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Simultaneous Hot Gas Desulfurization and Improved Filtration

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Introduction

Although the United States has some of the greatest coal reserves in the world, much of it will remain unusable until technology is developed to meet both Clean Air Act mandates and New Source Performance Standards (NSPS) for particulate, SO₂, and NO_x emissions effectively and economically. Recent breakthroughs in particulate control, specifically ceramic filtration technology, have shown that NSPS limits on particulates can be achieved at high process temperatures, thereby minimizing thermal losses and system complexity. While both calcium based and regenerable metal oxide sorbents are currently utilized for sulfur mitigation, problems such as sintering, temperature limitations, physical attrition, and cost have limited their success.

This research suggests the use of waste metal oxide materials for the removal of sulfur in hot gas streams as an alternative to either traditional calcium based sorbents, or regenerable metal oxide sorbents. When classified to a desired particle size and injected into a high temperature coal utilization process, such a “once-through” sorbent can effectively remove sulfur and simultaneously increase the permeability of dust collected at a downstream ceramic filter station in a highly cost effective manner.

There is considerable technical and economic promise in the use of waste metal oxides for the removal of sulfur dioxide (SO₂) and hydrogen sulfide (H₂S) from coal gas streams containing these components, based upon results from tests under controlled laboratory conditions. Several waste metal oxides, including the oxides of iron, tin, and zinc, have been evaluated both individually and in combination to assess their capacity for sulfur capture in both oxidizing and reducing atmospheres. Additionally, inert materials such as silica sand as well as more traditional materials such as dolomite and limestone, were evaluated as sorbents under identical test conditions to serve as reference data. Efforts also explored the overall domestic availability

of the best performing waste metal oxide sorbents, taking into account their geographic distributions, intrinsic value, etc. to provide the groundwork for commercial implementation of a low cost, highly effective sulfur sorbent for eventual use in both coal combustion and coal gasification processes. Recent elevated temperature thermogravimetric analysis (TGA) testing of these samples, performed at the Institute of Gas Technology (IGT), has further confirmed the trends in sulfur affinity which were observed in the preliminary testing. In that all of the sorbent samples tested were of an identical, carefully selected particle size, the data collected will serve as the basis for future research efforts which will additionally evaluate these waste metal sorbents as a means of increasing or maintaining the permeability of the dust collected on downstream particulate control devices, such as ceramic filters.

Objectives

The primary goal associated with this research is to promote the dual use of waste metal oxides as sorbents and filter aid additives in gas streams requiring both desulfurization and enhanced particle removal efficiency at elevated temperatures.

Specific goals related to this project include the following:

- Determination of the most prevalent types of domestically available waste metal oxides and evaluate their current and future availability, geographic distribution, purity, and intrinsic value;
- Assessment of the potential reactivity of several waste metal oxides with sulfur in both oxidizing and reducing atmospheres;
- Performance of a series of ambient laboratory screening tests to ascertain the affinity for sulfur, by way of chemisorption, of the waste metal oxides in both oxidizing and mildly reducing atmospheres, and compare these data with similar tests involving non-reactive materials and calcium-based sorbents;
- Performance of a series of TGA tests on the more promising waste metal oxides, in both oxidizing and reducing atmospheres, to determine their activities and capacities in comparative sulfation and sulfidation tests at several elevated temperatures;
- Performance of a series of packed bed reactor tests on the most promising waste metal oxides, in both oxidizing and reducing atmospheres, to further validate their desulfurization capacity in simulated fuel and flue gas conditions;
- Assessment of the most promising waste metal oxide materials as high temperature additives for improved filtration in a ceramic candle filter station at elevated temperature.

Upon completion of the above objectives, efforts will be made for implementation of this technology within the private sector.

Approach

In recent years, ceramic filtration devices have shown that particle removal levels well within New Source Performance Standards (NSPS) limitations can be achieved at high temperature, thereby improving the efficiency and overall performance of processes such as Integrated Gasification Combined Cycle (IGCC) and Pressurized Fluidized Bed Combustion (PFBC). Unfortunately, removal of the high levels of sulfur indigenous to much of America's coal reserves has been problematic, requiring exotic (and expensive) sorbents, substantial coal feed pretreatment, or a reduction in off-gas temperature to obtain acceptable sulfur emissions.

Many researchers are aware that metal oxide sorbents can be used to effectively reduce sulfur emissions in such processes. However, because of the high cost of most metal oxides, especially such materials as zinc titanate and zinc ferrite, economic studies have shown that for such materials to be cost effective they must be used, regenerated, and reused as many as several hundred times¹ before a return on investment is realized. Additionally, preliminary testing of such sorbents in a pelletized bed configuration, which lends itself to such a regenerative process, has shown that the strength of the pelletized metal sorbent can significantly decrease in as few as five six regenerative cycles. In view of this, it is apparent that a "once through", non-regenerable metal oxide sorbent can be a much more attractive solution from the standpoints of capacity, overall sulfur removal efficiency, and process economics, particularly if a low cost (or no cost) source of sorbent is readily available. Moreover, in combination with ceramic filtration technology, the use of such a sorbent becomes even more practical in that the sorbent can be introduced well upstream of a ceramic filter station, have sufficient residence time for sulfur removal to take place, and then be easily collected on the surface of the filter, along with the ash and other particulate. By properly classifying and sizing the waste metal oxide sorbent particles, the permeability of the dust accumulating on the filter surface can be enhanced, resulting in lower pressure differentials, better pulse cleaning efficiency, and less susceptibility to filter pore "blinding".

The test results reported herein show that significant sulfur removal capacities can be achieved using classified, spent metal oxides. Such materials are generated in tremendous volume as a result of metal processing, smelting, and refining operations, and are generally available for little if any cost.

Project Description

Preliminary Tests

Preliminary tests involved the assessment of the sulfur affinity of waste metal oxides under controlled laboratory conditions by exposing a prepared bed of each material to sulfur dioxide (SO₂) and hydrogen sulfide (H₂S), in separate trials. The testing was performed at the Research & Development Department of Industrial Filter & Pump Mfg. Co., Inc. The waste metal oxides tested are listed in Table 1 which follows:

Table 1. Waste Metal Oxides Evaluated in Preliminary Test Series

<u>Sorbent</u>	<u>Source</u>
Iron oxide	Basic Oxygen Furnace (BOF)
Zinc oxide	Chicago area zinc smelter
Zinc oxide	2nd Chicago area zinc smelter
Tin oxide	Chicago area tin refiner
Zinc/iron/lead oxide mixture	Chicago area smelter

Although waste copper oxide was readily available and considered as yet another material suitable for testing, it was decided that since many waste copper oxide sources contain significant amounts of arsenic, no testing of this material would be undertaken for safety reasons.

In addition to the testing of the above waste metal oxides, test trials were performed without any sorbents, with commercially available dolomite and limestone, and with inert or moderately inert sorbents, such as silica sand and diatomaceous earth, for reference purposes.

In all of the above test scenarios, the flowrate of the SO₂ or H₂S gas and nitrogen carrier gas, which was used as a diluent to the SO₂ or H₂S, was held constant. Likewise, the sample volume and temperature for each test were maintained constant. By bubbling the effluent gas through analyzed collection water, the elapsed time required to depress the pH of the collection water was recorded and indicated the end point of sulfur removal for each sample being tested. Table 2 below shows the preliminary test series conditions; Figure 1 schematically depicts the test apparatus used in the research effort. By plotting the reduction in collection water pH as a function of time for each sample tested, a series of “break through” curves were generated and proved useful in directly comparing the sulfur affinity of each material.

Table 2. Preliminary Test Series: Test Conditions

Test Temperature:	Ambient
Test Pressure:	3 psig
Sample Size:	50 cm ³
SO ₂ or H ₂ S Gas Flowrate:	38 cm ³ /min
N ₂ Carrier Gas Flowrate:	82 cm ³ /min
Sample Particle Size:	75-106 micron; 90 micron average
pH Endpoint:	5.00 (SO ₂); 6.5 (H ₂ S)

Initial “shakedown” trials involving nitrogen carrier gas and either SO₂ or H₂S, without a test sample bed, were conducted to determine the time delay (due to piping lengths and volumes) from the onset of the test until pH depression in the collection beaker.

Both the effect on pH of the nitrogen carrier gas as well as the “time delay” associated with the internal volume of the test apparatus were used in the final data analysis. All tests involving sample test beds were conducted in an identical fashion. Test samples were prepared by drying in an air-circulated oven, after which the weight of the sample stabilized, indicating the removal of any moisture present. The samples then underwent particle size classification using a

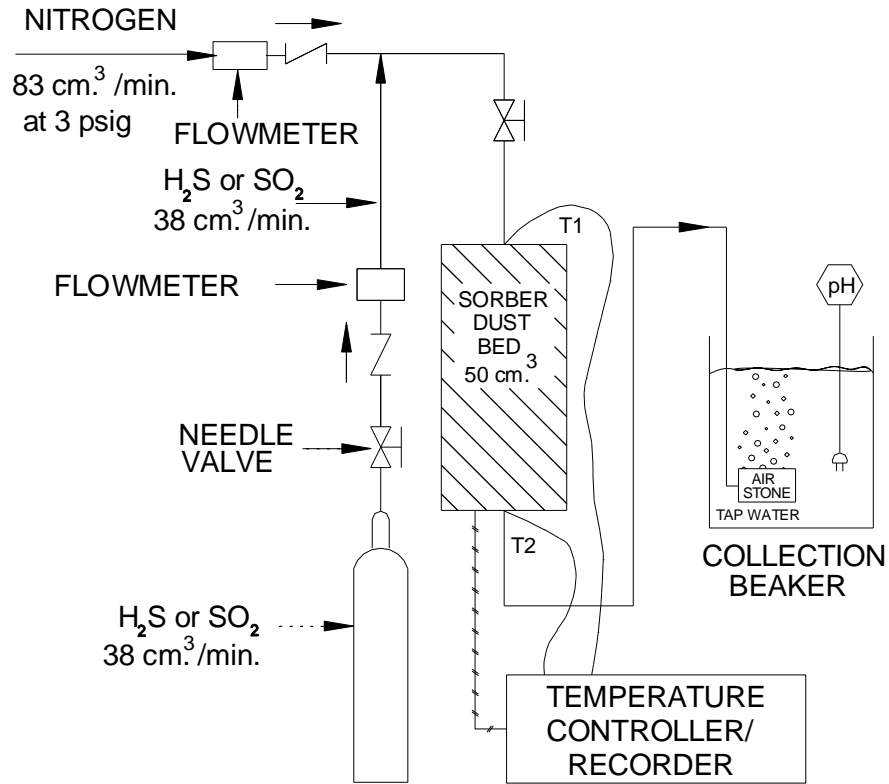


Figure 1. Preliminary Test Series Apparatus

CE Tyler Sieve Products, Inc. portable sieve shaker. Each sample material was classified and the particle fraction passing through a 140 mesh (106 micron opening) screen which was retained on a 200 mesh (75 micron opening) screen was utilized for each test specimen. This particle size is representative of that which would be used to enhance filter cake porosity in the eventual and effective use of IF&P U. S. Patent #4,865,629, which is the focus of future research efforts. By using an identical particle size fraction for each sample tested, it was hoped that the bed permeability in each sample trial would be essentially constant at constant gas flowrate conditions; also, the total available surface area exposed to the sulfur laden gas would be similar from one test to the next. Just prior to each test, the sample material was again dried in an air circulated oven to insure no moisture was retained, after which the classified sample was extracted and weighed for test purposes.

Thermogravimetric (TGA) Testing

Selected waste sorbents for TGA testing included tin oxide, zinc oxide, iron oxide, and a mixture of metal oxide and iron oxide, and was conducted by the Institute of Gas Technology in Des Plaines, IL. These sorbents were evaluated for their reactivities and absorption capacities with respect to H_2S and SO_2 using a high pressure, high temperature thermogravimetric analyzer (HPTGA) unit. The comparative sulfidation tests were conducted at 538°C (1000°F) using fuel gas containing H_2S , H_2 and N_2 ; sulfation tests were conducted at 650°C (1200°F) using flue gas containing SO_2 , O_2 , and N_2 .

During a typical TGA test, the sample weight, the rate of weight change, and the temperature of the furnace are recorded. The sample is contained in a platinum basket, suspended from a recording balance by a platinum wire chain, while a metered gas flow is introduced at the bottom of the reactor chamber. The desired composition of the reactant gas is obtained by mixing different streams of gases at pre-determined ratios. Any movement of the balance arm, because of a change in sample weight, is sensed by a linear differential transformer on the sample arm of the balance. A restoring force that is proportional to the change in weight is supplied to the opposite arm with an electromagnet. The recording balance control unit senses the force required to maintain a null and converts this into a signal proportional to the weight of the sample. The procedure for these tests includes heating the sorbent in a nitrogen atmosphere to a pre-determined temperature. At this point the reactant gas mixture containing H_2S or SO_2 is allowed to flow past the sorbent while the change in the sample weight is continuously monitored. The sample is exposed to the reactant gas until the sorbent is converted to its peak value. The weight gain-versus-time curve produced in these tests is used as a measure of reactivity and capacity of the sorbent tested. The TGA test apparatus employed in this phase of testing is depicted schematically in Figure 2.

Results

Preliminary Tests: SO_2 Trials

In the preliminary tests, an end-point pH of 5.00 was chosen for the SO_2 test series. Of the various materials tested using SO_2 gas, waste iron oxide and especially tin oxide appeared to have a significant potential for sulfur removal, as shown in Table 3 which follows.

Preliminary Tests: H_2S Trials

Because H_2S is a weaker acid than SO_2 when dissolved in water, and because tap water (which was purposely selected in favor of distilled or demineralized water) was used in the collection beaker, the pH depression observed upon exhaustion of the sample bed in the H_2S test series would not be nearly as notable as that observed in the SO_2 test series. Consequently, for the preliminary tests, an end-point of 6.50 was selected for all tests involving H_2S . In addition to pH depression, the total suspended solids (TSS) and total sulfites were periodically monitored and recorded in the H_2S test series to serve as two other means of validating the data.

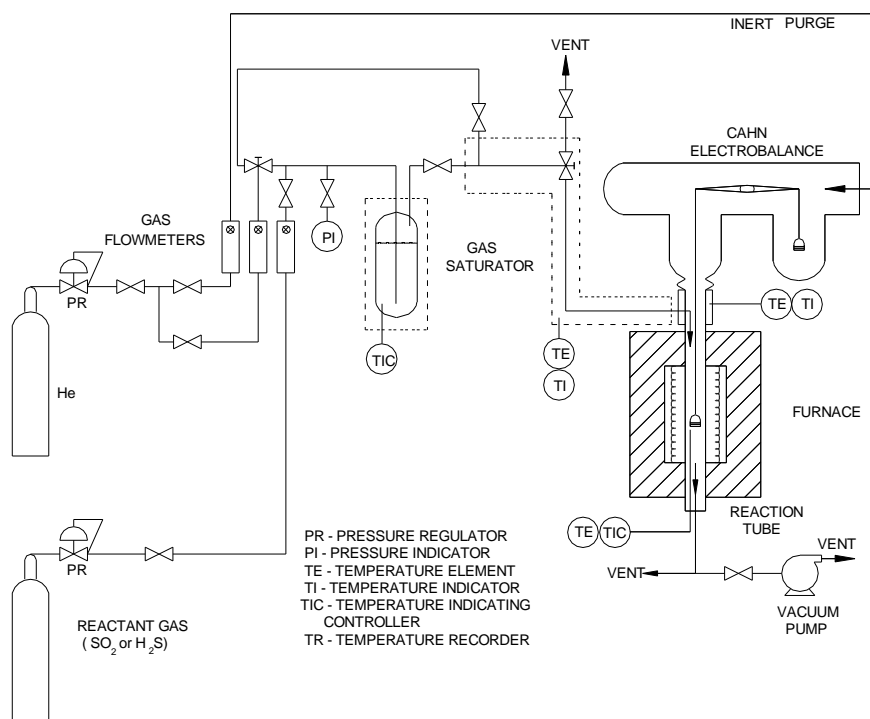


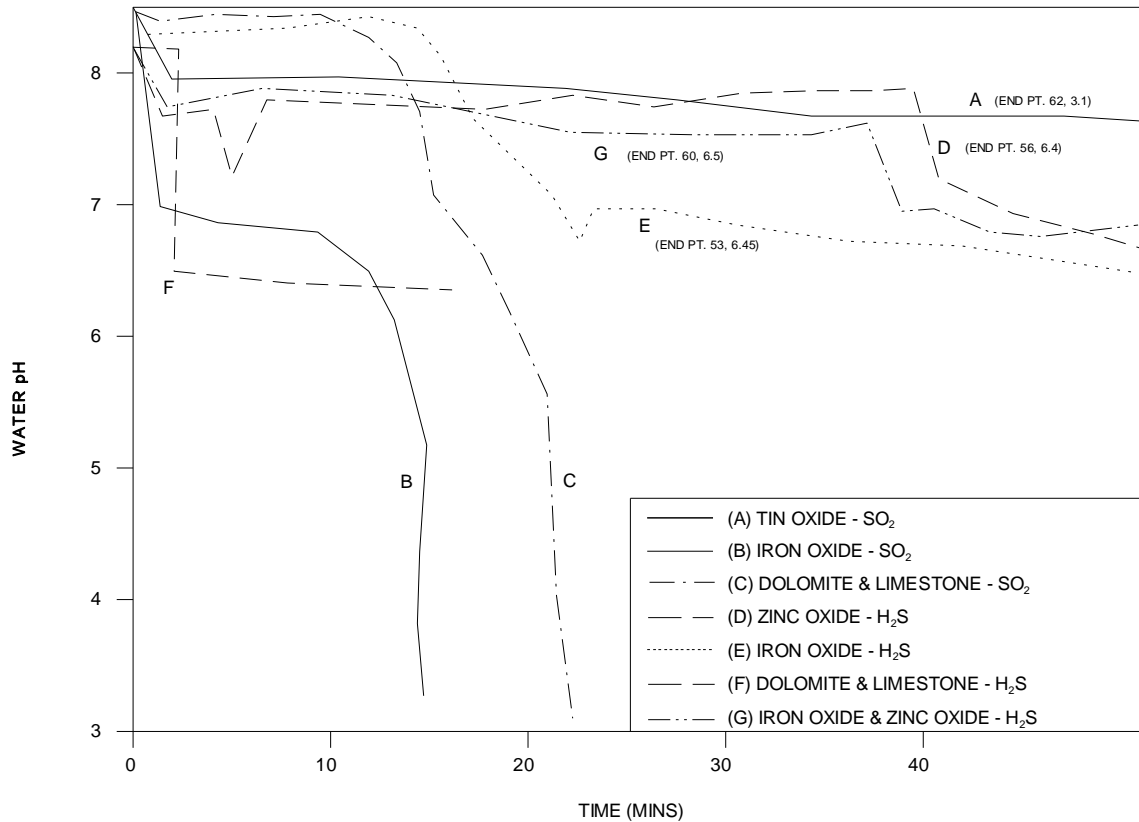
Figure 2. Thermogravimetric (TGA) Test Apparatus

Of the materials tested in an H₂S laden atmosphere, iron and zinc oxides appeared to exhibit high affinity for sulfur. Table 3 shows the various sorbent capacities for H₂S; Figure 3 shows the actual breakthrough plots for both SO₂ and H₂S.

Table 3. Preliminary Test Trials: Sulfur Removal Capacity
 (grams of sulfur/kilogram of sorbent)

<u>Sorbent*</u>	<u>SO₂ Capacity</u>	<u>H₂S Capacity</u>
Tin oxide	66.02	19.13
Iron oxide	21.22	59.86
Zinc oxide	14.92	70.22
Iron & zinc oxide	20.99	82.70
Dolomite & limestone mix	16.09	4.23

(*) normalized to 85% purity (typical)

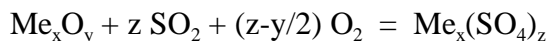


BREAKTHROUGH CURVES AT AMBIENT TEMPERATURE: pH vs. ELAPSED TIME

Figure 3. Preliminary Test Series Breakthrough Plots

TGA Tests: Sulfation Conditions

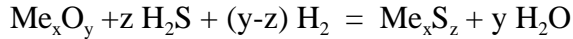
In the case of sulfation, the reaction may be represented by the following equation:



Initial sulfation tests at high temperature (1600°F) indicated no significant sulfation reaction with the zinc oxide waste at such a high temperature. This is consistent with the theoretical thermodynamic limitation of the metal oxide sorbents tested. Comparative sulfation tests were carried out at 650°C (1200°F). Since each mole of oxygen is replaced by 1 mole of sulfur and 4 moles of oxygen, the weight gains during the sulfation reaction are much more significant than during sulfidation. The results indicate that in terms of the overall sulfur capacity, zinc oxide waste is the best sorbent, followed by tin oxide waste and iron oxide. As in the sulfidation tests, both the reaction kinetics and final weight gain of the ZnFe mixed oxide waste are intermediate between those obtained with each of the iron oxide waste and the zinc oxide waste, further indicating the consistency of the results.

TGA Tests: Sulfidation Conditions

For a metal oxide Me_xO_y , the sulfidation reaction may be represented by the following equation:



The weight gain is therefore due to the exchange of sulfur (M.W.=32 g/mole) and for oxygen (M.W.= 16 g/mole) during the sulfidation reaction. The results from comparative sulfidation tests at 538°C (1000°F) using all four metal oxide waste materials indicate that in terms of overall sulfur capacity, iron oxide waste is the best sorbent, followed by zinc oxide waste and tin oxide waste. Both the reaction kinetics and final weight gain of the ZnFe mixed oxide waste are intermediate between those obtained with each of the iron oxide waste and the zinc oxide waste, further indicating the consistency of the results.

Waste Metal Oxides: Availability

As mentioned earlier, an additional task involved the compilation of information related to the availability, geographical location, and processes which generate the various waste materials tested in this research effort. Among the waste materials tested, namely the oxides of tin, zinc, and iron, waste iron oxide appears to be the most promising because of its tremendous availability and very low cost. Highlights of the availability for each of these materials are given below².

Iron

Iron is the most widely used of all the metals. In 1990, the iron and steel shipments in the United States consisted of steel mill products (90%), iron castings (9%), and steel castings (1%). Iron and steel products make up about 75% of the weight of an automobile. Steel is widely used in building, highway, industrial and all other forms of construction, and industrial machinery.

Consumption of steel mill products in the United States amounts to about 100 Mmt/yr. Steel production generates a number of wastes that contain ferrous and nonferrous metal residues. Junked automobiles are the largest source of obsolete or post consumer scrap.

Tin

Tin is one of the earliest metals known to humankind, and is commonly used as a protective coating or as an alloying metal with other metals. The major uses for tin are: cans and containers, 32%; electrical, 22%; construction, 10%; transportation, 11%; and other, 25%.

Waste tin oxides are available from new and old tin scrap by recycling and recovering. In 1991, about 50,000 metric tons of tin was consumed; 98% of the new tin scrap and 96% of the old tin scrap generated was recovered.

Zinc

Zinc is the fourth most widely used metal after iron, aluminum, and copper. More than 90% of the metal is used for galvanizing steel and for alloys; the remainder is used to produce dust, oxide, and various chemicals. In 1991, about 354,000 mt of secondary zinc valued at about \$412 million, was recovered in basic forms--refined metal, alloys, dusts, and chemicals. Scrap, containing about 96,000 mt of zinc and valued at \$62 million, was exported in 1991, whereas 38,000 mt of zinc in scrap, valued at \$19 million, was imported into the United States.

Application

As a result of the preceding discussions on tin, zinc, and iron oxide, it becomes apparent that extremely large quantities of these materials are and will continue to be readily available in America. In instances where such classified particles are not available, the use of "off-the-shelf" bulk handling, particle size reduction, and classification equipment can be easily used to achieve the desired particle size fraction, and to optimize sorbent capacity and filtration performance. In view of the availability of these three waste materials, one further remaining aspect from an economic standpoint (assuming handling costs, permits, and particle size reduction and classification are similar) is the intrinsic value of each material.

As of June 1996, the intrinsic value of the three base metal materials was as follows:

Tin (composite)	\$4.16/lb.
Zinc (high grade)	\$0.49/lb.
Iron (steel)	\$0.07/lb.

In contrast, pelletized zinc ferrite or zinc titanate is significantly higher in cost. Even the most novel, fluidized zinc titanate formulations, such as "ZT-4", were reported to be \$7.91/lb, as of June, 1994.³ It should be emphasized that the intrinsic values shown above are commodity prices for the base metals of each material, and do not represent the cost of the corresponding waste metal oxides, which are much less. The prices do, however, provide an idea of the value of each material after it has been recycled and recovered for sale as pure metal, and are indicative of the relative value of the three metal oxides which showed the most significant affinity for sulfur. By using the sulfur removal capacity recorded in Table 3 and the intrinsic value noted above, a relative cost comparison for sulfur removal, in grams of sulfur removed per dollar value, is shown in Table 4 as follows:

Table 4. Waste Metal Oxide Sorbents: Cost Comparison

<u>Sorbent</u>	<u>SO₂*</u>	<u>H₂S*</u>
Iron oxide	137.79	388.70
Zinc oxide	13.84	65.14
Tin oxide	7.21	2.09

(*) in grams of 'S' removed/dollar value of pure metal

Future Activities

Future efforts will focus on conducting packed bed testing at IGT with the most promising waste metal oxide sorbents, followed by a series of tests at IFP to determine their additional capability as a high temperature filter aid. Given their high affinity for sulfur, overall availability, and low cost in relation to other metal oxide sorbents, the select use of waste metal oxides as a “once-through” sorbent in combination with ceramic filtration technology will provide effective sulfur removal and enhanced filter performance in a cost-effective manner.

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