between the gas reservoir and the blow-tube.

According to pulse testing, it appeared that the strength of the pressure level of the pulse pressure reservoir needs to be increased sharply as the I.D. of the blow tube decreased to perform an efficient dust cake dislodging task. The frictional loss of gas jet stream experienced as it traveled along the back pulse plenum; jet pressure losses through various area changes along the pulse plenum system, its valves and the energy loss due to the reduction of blow-tube cross section area. High energy loss were responsible for the requirement of a high pressure of gas reservoir. A healthy back pulse cleaning setup could perform successful dust dislodging task repeatedly safely with ease.

Based on the test results acquired, it was then concluded that 1) back pulse cleaning is an efficient technique for dust cake dislodging application, 2) the gas stream plenum shall be designed with minimum energy loss as the jet gas stream travels along it.

2.1.4.2 Study on particulate effect during filtration process

To evaluate the filtration performance on various mixtures of iron oxide and coal ash, the differential pressure values (Delta P) across the cleaned filter and the filter with dust cake buildup were measured throughout the filtration process. The Delta P value measured from a cleaned filter is the total resistance induced by a clean filter and the filtrated flow plenum system. The difference of Delta P measured between a dust cake coated filter and a clean filter is the gas flow resistance through the dust cake. With the measurement of Delta P throughout the filtration testing, the performance of the filtration system can be characterized.

To gain insights of particulate effect on filtration process, different mixtures of particulate were evaluated in this study. Observation of dust reentrainment and measurement of dust cake thickness were also conducted in the transparent cold flow filtration chamber.

Dust cake made of waste iron oxide and coal ash, originating from the Curtis-Wright PFBC facility, were evaluated first. Coal ash did not have a strong affinity to moisture, which makes it easy to load and retrieve it from the filter chamber for filtration testing. Even though coal ash is heavier than iron oxide, a gas flow with heavy coal ash loading can be generated with a compressed air flow of 2.0 scfm flow rate. Higher mass flow rate, 6.0 scfm, was strong enough to agitate the coal ash to every where in the 6.0-inch I.D. filter chamber.

Different flow rate, with a ratio of 3, were applied on various mixtures for particulate cleanup testing. Higher flow rate created a thicker layer of dust cake on filter surface than a lower flow rate. The higher flow rate gas stream developed thicker dust cake faster than a lower flow rate, and the rate increase of dust cake build up for high flow rate was non-linear to the change of flow rate. Therefore, higher flow rate gas stream requires higher frequency of back pulse cleaning to keep Delta P in a manageable level.

Coal ash dust cake can be cleaned by back pulse cleaning without difficulty. However, iron oxide was very difficult to work with. The key problem of handling iron oxide was due to its strong affinity to moisture and the agglomeration of iron oxides into many large sized particulate.

These adhesive properties of iron oxides to every material made it very difficult to feed or retrieve during filtration testing because it plugged the feeding conduit easily. Wet iron oxide has a very strong adhesion force toward the materials it contacted, it can not be wiped off the contact surface even with brushes. This strong bonding force accelerates the agglomeration of iron oxides to coal ash particulate into large and heavy sized particles, which assists maintaining a high porous dust cake and aids the particulate falling off filter surface due to its heavy weight. The heavy weighted agglomeration of coal ash and iron oxide also minimized the reentrainment flow of particulate in the filter vessel.

Various mixtures of coal ash and iron oxide were utilized to buildup different kinds of dust cakes on candle filter. With the use of the same back pulse cleaning setup, every dust cake developed on filter surface had been successfully removed. After drying the particulate, dust cake dislodging task was easier than working with wet particulate. The lower output of Delta P values measured through different dust cakes indicated that the adding of iron oxides to coal ash could help maintain a lower Delta P value than that of coal ash cake without iron oxides additive during the filtration process as expected. The higher permeability of iron oxides loaded dust cake helped the filtration operation of dirty gas stream.

2.1.4.3 Procedures and test results of particulate filtration testing

Dust cake of coal ash, originating from the Curtis-Wright PFBC facility, and its mixture with iron oxide had been successfully removed from IF&P ceramic filter with the use of back pulse cleaning technology. Prior to hot gas desulfurization testing, ratio effect of iron oxide to coal ash of its mixtures on dust cake permeability was evaluated; and dust cake removal was performed at room ambient temperature.

Particulate filtration test results indicated that a specific threshold pulse pressure is required to clean the dust cake. Pulse pressure slightly above the threshold pressure seems strong enough to clean the dust cake over a short period of time. If the back pulse strength is too weak, the residual patch left on the filter will grow with ensuing particulate filtration process; and higher pressure will be needed to dislodge the dust cake for the increased pressure drop through the dust cake.

However, the use of a strong pulse pressure to start with, will help maintain a clean filter surface after pulse cleaning. To handle excess dust loading and investigation on the repeatability of dust cake cleaning, each dust cake was cleaned during the filtration testing. Measured Delta P was repeatable after cleaning for all kinds of dust cake dislodging, the test results confirmed that the dust cake of coal ash and mixtures of coal ash and iron oxides can be well cleaned to the initial condition prior to the filtration process started with the back pulse cleaning technique.

The test mixtures were prepared in a systematic manner to ensure that the output of Delta P and the efficiency of dust cake dislodging were procedures independent. Details of mixture preparation for iron oxides and coal ash are listed as follows.

The filtration testing on coal ash and its mixtures with iron oxide was performed with the following mixture ratio with a batch of 1,500 grams of sample material each. Each batch of 1,500 grams of coal ash or the mixture were carefully weighed with the use of an precision electronic scale.

(1) 100% of coal ash
(2) 2/3 of coal ash and 1/3 of iron oxide
(3) 1/2 of coal ash and 1/2 of iron oxide
(4) 1/3 of coal ash and 2/3 of iron oxide

Each mixture was sealed within a steel container and well mixed on two rollers of a mixing machine. All of the mixed sample materials were dehydrate within a metal tray heated by a hot plate. The mixtures were well stirred during dehydration process.

Each dehydrated sample was filled into the filtration testing chamber and a 3.5-inch thick dust bed was developed at the bottom of the chamber. Nitrogen and compressed air were used to develop a very high dust loading to have the dust cake deposited on filter surface. A 2 SCFM and 7 scfm mass flow rate were used to developed the dust cake. To protect the differential pressure sensor from being burst damaged by high static pressure and contaminated by purged particulate, the 7 CFPM mass flow rate was used to develop the dust cake and the 2 CFPM flow rate was used when the differential pressure was measured across the dust cake and the filter assembly.

The differential pressure was measured twice after every two minutes of 7 CFPM gas flow, and the dust cake was deposited on the filter surface after 5 to 6 filtration cycles. The dust cake was dislodged with back pulse cleaning technique after the dust cake was built on the filter or when the dust loading became very low.

The differential pressure variations across dust cake and filter assembly for coal ash and mixtures of coal ash and iron oxide with different ratio are shown in Figure 1, 2, 3, and 4. The overall differential pressure measurements for all of the dust cake materials is shown in Figure 5 and 6. The test data of the differential pressure measurements is shown in Data Sheet 1.

Based on the test data and the observation of filtration testing in the transparent filter test chamber, the following conclusions are derived.

(1) High permeability can be maintained in various dust cakes, because the output of the pressure differential measured for mixtures of coal ash and iron oxide are less than that of pure coal ash.

(2) Iron oxides and coal ash mixtures with high iron oxide ratio experienced less pressure differential (Delta P) across the dust cake and filter assembly.

(3) The lower values of Delta P for mixtures with iron oxides additive indicated that iron oxide can be used to maintain a high dust cake permeability during the filtration process, even a very high dust loading is required for hot desulfurization purpose.

(4) The more iron oxide has in the mixture, the heavier the agglomerated mixture particles will be. Because iron oxide has a very strong adhere bond to coal ash particulate, iron oxide loaded mixture would be heavier than that with less iron oxide in it.

(5) The heavier iron oxide mixture needs a larger mass flow rate to agitate the mixture up in the chamber to be deposited on filter surface. This results demonstrated that the heavy mixture particles could aid the burst dust particulate to fall into dust hopper after back pulse cleaning and the reentrainment would be less significant in mixture of iron oxide and coal ash than pure coal ash.

(6) All kinds of dust cake can be successfully dislodged with the use of back pulse

cleaning technique. And the delta across the filter itself repeated as back pulse cleaning technique was applied. This confirms the fact that iron oxide mixtures will not create difficulty for dust cake cleaning with the use of current back pulse cleaning technique.

(7) The current dust loading is very high, because the dust mixture bed was blown up with a high mass flow rate, and a 4 millimeter or thicker coal ash cake was developed on filter surface within a 5-minute filtration period. This dust cake deposition rate far exceeds the dust loading might be needed for hot gas desulfurization purpose. This result indicates that there shall be no problem to use waste iron oxide as a desulfurization sorbent from filtration point of view.

(8) Measured Delta P values kept decreasing as the percentage of iron oxide increases in the mixture.

(9) The test data repeated fairly well, except a deviation displayed in 1 to 1 ratio, which might be caused by processing error.

(10) Filtration test system can be designed according to the results acquired in the subject research of the hot gas desulfurization testing to optimize the iron oxide ratio in the mixture, or the space velocity as required.

2.2 Summary of hot gas desulfurization testing

During the hot gas desulfurization testing, mixture of particulate with 1:1 and 1:2 coal ash to iron oxide ratios were performed. Effects of reaction time and iron oxide mass provided were studied for hot gas desulfurization. The test data were converted into space velocity based on the mass and ratio of iron oxides to coal ash. According to hot gas desulfurization test results, it appears that waste iron oxides can be utilized as a disposable sorbent alternative to replace other sorbent candidates developed in the last decade.

To characterize the temperature effect on hot gas desulfurization, testing was performed at 625, 750, 875 and 1,000 degree F. To further characterize the sulfur absorption capacity at low temperature, hot gas desulfurization testing was also performed at 350 degree F for post desulfurization gas treatment testing.

Test data were plotted to show the effect of temperature, space velocity and residence time to develop a road map for hot gas desulfurization optimization design.

According to the test results of the subject research, it concludes that the success of hot gas desulfurization and particulate filtration with the use of waste iron oxides ensures the feasibility of using waste iron oxides for simultaneous operation of hot gas desulfurization and particulate filtration processes. The test results revealed from this study can be served as a guideline for future system design optimization.

2.2.1 Evaluation of waste metal oxides for desulfurization sorbent candidates

Many researchers have learned that metal oxides can be used for hot gas desulfurization purpose. Due to the high cost of currently developed reusable sorbent candidates, people started to look into the use of waste metal oxides as an alternative for the removal of sulfur in hot gas cleaning. Typical sorbent candidate will cost more than \$7.00/lb, which is two orders more expensive iron oxide (\$0.07/lb), according to the analysis of IF&P. The new low operation temperature limit of 1,000 degree F makes the use of iron oxides as disposable sorbent candidates more attractive because the current filtration study indicates this new approach is feasible. At PV A&MU, iron oxide powder was evaluated with a parametric study on effect of temperature, residential time and space velocity effect for hot gas desulfurization.

The subject hot gas desulfurization research work was concentrated on the factors of the following parameters: 1) Iron oxides residing time for hot gas desulfurization with different reaction temperature, 2) studies on the ratio effect of iron oxide to the coal ash, 3) studies on desulfurization for ash and iron oxide mixture with two space velocities, and 4) studies on integration testing of hot desulfurization in a high temperature reducing atmosphere (KRW-Gas) and a post desulfurization filtration testing performed at room ambient temperature.

2.2.2 Description on hot gas desulfurization test setup

The hot gas desulfurization tests for waste iron oxide were carried out in a high pressure bench scale reactor and coil tubing setup capable to withstand pressure of more than 800 psi and temperature up to 1,000 degree F. The sorbent test facility was designed also to operate with a continuous operation of simultaneous hot gas desulfurization and particulate filtration; when this setup was connected to a heat exchanger, a post gas treatment setup, and the filtration system.

Figure 7 shows the pictures of the test setup. For ease of connectivity and transportation, the test unit was constructed as a skid mounted system. Most of the system components were constructed with 316 and 304 stainless steel to prevent corrosion attack by hot, steamed sulfur gas throughout the hot gas desulfurization testing.

The bench test facility consists of : 1) a gas supply assembly, 2) a reactor assembly, 3) a gas sampling assembly and 4) a residue gas collecting assembly.

The gas supply assembly was provided from a pre-mixed gases bottle prepared by Scott Specialty Gas Company. The coal gas compositions simulating the KRW-gas with 5% steam, a highly reducing medium BTU gas, was utilized for hot gas desulfurization testing. Research institutes utilized three kinds of simulated KRW-gas for desulfurization testing with several kinds of regenerable sorbent candidates.

To investigate the feasibility of using waste iron oxides as a disposable sorbent alternative, the KRW-gas with highest value of reducing power (5% steam) was selected as the reducing environment gas to react with waste iron oxides. The "reducing power", Rp, was arbitrarily defined by sorbent research institutes as a molar ratio of (CO + H_2) to (Steam + CO_2).

The simulated reducing KRW-gas utilized before and their gas composition and its Rp values are listed as follows:

Gas	KRW-Gas (20% Steam)	KRW-Gas (5% Steam)	Texaco O_2-Blown Gas
H_2	8.85	11.65	27.70
CO	15.01	18.97	39.44
CO_2	6.89	6.75	13.10
H_2O	19.17	5.12	18.64
H_2S	0.44	0.55	1.12
N_2	49.54	56.95	0.00
Rp	0.92	2.58	2.11

The design of the hot gas desulfurization setup is described as follows:

One MKS mass flow controller was connected to the stainless steel regulator installed on the simulated KRW-Gas bottle. A water injection pump was connected to a mixing manifold, which is also connected to the exit of the mass flow controller. The exit port of the mixing manifold was then connected to the inlet end of a 1/4 inch O.D. stainless steel coil tubing installed in a high temperature oven heated up to 1000 degree F. The pre-heated gas stream exited from the pre-heated temperature oven, and was guided into the reactor installed within the high temperature reacting oven with operating temperature up to 1000 degree F.

The hot gas stream reacted with a fixed bed of coal ash and waste iron oxides mixture, sealed in a reactor. The reactor is made of 304 stainless steel with 2.5 inch O.D., 2.375 inch I.D., 8.0 inch long and a 1/2 inch thick flange of 5.0 inch O.D. on each end of the reactor. A 12.0 inch long 1/4 inch O.D., 0.150 inch I.D. 316 stainless steel tubing was welded to the center of the sealing cap. A high temperature sealing material template was inserted between the reactor chamber and the sealing flange on each end of the reactor. Each sealing flange was bolted to the reactor flange with 4 sets of 1/2 O.D. bolt and nut.

A sampling device was utilized for hydrogen sulfide concentration measurement after each of desulfurization testing. The sampling device was connected to the exit end of the reactor chamber, and the other end of the sampling device was connected to a flexible tubing leading to a Industrial Scientific single H2S detector. Four needle valves were connected on a four way steel junction union for gas sampling process control.

Figure 8a shows the layout of the KRW-Gas supply, the preheat temperature oven (Blue M) and the reactor high temperature oven (The Grieve Corp.). Figure 8b shows the coil tubing assembly installed in high temperature oven (for both preheater and reactor oven each). Figure 8b shows the reacted gas sampling setup and Figure 8d shows the 1000 degree F tested reactor chamber.

A fix bed of composite layers of coal ash and iron oxides were installed within the reactor chamber. Three kinds of fixed bed design were utilized for hot gas desulfurization testing.

Design version one of the fixed bed consists of layers of 2.375 inch O.D. and 1.50 inch O.D. Zircar Alumina Boards with 0.25 inch thickness for both boards, layed in series, to fill the entire reactor chamber. And the annulus space between the 1.5 inch alumina board and the 2.375 inch I.D. of the reactor chamber was filled with 50% of mixture of coal ash and waste iron oxides to form a multi-layer coal ash mixture bed. Hot gas stream was able to flow through the high porous alumina boards during hot gas desulfurization testing.

Design version two of the fixed bed is similar to that of version one except that a 2.0 inch O.D., 1.745 inch I.D. and 2.995 inch long steel tubing was installed at the bottom of the reactor to provide more space for hot gas to be trapped within the reactor chamber for desulfurization testing.

Design version three was simply the use of 50-foot long 1/4 inch O.D. and 0.150 inch I.D. coil tubing to install coal ash and iron oxide mixture and hot gas stream for desulfurization testing.

2.2.3 Description on integrated hot gas desulfurization and particulate filtration test setup

The test facility of the integrated hot gas desulfurization and particulate filtration testing is the integration of the hot gas desulfurization testing facility and the particulate filtration testing facility. The bench test facility consists of : 1) a gas supply assembly, 2) a gas stream preheat assembly, 3) a reactor assembly, 4) a heat exchanger assembly, 5) a gas stream post treatment assembly, 6) a gas sampling assembly, 7) a particulate filtration testing assembly and 8) a residue gas collecting assembly.

The gas supply, gas stream preheat, reactor assembly and the gas sampling assembly was the same as the that described in section 2.2.2. The hot gas desulfurization assembly exit was connected to a heat exchanger assembly to cool the hot reacted gas to a lower temperature prior to its entry to the post gas stream treatment assembly, where residual hydrogen sulfide concentration was to be absorbed by a very thick layer of waste iron oxides bed, either design version one or version 2. The post treated gas stream was then led into the particulate filtration chamber for dust filtration.

The pictures of each sub-assembly of the integration test facility are shown in Figures 9a, 9b and 9c. Figure 9a shows the heat exchanger assembly and the particulate filtration assembly. Figure 9b shows the gas supply assembly and post gas treatment assembly. Figure 9c shows the preheat assembly, the reactor oven assembly and the tubing connection between preheater and reactor oven.

The close view of the filtration assembly are shown in Figures 10a, 10b, 10c and 10d. Figure 10a shows the K-Tron dust feeder, Figures 10b and 10c show the fast response solenoid valves and Figure 10d shows the candle filter after dust cake dislodging. Two solenoid valves were mounted on the top section of the filtration system. The one installed on top of the filtration chamber is a normally open valve; the one connected between the positive pressure back pulse cleaning plenum between the filtration chamber Figure 10b and the medium pressure storage tank Figure 10c is a normally closed valve.

The normally closed valve is designated to seal the pressurized gas in a 1.2 cubic foot tank from entering the filtration chamber. The normally open valve is designated to vent the filtrated gas to the ambient environment. When the dust cake developed on the candle filter was about to be dislodged, both valves were energized to reverse the close and opening position.

The normally open valve was then closed to get ready for back pulse cleaning, and the normally closed valve was opened immediately after the other valve was closed. The pressurized back pulse gas stream was then released into the filtration chamber to dislodge the dust cake. The close look view of the bottom portion of a cleaned candle filter was shown in Figure 10d; the rest of the cleaned filter was blocked by the mixture of coal ash and waste iron oxides.

The hand held pressure calibrator (Ashcroft), measured the differential pressure across the filter chamber and the filtrated gas stream, and the 120 psi air compressor is shown in Figure 11.

2.2.4 Hot Gas desulfurization testing on mixtures of coal ash and iron oxide

2.2.4.1 Philosophy and preparation of hot gas desulfurization testing

To ensure the safety of the hot gas desulfurization testing, nitrogen was utilized to pressurize the test setup to check the fitting and chamber sealing integrity. The test setup was tested to 60 psig at room temperature prior to the installation and connection to the test assembly.

Gas sampling assembly was tested at room and high temperature to ensure the sampling process was safe and repeatable. All valves and fittings were also leak detected prior to testing.

After the preliminary test checkup, mixture of coal ash and iron oxide with 1:1 and 1:2 ratios were installed in the reactor chamber and then connected to fittings and valves for high temperature testing. During the first few testing at 1000 degree F, the fan of the Grieve high temperature oven generated intermittent noise and the testing setup was then shut down to inspect the problem. After few iterations of high temperature operation up to 1000 degree F, the noise problem of the circulation fan disappeared, and the reactor assembly was then reconnected and leakage tested afterwards.

However, before the hot gas desulfurization testing was resumed, a minor leak was located around one of the eight locking bolt and nut area. The test setup was then changed again for safety reasons. Because a chemical leakage was detected in the gas bottle storage cage area outside of PV A&MU engineering building, leading to the shut down of the entire engineering building per the request of off campus police and fire department. The safety regulations for hazard gas handling at PV A&M University turned out to be extremely stringent prior to the hot gas desulfurization testing was processed.

Because the simulated KRW-Gas is flammable and poison, for safety reason, the reactor chamber was disconnected and replaced with 2 pieces of 50-foot long, 1/4 O.D. and 0.150 inch I.D. 316 stainless steel coil tubing to carry out the testing.

Operation procedures, feeding KRW-Gas and particulate mixture of coal ash and iron oxides through the coil tubing, were developed and tested. Small amount of particulate feeding was tested for dehydrated coal ash mixture. However, technical difficulty was experienced when wet coal ash mixture was injected into the coil tubing. The coil tubing was plugged by wet particulate mixture after a short period time of particulate feeding.

High pressure jet was applied to the coil tubing to drive the plugged particulate mixture out immediately after the plugging was detected, otherwise coil tubing could be severely plugged. After few iterations, it was decided that it was very difficult to feed the gas and wet particulate mixture simultaneously throughout the 100 to 150 foot long coil tubing for a continuous run with the feeding of particulate and KRW-Gas stream at the same time.

The objectives of hot gas testing at different face velocities were to find out the effect of space velocity and the residence time on the reaction rate of waste iron oxide to hydrogen sulfide at high temperature. The coal ash and contaminant mixed with waste iron oxides tend to coat the surface of iron oxides, thus interfering with the process of adsorption and/or absorption of hydrogen sulfide. To resolve the technical difficulty, several different test procedures were developed to carry out hot gas desulfurization testing. The residence time of waste iron oxides in KRW-Gas vs the concentration level of hydrogen sulfide was measured with a hydrogen sulfide gas detector at the outlet sample port of reactor at the end of each batch testing. The test data could be utilized as a guideline for future hot gas desulfurization process design.

To evaluate the performance of waste iron oxides as a disposable sorbent alternative, the philosophy of hot gas desulfurization testing design at two different face velocities (two different residence times) is summarized below.

Hot gas desulfurization testing was initially designed at two space velocities; 2000/hr and 6000/hr. Due to the technical difficulty in particulate feeding control, few more space velocities were tested and the space velocities were matched as close as possible with best effort. Different space velocities were derived from 1:1 and 1:2 coal ash to waste iron oxide ratio. The test design was also utilized to evaluate the reaction rate of hot gas desulfurization vs particulate mixing ratio or contaminant effect on iron oxides. Final test data were converted to space velocity vs the concentration level of hydrogen sulfide at different reaction temperatures. After the testing of two space velocities, loading of iron oxides were reduced due to the difficulty experienced on particulate feeding into reacting devices. Residence time vs temperature were also evaluated to gain more insights into the process of hot gas desulfurization with waste iron oxides.

Because the desulfurization reaction is surface area limited and the adsorption and absorption of hydrogen sulfide process of iron oxide took a finite period of time, the volume of gas stream determines the amount of waste iron oxide required. The amount of iron oxide needed for hot gas desulfurization was determined by the space velocity for particulate loaded gas stream. Space velocity is defined as the ratio of gas flow rate to the volume of the sorbent utilized in cubic feet. Sorbent candidate needs evaluated vs space velocity to reach a good absorption result. Waste iron oxides mixed with coal ash may need a low space velocity for successful desulfurization due to the masking obstacles derived from coal ash barrier and contaminant in waste iron oxides.

$$\text{Space Velocity (1/HR)} = \frac{\text{Gas flow rate (scfh)}}{\text{Volume of sorbent (iron oxides)}}$$

The depth of iron oxide bed was also evaluated with the use of a large diameter reactor vs a small I.D. coil tubing with fixed ratio of gas volume to iron oxide. The large diameter reactor provided a thick and packed sorbent bed; while the long length of coil tubing had a much thinner population of particulate scattered along the length of the tubing with a non-uniform pattern.

To simulate a continuous hot gas desulfurization testing, mixture of waste iron oxides and coal ash was installed into the reactor chamber or a 50-foot long stainless steel coil tubing prior to the feeding of the reducing gas. The volume of gas and iron oxide was calculated and fed into the test reactor or tubing with the best effort to the designated values. Since the mass of the particulate was small and the amount of the steam is only 5% of the small mass, the water droplets required for steam were absorbed by mixture of dehydrated coal ash and iron oxides prior to the feeding of particulate to reactor or coil tubing.

Before the feeding of KRW-Gas into the reactor or the tubing, the reacting device was vacuum first to ensure KRW-Gas would not be diluted when the gas was fed into the reacting device during desulfurization process. The feeding of reducing gas into the reactor was managed with the use of controlled valves and pressure gages. The amount of gas fed was verified with pressure gages mounted on the test setup. Since the amount of gas mass is small, the gas could be heated up to the test temperature less than a minute because the reacting device was preheated in the temperature oven. To minimize the effect of the short period of time for gas heating, the residence time for hot gas desulfurization reacting was set at 5, 15 and 25 minutes. The span of residence time could be utilized as a guide for process plenum length vs gas stream speed design.

The reducing gas was fed into the reactor and reached gas supply reservoir pressure in about one second; and the gas inlet valve was closed immediately after the gas pressure in the reactor or the coil tubing reached equilibrium with the large gas supply reservoir. The reducing gas, trapped in the reactor or the tubing, reacted with pre-installed particulate of coal ash and waste iron oxides for preset residence time.

Because the ratio of the gas flow rate to the volume of iron oxide was fixed to a preset space velocity for each batch of testing, the closed system of KRW-Gas and particulate mixture could be viewed as a simulation of a closed system of a steady state flow, traveling throughout the plenum of the hot gas desulfurization system with the same amount of gas and mixture of coal ash and iron oxides.

Different residence time for each set of the simulated steady state hot gas desulfurization was carried out to weigh the importance of each variable affecting desulfurization process. After the gas sampling at the end of each testing, the pre-tested particulate was purged out of the reactor or tubing prior to the setup of the next testing.

2.2.5 Hot gas desulfurization testing

To feed particulate mixture into the coil tubing at high temperature, both positive pressure and vacuum pressure were applied to each end of the coil tubing while the particulate was fed from the other end. Finally, it was decided that an intermittent vacuum pressure pulse was capable to suck the particulate into the coil tubing periodically. To prevent the particulate from being sucked out of the vacuum end of the tubing, an alumina board was installed into the internal cavity of a swage locked elbow, connecting the tubing to elbow, with 0.001 to 0.002 inch tolerance along the circumference between the alumina board and the elbow throughout the dust feeding process. To provide a best effort uniformly distributed particulate loading in the coil tubing, pulsed vacuum pressure was applied throughout the feeding operation.

A 0.15 pound mass of particulate mixture with a 1:1 coal ash to iron oxide ratio was installed into one piece of 50-foot long coil tubing. Both 0.11 and 0.075 pound mass of particulate mixture with a 1:2 coal ash to iron oxide ratio were installed into different pieces of 50-foot long coil tubing. Both coil tubing were installed into the 1000 degree F reactor temperature oven prior to hot gas testing, connected with proper fittings and valves.

The operation procedures for hot gas desulfurization testing of each batch run are listed as follows:

1) The oven temperature was set and adjusted to 1000 degree F.
2) Prior the injection of reducing gas, the air trapped in the coil tubing was vacuum out with a vacuum of better than 25 inch of mercury.
3) KRW-Gas was injected into each coil tubing at 20 psig.

4) Feeding ball valves were closed immediately after the pressure stabilized in the coil tubing.
5) The trapped KRW-Gas was sampled after a preset period of reacting time; 5, 15 and 25 minutes of residence time.
6) To prevent hazard gas pollution, the residual gas, trapped in the coil tubing or the reactor, after gas sampling was evacuated out of the coil tubing with a high vacuumed 5-gallon steel tank.

The same procedures were followed when hot gas desulfurization testing were performed at different temperature levels after 1000 degree F testing.

2.2.6 Discussion on hot gas desulfurization testing

The test data were analyzed and categorized as follows: The concentration level of hydrogen sulfide after desulfurization testing was plotted to show the relationship between space velocity vs reaction time and reaction temperature vs residence time. In **Figure 12, 13, 14 and 15**, hydrogen sulfide concentration is plotted vs temperature for space velocity 2540, 4560, 5500 and 9100 1/HR respectively. In **Figure 16, 17 and 18**, hydrogen sulfide concentration was plotted vs residence time at 1000, (625, 750, 875 and 1000), and 350 degree F with different space velocities.

Based on the test results of Figures 12, 13, 14 and 15, the general trend of desulfurization output appears that the lower the space velocity was, the lower the hydrogen sulfide concentration left after desulfurization testing. The concentration also could be further reduced with a longer span of residence time, as shown that 15 and 25 minutes residence time could bring the concentration to a very low level. However, as the space velocity

In Figure 14, it was demonstrated that the reaction rate of desulfurization increased as the reaction temperature increased proportionally at a space velocity of 5500 1/HR.

In Figure 12, it was shown that waste iron oxides could bring the concentration of hydrogen sulfide to a fair low level even reacted at 350 degree F. These test results indicated that the space velocity plays a significant role as the residence time for hot gas desulfurization. The space velocity has same magnitude of significance as reaction temperature for hot gas desulfurization.

It also appeared that there was a threshold level for space velocity selection to reduce the concentration of hydrogen sulfide with a long residence time. Higher space velocity could only carry limited iron oxides in the gas stream which limited the sulfur capacity for the fixed iron oxides available in the gas stream. It is important to calculate the space velocity and residence time for hot gas stream to travel from upstream to the filtration chamber to reduce the concentration of hydrogen sulfide to designated low ppm level.

In Figure 16, the concentration level of hydrogen sulfide was plotted vs residence time at three space velocities. The general trend showed that the higher the space velocity, the less hydrogen sulfide could be removed. The 9100 1/HR space velocity showed a deviation for concentration removal at longer residence time period; the deviation could be derived from the mixing quality and the contaminant of the coal ash and waste iron oxide mixture.

In Figure 17, the test results revealed that high temperature and longer residence time could help minimize the concentration of hydrogen sulfide.

In Figure 18, the test results illustrated that slow space velocity could reduce the concentration of hydrogen sulfide even at low reacting temperature. This finding is important to use waste iron oxides as a disposable sorbent alternative at mild reaction temperature.

A good control of space velocity, reaction temperature and residence time will make the use of waste iron oxides an attractive sorbent to replace other expensive regenerable sorbent candidates.

The typical superficial linear velocity of the gas stream operated by other research institutes during hot gas desulfurization testing was in the range of 3.0 to 6.0 inch per second. With this range of linear velocity, the gas flow rate through a 0.15-inch I.D. tubing would require a flow rate of 6.25 liter/hr, which would carry a very small amount mass of particulate for filtration, compared with the filtration testing performed in this research work. The dust loading of the filtration testing described in section 2.1.4 of this report overwhelmed the dust loading required in hot gas desulfurization testing. The integration of continuous desulfurization and filtration testing was similar to the hot gas desulfurization testing.

Due to the difficulty experienced in feeding particulate through the 1/4 inch O.D. tubing with wet particulate in the integration testing trials and hot gas cleanup testing was investigated into two parts: hot gas desulfurization testing and cold flow particulate filtration and dust cake removal evaluation. Water content in wet mixture of coal ash and iron oxide can be shown in sample pictures taken before and after the testing.

In **Figure 19,** sample pictures of mixture of coal ash and iron oxides were taken to illustrate the wet, dried and reacted mixtures. Picture of sample A is a wet mixture of coal ash and iron oxides prepared at room temperature, picture of sample B is the same mixture dried in the oven at 1,000 degree F without reacting with KRW reducing gas; picture of sample C is a dried mixture after reacting with KRW reducing gas. Compared with wet mixture, dried mixture had more brown shade and dried sample was much easier to be carried by gas stream than the wet one. The reacted sample distinguished itself from the other two samples with a strong black appearance, characterizing its reaction with hydrogen sulfide. Consistent low concentration of hydrogen sulfide of every reacted gas samples confirmed that iron oxide material was capable to absorb hydrogen sulfide even iron oxides were well mixed with coal ash and coated by contaminant acquired from waste iron oxides.

Even though these two section of testing were evaluated independently, each testing was performed under stringent environment, such as heavy dust loading and a wide range of space velocity and flow rate. Without losing generality, the test data acquired from each part of research can be utilized as a general guideline for integrated testing of continuous hot gas desulfurization and particulate cleanup testing.

2.2.7 Cost analysis on hot gas desulfurization testing with waste iron oxides

According to the test results of sulfur loading capacity of zinc ferrite, conducted by Thomas Grindley in "Development and testing of regenerable hot coal gas desulfurization sorbents" in 1981 (DOE/MC/16545-1125), operated at 1,000 degree F was 13 g S/100 g fresh sorbent. The sulfur capacity of various ZT sorbent, operated at 1,000 degree F, was 8 to 17 g S/100 g, conducted by R. P. Gupta and S. K. Gangwal in their study of "Enhanced durability of desulfurization sorbents for fluidized-bed applications". The sulfur removal capacity of waste iron oxide, investigated by P.M. Eggerstedt, J. F. Zievers and P.C. Patel in "Simultaneous hot gas desulfurization and improved filtration", was 59.86 g S/1000 g of sorbent or 6.0 g S/100 g of sorbent.

According to these test results, it appeared that the sulfur capacity of waste iron oxide is about 50% of fresh regenerable sorbents of zinc oxide and ZT sorbents. However, the cost of the waste iron oxide is about 1% of the regenerable ZT sorbent, and the regenerable sorbents are limited to 50 to 100 cycles of application for hot gas desulfurization with excellent regenerable performance required.

For fixed bed or fluidized bed desulfurization application, the residence time and space velocity for regenerable sorbents are limited by system design. Typical residence time might be less than a second and the space velocity might be less than 5000/HR. On the contrary, the use of waste iron oxides would have flexible dimensions for residence time and space velocity control to optimize hot gas cleanup.

The use of disposable iron oxides can help maximize the use of the sulfur capacity of iron oxides in two aspects: 1) the optimization of space velocity and residence time for iron oxide to travel with sulfur contained gas stream; and 2) there will be a 10 to 20 minutes waiting period after the deposition of iron oxides on filter surface prior to the back pulse cleaning of iron oxide loaded dust cake. During each stage of the reacting phase between hydrogen sulfide and iron oxide, the pattern of chemical mixing and the very long residence time will help the maximization of sulfur capacity of iron oxides.

Based on the hot gas desulfurization testing performed at PV A&MU, a layer bed structure design of mixture of iron oxide and coal ash did facilitate the absorption of hydrogen sulfide from KRW reducing gas. When iron oxide loaded particulate starts to be deposited on filter surface, a similar layer bed structure is developed over filter surface. Prior to the back pulse cleaning, iron oxide loaded dust cake serves as a fixed bed of iron oxide for hot gas desulfurization.

Therefore, it is beneficial to use disposable iron oxides for hot gas desulfurization. The maximization of sulfur capacity and the elimination of expensive sorbents and high capital investment for sorbent regeneration will yield a dramatic saving for hot gas desulfurization.

A bench scale hot gas desulfurization system will cost more than $100,000.00 for equipment and system control. The regeneration system will also cost $100,000.00 plus the transition operation fees and supplies for sorbent regeneration. Therefore, even for a very small scale hot gas desulfurization system for power plant application, it will save several million dollars just for the fabrication of equipment, control and operation setup. The additional savings of system operation and maintenance and the use of off shelf components for the operation of new IGCC and PFBC systems at the temperature range less than 1,000 degree F will justify the use of disposable iron oxides for hot gas desulfurization application in the future.