**Enhanced Durability of High-Temperature
Desulfurization Sorbents for Moving-Bed Applications
Option 2 Program: Development and Testing
Of Zinc Titanate Sorbents**

Topical Report

R.E. Ayala

April 1993

Work Performed Under Contract No.: DE-AC21-88MC25003

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

**By
GE Corporate Research and Development
Schenectady, New York**

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ABSTRACT

One of the most advantageous configurations of the integrated gasification combined cycle (IGCC) power system is coupling it with a hot gas cleanup for the more efficient production of electric power in an environmentally acceptable manner. In conventional gasification cleanup systems, costly heat exchangers are necessary to cool down the fuel gases for cleaning, sometimes as low as 200-300 °F, and to reheat the gases prior to injection into the turbine. The result is significant losses in efficiency for the overall power cycle. High-temperature coal gas cleanup in the IGCC system can be operated near 1000 °F or higher, i.e., at conditions compatible with the gasifier and turbine components, resulting in a more efficient overall system.

GE is developing a moving-bed, high-temperature desulfurization system for IGCC power systems in which mixed-metal oxides are currently being used as desulfurization sorbents. The objective of this contract is to identify and test fabrication methods and sorbent chemical compositions that enhance the long-term chemical reactivity and mechanical durability of zinc ferrite and other novel sorbents for moving-bed, high-temperature desulfurization of coal-derived gases. Zinc ferrite was studied under the base program of this contract. In the next phase of this program novel sorbents, particularly zinc titanate-based sorbents, are being studied under the remaining optional programs. This topical report summarizes only the work performed under the Option 2 program.

In the course of carrying out the current program, more than 25 zinc titanate formulations have been prepared and characterized to identify formulations exhibiting enhanced properties over the baseline zinc titanate formulation selected by the U.S. Dept. of Energy. Fabrication variables studied were: pellet shape (cylindrical extrudates and rounded spheres), pellet size (5-12 mm), zinc-to-titanium molar ratio (0.8-2.0), type (molybdenum, organic burnout) and concentration (0-10%) of additives, and calcination temperature (1400-1800 °F).

The presence of molybdenum (< 2.5% wt. MoO_3) and organic burnout (< 10% wt.) additives was found to be beneficial in maintaining the mechanical strength and chemical reactivity of rounded sorbents over extended testing of 10 cycles of absorption and regeneration in the bench-scale reactor system. This beneficial effect is believed to be a result of modifications in the pellet porosity and pore structure characteristics by the additives, as well as the result of differences in sulfur distribution within the pellet during desulfurization.

ACKNOWLEDGMENTS

Special thanks to T. Chuck at GE-CRD who performed the bench-scale tests, to E. Gal and M. Arnold at GE Environmental Services, Inc., who contributed with the mechanical characterization measurements, and to R. Gupta and S.K. Gangwal at Research Triangle Institute, who contributed with the TGA and porosimetry measurements. The author also acknowledges the helpful discussions with Mr. S. Jain, DOE's Program Contracting Office Representative. This work was sponsored by the U.S. Dept. of Energy under Contract DE-AC21-88MC25003.

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EXECUTIVE SUMMARY

BACKGROUND

The integrated gasification combined cycle (IGCC) power system using high-temperature coal gas cleanup is one of the most promising advanced technologies for the production of electric power based on coal in an environmentally acceptable manner. In conventional cleanup systems, costly heat exchangers are necessary to cool down the fuel gases for cleaning. Unlike these conventional low-temperature cleanup systems, where the coal gas from the gasifier has to be cooled down from 1000-2000 °F to below 300 °F, high-temperature coal gas cleanup systems can be operated at near 1000 °F or higher. These conditions are compatible with the gasifier and turbine components in the IGCC system. The result is a more efficient overall system (Corman, 1986).

GE is developing a moving-bed, high-temperature desulfurization system for IGCC power systems in which mixed-metal oxides are currently being used as desulfurization sorbents (Cook et al., 1991). In addition to zinc ferrite, zinc titanate and other novel mixed-metal oxides are currently being considered as promising sorbents, particularly for cases of highly-reducing coal gases where the use of iron-containing sorbents, such as zinc ferrite, is limited by the formation of iron carbides and other iron compounds that result in sorbent degradation (Geizer, 1983).

OBJECTIVES

The objective of this contract is to identify and test sorbent fabrication methods and chemical compositions that enhance the long-term chemical reactivity and physical strength of zinc ferrite and other novel sorbents for moving-bed, high-temperature desulfurization of coal-derived gases. Zinc ferrite was studied under the base program of this contract while novel sorbents, particularly zinc titanate-based sorbents, are being studied under the remaining optional programs. This topical report summarizes only the work performed under the Option 2 program.

ACCOMPLISHMENTS

- A total of 19 cylindrical extrudate formulations of zinc titanate were prepared and characterized to identify sorbent compositions with better desulfurization characteristics. The presence of molybdenum as an additive to zinc titanate was identified as a useful pore size distribution modifier for the zinc titanates.
- Based on the desulfurization performance of cylindrical extrudates, eight rounded spherical formulations were prepared to study the effect of

rounding on sorbent performance during bench-scale testing. As in previous work on zinc ferrite (Ayala, 1991), rounding was found to enhance the mechanical/physical durability of zinc titanate formulations while maintaining satisfactory chemical reactivity toward desulfurization.

- Ten runs of 10 cycles of absorption and regeneration each were conducted in the bench-scale reactor system to determine the long-range performance of the rounded zinc titanate formulations. The usefulness of molybdenum oxide was identified as a porosity modifier that helps preserve the mechanical strength in formulations exhibiting enhanced durability. Formulation 2A1.7M (designated as L-3787M by United Catalysts, Inc., UCI) containing 1.7% molybdenum (i.e., 2.5% MoO_3) was identified as the best performer of all the enhanced formulations tested because of a good balance in chemical reactivity, mechanical strength, and pore structure.

RESULTS AND CONCLUSIONS

The following conclusions can be drawn from the characterization of cylindrical formulations:

- Formulations containing a 0.8 Zn:Ti ratio produced mixtures of several stoichiometric titanates: $\text{Zn}_2\text{Ti}_3\text{O}_8$, ZnTiO_3 , and Zn_2TiO_4 , with the relative amount of each component depending on calcination temperature. Formulations containing a 2.0 Zn:Ti ratio exhibited exclusively the Zn_2TiO_4 structure, which is more desirable because of its higher sulfur capacity.
- The higher calcination temperature of 1800 °F (982 °C) significantly reduced the porosity available for chemical reactivity in Mo-doped formulations, while the lower calcination temperature of 1400°F (760 °C) produced, in some cases, formulations with traces of residual unreacted zinc oxide and anatase titanium dioxide. The desirable calcination temperature range was found to be 1400-1550 °F for Mo-doped formulations and up to 1800 °F for straight zinc titanates.
- The crystalline form of the MoO_3 additive was absent after calcination, even at a 10% concentration, which suggests that Mo dissolves within the zinc titanate structure forming zinc molybdates or, alternatively, becomes an amorphous phase to x-ray diffraction.

- Addition of MoO_3 modifies the pore structure of the pellet: MoO_3 -containing formulations exhibited higher median pore diameter (MPD) (5000-7000 Å vs. 3000-3500 Å), and higher bed bulk density (1.63-2.37 vs. 1.12-1.36 g/cc). This modification of the pore structure is considered to be beneficial for the process of desulfurization. Crush strength and specific pore volume (SPV) were functions primarily of calcination temperature rather than of Mo content.

The following conclusions can be drawn from the characterization of rounded pellets:

- Modification of the extrudate shape by further rounding into spherical pellets prior to calcination resulted in an increase in attrition resistance from 88.0-96.0% for cylindrical extrudates to 91.7-98.9% for rounded spherical pellets. All rounded zinc titanate formulations with a 2.0 Zn:Ti ratio had attrition resistances in the range 96.7-98.9%, which is higher than those with lower zinc-to-titanium ratios.
- Addition of up to 10% organic burnout material was necessary in the Mo-doped formulations in order to maintain the SPV above the desired 0.20 cc/g after calcination while maintaining satisfactory chemical reactivity. The presence of organic burnout material did not affect the median pore diameter, MPD, of the formulations.
- Differences in chemical reactivity between cylindrical extrudates and rounded spherical pellets during single-pellet TGA tests were explained by differences in SPV, rather than by differences in the presence or absence of molybdenum.
- Differences in mechanical durability of rounded spherical pellets during bench-scale tests were explained by the presence or absence of molybdenum. Spalling and pellet physical degradation during bench testing were inhibited by the addition of molybdenum and the resulting modification of the pore structure and sulfur distribution profile within the pellet. Straight zinc titanate pellets, having only bentonite as a binder, exhibited heavy spalling, while those pellets with added molybdenum showed very little or no spalling at all over the whole range of Zn:Ti ratios (1.0-2.0) and 10 cycles of testing.
- During bench-scale testing, pre-breakthrough H_2S concentrations were below 20-25 ppmv at 1% H_2S in the inlet gas, regardless of the concentration of Mo additive. This desulfurization level corresponds to 99.8% H_2S removal from the gas stream. Sulfur loading in the sorbent gas

inlet samples removed at the 200 ppm H₂S breakthrough ranged from 8% to 35% of the theoretical value for zinc titanates, with a bed average value of approximately 12% to 14% for the Mo-doped formulations

- Levels of carbon, residual sulfur, and sulfate sulfur were low enough after the tenth regeneration in the bench reactor and did not represent a concern during scaleup, provided that similar conditions are maintained.

The overall conclusion of the Option 2 program work is that the more promising formulations were those with a 2:1 Zn:Ti ratio containing molybdenum additive. Formulation 2A1.7M (UCI formulation L-3787M), containing 2.5% MoO₃ (1.7% Mo) additive, was the best performer in the family of sorbents tested because of a good balance of chemical reactivity, mechanical strength, and pore structure. The 2:1 zinc-to-titanium ratio is the optimum ratio for the formation of the stoichiometric zinc titanate, Zn₂TiO₄, crystalline structure with the highest sulfur capacity. The molybdenum concentration was not optimized over the range 0-10% MoO₃ and, hence, a lower molybdenum concentration (<1.7% Mo reported here) may be optimum for desulfurization sorbents. The Mo additives were found to modify the pore structure of the pellet by increasing the MPD, a result thought to be favorable for the accommodation of the products zinc sulfide or zinc sulfate (of higher molar volumes than zinc oxide) in the zinc titanate structure thus minimizing pellet internal stresses induced during reaction. MoO₃ also reacts with hydrogen sulfide forming Mo sulfide, MoS₂, which in turn is well known for being catalytically active in hydrodesulfurization and hydrodenitrification reactions in the petroleum industry (Sittig, 1978).

RECOMMENDATIONS

Based on the overall conclusions presented in the previous section, it is evident that the presence of molybdenum oxide enhances the desired properties for moving-bed sorbents. However, a careful choice of molybdenum concentration is necessary to achieve the optimum performance of Mo-doped formulations. Since Mo concentrations were tested at discrete points in the range 0-10% MoO₃ (0.8-6.7% Mo) under the Option 2 program, more work is needed to optimize the sorbent properties with respect to molybdenum concentrations. It is recommended that this work be performed using molybdenum concentrations between 0 and 2.5% MoO₃.

The addition of molybdenum prior to calcination up to 1600 °F was found to be useful in modifying the pellet pore structure. Since bench-scale testing was restricted to temperatures up to 1400 °F, no bench-scale sorbent performance was evaluated above this temperature. Routine regeneration operation above 1500 °F will require further evaluation of the sorbent for potential molybdenum evaporation, excessive pellet sintering, or appearance of pellet cohesiveness (i.e., stickiness) caused by formation of low-temperature eutectic phases at the contact points. The use of structural promoters to stabilize the

molybdenum phase after calcination may further increase the temperature window of operation of Mo-doped zinc titanate above 1500-1600 °F. Further study in this area is highly recommended.

A second approach to altering the pore structure and mechanical properties of sorbents is to use substrate modifiers. During desulfurization with zinc titanate, the TiO_2 phase acts as an inert microscopic support that keeps the pellet structure in place while the ZnO is undergoing phase changes and forming sulfides and/or sulfates. The selection of materials that will increase the strength of TiO_2 is worth considering for future sorbent preparation. Close work with sorbent manufacturers is very critical for evaluating other avenues of sorbent fabrication and to keep manufacturing costs at reasonable levels.

To summarize: It was found during the course of performance of the Option 2 program that the use of additives for the modification of the pore structure of zinc titanate was beneficial within the range of calcination temperatures (1400-1600 °F) and Mo concentrations (0-2.5% MoO_3). Further work is highly recommended to optimize this new family of Mo-containing sorbent materials or to explore new non-Mo containing additives that perform the same functions of pore modification and mechanical strengthening.

SECTION 1 INTRODUCTION

1.1 CONTRACT OBJECTIVES

The objective of this contract is to identify and test sorbent fabrication methods and chemical compositions that enhance the long-term chemical reactivity and mechanical strength of zinc ferrite and other novel sorbents for moving-bed, high-temperature desulfurization of coal-derived gases. Zinc ferrite was studied under the base program of this contract while novel sorbents, particularly zinc titanate-based sorbents, are being studied under the remaining optional programs. This topical report summarizes only the work performed under the Option 2 program which addresses the current development of zinc titanate sorbents.

Desired properties to be enhanced for moving-bed sorbent materials are: (1) high chemical reactivity (sulfur absorption rate and total sulfur capacity), (2) high mechanical strength (pellet crush strength and attrition resistance), and (3) suitable pellet morphology (e.g., pellet size, shape, surface area, and pore size distribution). In addition, it is desired to maintain the sorbent properties over extended cyclic use in moving-bed systems.

1.2 BACKGROUND

1.2.1 High-Temperature Desulfurization Systems

The integrated gasification combined cycle (IGCC) power system using high-temperature coal gas cleanup is one of the most promising advanced technologies for the production of electric power from coal in an environmentally acceptable manner. In conventional cleanup systems, costly heat exchangers are necessary to cool down the gases for cleaning. Unlike these conventional low-temperature cleanup systems, where the coal gas from the gasifier has to be cooled down from 1000-2000 °F to below 300 °F, high-temperature coal gas cleanup systems can be operated at near 1000 °F or higher, i.e., at conditions compatible with the gasifier and turbine components in the IGCC system. The result is a more efficient overall system (Corman, 1986). A description of high-temperature desulfurization systems is given below.

Over the last decade, the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) has sponsored development of various configurations of high-temperature desulfurization systems (Bossart et al., 1990). Fixed-bed systems (Haldipur et

al., 1989) have operated using several fixed-bed reactors of sorbent using one of the approaches that, at any given time, one reactor is undergoing desulfurization of the coal gas, one is undergoing oxidative regeneration, and at least one other is undergoing reductive regeneration or oxidative regeneration. The need for a minimum of three reactor vessels— all rated for high pressure/high temperature operation— is determined by the restriction that the regeneration step may not be easily accomplished in less time than the absorption step because of the highly exothermic nature of regeneration and the need to control the maximum sorbent temperature.

Fluidized-bed systems (Gangwal and Gupta, 1991) are also under development with DOE/METC sponsorship. They have the advantage over fixed-bed systems in that better temperature control can be achieved during regeneration because of better gas-solid mixing. However, sorbents are subject to higher levels of attrition in a fluidized bed, and stronger sorbent materials are necessary. Current development work on fluidized beds for desulfurization is at the bench scale.

Moving-bed systems are under development at GE (Cook et al., 1991). Pelletized sorbents move slowly between the absorber and regenerator vessels. Unlike fixed-beds, moving beds can decouple the vessel construction requirements for the two reactions (sulfur absorption and sorbent regeneration) by carrying them out in two separate vessels such that lower pressure regeneration (compared to full pressure in the absorber) reduces the regeneration system capital costs.

1.2.2 Sorbent Development

GE is developing a moving-bed, high-temperature desulfurization system for IGCC power systems in which mixed-metal oxides are currently being used as desulfurization sorbents (Cook et al., 1991). In addition to zinc ferrite, zinc titanate and other novel mixed-metal oxides are currently being considered as promising sorbents (Ayala and Gal, 1991), particularly for cases of highly reducing coal gases where the use of iron-containing sorbents such as zinc ferrite, are limited by the formation of iron carbides and other iron compounds that result in sorbent degradation (Geizer, 1983).

In order for a metal oxide to be considered suitable for high-temperature desulfurization, the material must exhibit desirable properties in the following areas:

1. Rate of H_2S absorption and low equilibrium H_2S achievable in the gas phase
2. Ease of regeneration of the sulfide species formed during absorption
3. Likelihood of sulfate formation and ease of sulfate decomposition
4. Metal/sorbent evaporation and temperature of incipient evaporation

5. Formation of low-melting eutectic phases
6. Reduction to metal during absorption due to highly reducing coal gases
7. Interactions between active metal oxide, stabilizers, and support
8. Sulfur loading of metal oxide and sulfur loading capacity limitations
9. Disposal of spent sorbent metals and deleterious effects of volatilized sorbent metals to other IGCC components (e.g., turbine)
10. Cost of support and/or cost of active metal oxide

The feasibility of operating a moving-bed high-temperature desulfurization system in an economically competitive and technically feasible manner currently restricts its use to a temperature window between 800-1400 °F and pressures above 10 atmospheres during absorption. Operation below 800 °F does not take full advantage of higher system efficiency compared to low-temperature cleanup systems, while operation above 1400 °F requires a tradeoff between more sophisticated material properties/higher capital costs and reliability of process operation. Although this window of operation may expand in the future, these current boundaries of operation are considered realistic.

Preliminary to the preparation of mixed-metal oxide sorbents under the Option 2 program, a review of the literature was done to identify pure metal oxides and combinations of metal oxides that had been evaluated in the past for high-temperature desulfurization of coal gases. In most laboratory studies of pure and mixed-metal oxides, the feasibility of removing H₂S to low levels (e.g., < 50 ppmv) from coal gases has been shown to be technically viable, but the major limitations for large-scale use may be the lack of long-range chemical or mechanical stability of the sorbents under reducing gas atmospheres or the difficulty of regeneration over many cycles.

Early thermodynamic predictions of stable phases for pure oxides under coal gas environments have been supported by more recent experimental data, including the data on mixed-metal oxides. A total of 28 metal oxides were initially considered by Westmoreland and Harrison (1976) in thermodynamic calculations of equilibrium among solid and coal gas phases. Of the original 28 oxides considered, many were discarded by the authors because of inadequate desulfurization (i.e., low sulfur capture). For instance, Al, Ce, Cr, Mg, Ti, and Zr formed unreactive oxides or carbonates throughout the temperature range of 360 to 1560 °C and 20 atm of pressure. Alkali metals Li, Na, K also formed unreactive carbonates under coal gas environments. Inadequate desulfurization was predicted for Ag, La, Ni, and Sb. Finally, Bi, Cd, Pb, and Sn were rejected because excess metal oxide could be reduced to a low-melting metal.

Experimental studies of mixed-metal oxides performed at the Massachusetts Institute of Technology, MIT, (Flytzani-Stephanopoulos et al., 1984; Flytzani-Stephanopoulos et al., 1987; Lew et al., 1989), Research Triangle Institute, RTI, (Gangwal and Harkins 1987, 1988), Electrochem (Jalan, 1989), U.S. Dept. of Energy/Morgantown Energy Technology Center, DOE/METC (Grindley, 1991), Texaco (Leininger et al., 1991), and the Institute of Gas Technology, IGT, (Anderson and Berry, 1987) were also included in our evaluation of metal oxides. Mixed-metal oxide sorbents have been studied in the past both as straight zinc titanates, (e.g., Zn_2TiO_4 and $\text{Zn}_2\text{Ti}_3\text{O}_8$) (Woods et al., 1989) or as combinations of oxides of vanadium, copper, manganese, cobalt, and others; see for instance (Flytzani-Stephanopoulos et al., 1987).

From the theoretical predictions of Westmoreland and the more recent experimental studies of pure metal oxides presented above, oxides of the following metals appear to meet, at least in part, our requirements for desulfurization in the temperature range 800-1300 °F (~400-700 °C): copper, iron, manganese, molybdenum, vanadium, and zinc. Iron-containing oxides, such as zinc ferrite, cannot be used for highly-reducing coal gases because eventually they tend to undergo excessive reduction to wustite, or even metallic iron, including formation of iron carbide compounds (Gangwal and Gupta, 1991) which promote sorbent decrepitation. Hence, iron-containing oxides would not be considered in this program. A closer look at the remaining five metals was taken to explore their advantages and shortcomings from previous tests by various investigators.

Copper:

The use of copper has been thought attractive for higher temperature applications (up to 1472 °F, 800 °C) in combination with iron or other active oxide and alumina (as in copper-iron-alumina systems) (Flytzani-Stephanopoulos et al., 1987) because copper maintains desulfurization capabilities in excess of 1650 °F. However, high exothermic reduction temperatures may hinder the application of copper for reducing coal gases where copper is present in the metallic form over the entire temperature range. At MIT, researchers have studied the Cu-Fe-Al-O systems and have found that Cu-based sorbents do not suffer from metal volatilization up to 800 °C (Flytzani-Stephanopoulos et al., 1987). Addition of alumina reduces the rate of reduction of Fe_2O_3 to FeO and CuO to Cu metal, both of which are undesirable. The contribution of alumina to undesirable sulfate retention (from absorption of SO_2) in the sorbent is negligible.

The major disadvantages of copper are related to the highly exothermic oxidation reaction from metal (the predominant form of copper in reducing coal gas) to oxide, which is very difficult to control in large-scale systems. Another current limitation of impregnated copper sorbents is that only relatively small amounts of copper can be impregnated onto a support such as alumina without inducing mechanical stresses during cycling. Recent work at DOE/METC (Gasper-Galvin and Atimtay, 1991) has demonstrated the stability of copper oxide impregnated on zeolites, but the sulfur capacities (i.e., mass of sulfur per unit mass of sorbent) are lower than for bulk metal oxides.

Manganese:

The main advantages of manganese are asserted to be its high reactivity for sulfur capture, decomposition at 1200 °F of any sulfates formed during regeneration, and reproducible sulfur capture over several cycles when combined with copper (Jalan and Desai, 1989). Manganese oxide stability and high fractional desulfurization are predicted for temperatures in excess of 1800 °F. Below 750 °F, MnCO_3 is the stable solid, while above 750 °F, MnO is stable (Westmoreland and Harrison, 1976). On the one hand, manganese shows desulfurization potential in the temperature range of 1100-1300 °F (~600-700 °C) where metal oxides currently known to be reactive with H_2S are unsatisfactory. On the other hand, the main disadvantage for current hot gas cleanup systems operating in the 900-1100 °F range is the high temperature needed for complete regeneration of the manganese sulfide (above 1517 °F, 825 °C). Degradation of manganese in copper/manganese systems occurs with high manganese contents, therefore the metal has to be supported or mixed with other active desulfurization oxides (Jalan and Desai, 1989). Disposal of heavy metals is also an important issue, and manganese emissions are strictly regulated by Title III of the 1990 Amendments to the Clean Air Act.

Electrochem (Jalan et al., 1989) has studied $\text{Cu}_2\text{O}\cdot\text{MnO}$ systems and found that manganese-rich systems suffered a very rapid decay in reactivity. Stoichiometric mixtures gave predictable breakthrough curves. The best performer was a copper-rich sorbent that exhibited the most consistent performance over several cycles. Mixed-metal sulfates of Cu and Mn are unstable at approximately 1200 °F, thus the regeneration scheme has to be carried out above this temperature.

Molybdenum:

Pure molybdenum oxide cannot be used for desulfurization at the temperatures of interest in moving-bed hot gas cleanup systems (i.e., $T > 900$ °F) because of vaporization of molybdenum at $T > 1100$ °F if not stabilized on a support or matrix (Flytzani-Stephanopoulos et al., 1985). A support is needed to keep the surface area constant when a Mo eutectic is formed at these high temperatures. However, copper-molybdenum sulfides formed during sulfidation of copper-molybdenum oxide mixtures have been shown to be easily regenerated when fabricated in an alumina support at MIT. In a similar fashion, one could consider fabricating other mixed-metal oxide sorbents (such as zinc titanates) with small additions of molybdenum as possible combinations for stabilization of zinc and molybdenum in a titanium matrix. At MIT, a high degree of desulfurization, even at temperatures above 1470 °F, was achieved with molybdenum, and easy regenerability was obtained with no evaporative losses of Mo when regenerating with dry gases (i.e., no steam). The temperature at which fractional desulfurization drops below 95% puts an upper bound to the practical temperature for desulfurization (~1562 °F, 850 °C), which corresponds closely to the temperature at which MoO_2 is reduced to the metal. This upper temperature bound is sufficiently high for current operation of moving-bed desulfurization systems.

Vanadium:

V_2O_3 is the stable form of vanadium when there is excess metal in the presence of coal gases. Essentially 100% desulfurization, with V_2S_3 as the sulfided product, is predicted up to the melting temperature of V_2S_3 near 1200 °F (Westmoreland and Harrison, 1976). At MIT, Flytzani-Stephanopoulos et al. (1984) have studied the system Zn-V-Al-O. ZnO/V_2O_5 alone forms a low melting eutectic at about 1220 °F (661 °C). This melt is held in place by the addition of alumina. Higher regeneration conversions were obtained by dry regeneration instead of steam regeneration. At high H_2O/H_2S ratios during absorption, the sulfur uptake by vanadium was minimal. Vanadium stabilizes zinc onto the support, and regeneration at high temperature (1382 °F) is feasible with no sintering, no V loss, and no elemental sulfur formation. Addition of vanadium also promotes formation of elemental sulfur in zinc ferrite (Akyurtlu and Akyurtlu, 1992).

For the use of vanadium-based sorbents in hot gas cleanup systems, a major drawback, and perhaps an unresolvable one, is that vanadium ions released in the gaseous fuel, even at concentrations of a few ppm, promote type-I hot corrosion in gas turbines just as much as alkali metals do and even more than sulfur species. Hot corrosion of alloys generally occurs by accelerated oxidation of the alloy in the presence of a molten salt (Shores and Luthra, 1990).

Zinc

The use of zinc oxide by itself is limited by zinc vapor formation at approximately 1300 °F (700 °C) under reducing gas environments (Westmoreland and Harrison, 1976). Research Triangle Institute (Gangwal and Harkins, 1988, Gangwal et al., 1988) and MIT (Lew, 1989) have studied the Zn-Ti-O system, which shows higher stability to zinc evaporation. DOE/METC (Gasper-Galvin and Atimtay, 1989) have explored supported ZnO on zeolites for high attrition resistance in fluidized beds also. A wet impregnation technique has been used. No resistance to gas diffusion existed, and no significant losses caused by zinc evaporation were observed at 1000 °F. Moreover, no significant deterioration because of zinc evaporation or dealumination of the zeolite structure was observed up to 1600 °F. Future work will be geared toward studying high silica zeolites. A major drawback of zeolite-supported sorbents is the low sulfur capacity per unit mass of sorbent, a result of low metal loadings. Zinc in the form of zinc titanate is currently the most promising material for novel sorbents because of less tendency towards zinc evaporation under reducing gas environments, ease of regeneration below 1300 °F, high sulfur loading, and absence of formation of low-temperature eutectics.

In summary, from an evaluation of predictions and experimental studies of metal oxide sorbents, zinc titanates are considered very promising sorbent materials for high-

temperature desulfurization. The use of manganese or vanadium brings too many potential problems to be solved in this project (e.g., regeneration of manganese at above 1500 °F requires sophisticated alloys for handling the hot gases, and vanadium induces high-temperature corrosion in gas turbines, even as a few ppm in the coal gas). Similarly metal oxides on alumina or any other type of support that is mostly inert solid (e.g., 75% inert) would be very costly and ineffective to transport in a moving-bed system. On these grounds, zeolites and alumina-based sorbents with less than 25% active oxides are also ruled out from consideration in this program.

From the above discussion, it is reasonable to conclude that the most promising formulations to study under the present program would be those containing Zn and Ti as in zinc titanates. Modification of the properties of zinc titanates can be studied by incorporation of molybdenum or other modifiers into the mixture to make Zn-Ti-Mo combinations.

1.2.3 Zinc Titanate Chemistry

When calcining mixtures of ZnO and TiO₂ powders at high temperature, three crystalline structures of zinc titanate may form depending on the ratio of zinc to titanium: ZnTiO₃, Zn₂Ti₃O₈, or Zn₂TiO₄. The highest zinc-to-titanium molar ratio zinc titanate, Zn₂TiO₄, would be the most desired crystalline phase from the point of view of its higher sulfur capacity. For this case, the overall reaction occurring during H₂S absorption from coal gases is as follows:

A secondary reaction that may take place during desulfurization is the reduction of zinc titanate by hydrogen and carbon monoxide to zinc metal, with the subsequent loss of Zn caused by evaporation. Zinc metal evaporation becomes significant if desulfurization above 1350 °F is desired (Gangwal et al., 1988). Since the GE moving-bed system carries out H₂S absorption around 1000 °F, zinc metal evaporation is not a concern. When regeneration is carried out under dry conditions in the presence of diluted air, the following reaction takes place:

In addition to the regeneration reaction, zinc sulfate formation may occur during regeneration, favored below 1200 °F (648 °C), and at high O₂ and SO₂ concentrations.

Zinc sulfate formation is undesirable because the sulfate occupies more volume than the sulfides in the pores (producing internal joint stresses) and decomposes during subsequent absorption releasing SO₂. Zinc sulfate thermally decomposes in the range of 1112 °F (600 °C) (Wheast and Astle, 1978) to 1364 °F (740 °C) (Perry and Chilton, 1973). These decomposition temperatures increase at higher concentrations of SO₂ and O₂. Hence, a regeneration scheme where the temperature is high enough at the end of regeneration to decompose sulfate is desired.

1.3 OPTION 2 PROGRAM DESCRIPTION

The goal of the Option 2 program was to identify and to test sorbent fabrication methods and sorbent chemical compositions that enhance the long-term chemical reactivity and mechanical strength of novel zinc titanate sorbent formulations for moving-bed, high-temperature desulfurization of coal-derived gases. The work was divided into five tasks with the following objectives:

Task 12 — Experimental Test Plan

To revise the experimental test plan according to the proposed work.

Task 13 — Sorbent Preparation

To prepare and characterize various formulations of novel sorbent suitable for moving-bed desulfurization of hot coal gases.

Task 14 — Bench-Scale Testing

To test 10 formulations of novel sorbents through at least 10 cycles of operation per the approved test plan.

Task 15 — Bench-Scale Test Analysis

To perform analyses of sulfided and regenerated sorbents extracted from the bench-scale reactor and to determine the amount of deterioration in mechanical as well as chemical properties that occur because of cyclic testing.

Task 16 — Topical Report

To provide a report containing detailed analysis of sorbent characteristics before and after long-term cyclic testing.

SECTION 2 EXPERIMENTAL PROCEDURES

2.1 SORBENT FABRICATION PARAMETERS

Zinc titanate sorbents were prepared by United Catalysts, Inc., (UCI) first as cylindrical extrudates and then as rounded pellets. The extrudates were prepared to screen a number of chemical formulations for chemical performance in desulfurization. The rounded pellets were prepared later to achieve a desired balance of mechanical properties (crush strength and attrition resistance) and chemical properties. The details of the preparation procedure are proprietary to UCI, but in general, the procedure involves mixing of the metal oxide powders followed by forming into shape and calcining at high temperature so that the mixed-metal oxide structure is created by solid-state reactions. The rounding procedure, when used in addition to extrusion, produces stronger pellets and has been shown to aid in the preparation of zinc ferrite sorbents more suitable for moving-bed applications (Ayala and Gal, 1991).

Fabrication variables that were studied during preparation are shown in Table 1. For all formulations, calcination time was held constant at two hours. Pellet size was generally held constant at 3/16 in. diameter and 1/2 in. length for cylindrical extrudates and 5-6 mm spheres for rounded formulations. One formulation, L-3140M, was prepared as a larger 8.3-mm diameter pellet.

Table 1. Cylindrical Extrudate Fabrication Variables

Fabrication Variable	Range
Zn:Ti molar ratio	0.8-2.0
Bentonite Binder:	2-3% wt.
MoO ₃ Additive:	0-10.0% wt.
Organic burnout additive	0-10% wt.
Calcination temperature:	1400-1800 °F (760-982 °C)

Formulation L-3140 (a cylindrical extrudate of zinc titanate containing a 1.5 Zn:Ti molar ratio and 3% bentonite binder/10% organic burnout additive) was selected by DOE as the baseline formulation for the purpose of evaluating performance of new formulations. Several guidelines were used to assess sorbent performance and to identify superior

formulations for moving-bed systems. Among the guidelines, a formulation had to meet mechanical strength requirements (crush strength and attrition resistance), chemical reactivity requirements (as measured by single-pellet thermo-gravimetric analysis, (TGA)), and pellet physical morphology requirements (size, shape, and pore structure). Crush strength is defined as the maximum dead-weight load a pellet withstands on compression prior to fracture; for cylindrical extrudates, the crush strength is divided by the length of the cylinder. Attrition resistance is defined as 100% minus the attrition loss when measured according to the ASTM D4058-81 method. Pore size distribution by mercury porosimetry, including median pore diameter (MPD) and specific pore volume (SPV) in cc/g of sorbent, and single-pellet TGA chemical reactivity were to be measured at Research Triangle Institute (RTI).

When calcining mixtures of ZnO and TiO₂ powders at high temperature, three crystalline structures of zinc titanate may form depending on the ratio of zinc to titanium: ZnTiO₃, Zn₂Ti₃O₈, or Zn₂TiO₄. The highest zinc-to-titanium molar ratio zinc titanate, Zn₂TiO₄, would be the most desired crystalline phase because of its higher sulfur capacity.

2.2 CHARACTERIZATION TECHNIQUES

2.2.1 Kinetic Performance

2.2.2.1 TGA Chemical Reactivity

Chemical reactivity of single-pellet sorbent samples was determined by measuring pellet sulfur capacity and regenerability in a thermogravimetric analyzer at RTI. The rate of sulfidation or regeneration was determined indirectly by relating pellet weight gained or lost as a function of time. Details of the procedure have been described elsewhere (Woods et al., 1989).

The TGA uses a Cahn Instrument Model 1000 balance having a sample capacity of up to 100 g, and capable of measuring weight changes with an accuracy of $\pm 1 \mu\text{g}$. The gas compositions used for sulfidation and regeneration in the Option 2 program are shown in Table 1. The sulfidation gas compositions simulated air-blown, fixed-bed gasifier coal gas and oxygen-blown, entrained-bed gasifier gas; the regeneration gas composition was the same for all cases. The TGA monitors the weight changes of a single pellet suspended from a hangdown wire attached to the electrobalance mechanism. Additional pellets (up to four) can be placed downstream on a stainless steel screen supported on the thermowell so that a total of five pellets can be exposed to the same gaseous environment and enough sample is available for further chemical analysis. The test procedure consists of a 30-minute reduction at 1022 °F (550 °C) in clean reducing gas (i.e., no H₂S) prior to each sulfidation. Sulfidation is then conducted at 1022 °F (550 °C) with 3% H₂S for both the half-cycle (i.e., sulfidation) runs and the 1½-cycle (i.e., sulfidation-regeneration-

sulfidation) runs. This concentration enabled us to complete a TGA run in one day or less. Tests are conducted for a minimum of three hours or until no weight change occurs.

After full sulfidation, oxidative regeneration is carried out at 1250 °F with 4% O₂ in N₂. At this point the run is interrupted, if necessary, to remove one pellet from the screen for characterization of pore size distribution. The remaining pellets are then subjected to a second reduction and sulfidation prior to termination of the run. All tests were conducted at 1 atm pressure. All of the sample pellets tested were selected to be of nearly equivalent size so that the comparison of results would be meaningful.

Table 2. Gas Compositions (Volume %) for TGA Tests

	Simulated air-blown gasifier gas	Simulated O ₂ -blown gasifier gas	Regeneration gas
H ₂	15.0	25.1	
CO	8.0	60.9	
CO ₂	11.0	3.0	
H ₂ O	30.0	3.0	
H ₂ S	3.0	3.0	
N ₂	33.0	5.0	96.0
O ₂			4.0

2.2.3.2 Bench-Scale Reactor Testing

Chemical reactivity was also determined by measuring sorbent sulfur loading (defined as grams of sulfur absorbed per 100 g of fresh sorbent) in fresh and in cycled samples from the bench-scale reactor. Only formulations that exhibited a good balance of chemical and mechanical performance as fresh pellets were selected for further cyclic testing in a bench-scale reactor system. Details of the bench-scale reactor and procedures associated with it have been given before (Ayala, 1991). The important aspect of the bench-scale testing is that both absorption and regeneration were conducted in a packed-bed reactor simulating the time/temperature environment in which the sorbent would be exposed in a typical full-scale moving-bed system. Absorption was carried out at 1000 °F (538 °C) using any of three gas compositions (Table 3), all having a deliberately high 1% H₂S concentration to accelerate testing.

Three simulated coal gas compositions were selected for bench-scale reactor testing (Table 3) to approximate gasifier gas compositions and to provide a means to screen the effect of: (1) reducing power, (CO + H₂)/(CO₂ + H₂O), (2) total concentration of (CO + H₂), and (3) steam concentration on the performance of zinc titanate sorbents.

Table 3. Simulated Coal Gas Compositions for Bench-Scale Testin

Component	Composition 1 (%)	Composition 2 (%)	Composition (%)
CO	8	39	33
CO ₂	11	10	0.4
H ₂	16	30	16
H ₂ O	30	20	10
H ₂ S	1	1	1
N ₂	34	0	39.6
Reducing Power	0.61	2.33	4.70
(CO + H ₂)%	24	69	49

Composition 1 is a high-steam, low-CO, low-H₂ gas composition, typical of a Lurgi fixed-bed gasifier. Composition 2 is a simulated oxygen-blown composition with high CO and high H₂ concentrations, but intermediate reducing power. This composition is different from that used in the TGA tests (O₂-blown gasifier gas in Table 2) so that carbon deposition on the stainless steel lines of the reactor system would be minimized and long-term operation could be carried out. Composition 3 is a high-CO, low-H₂, low-CO₂ composition that has nitrogen included to decrease the total (CO+H₂) concentration below that of gas composition 2 while increasing the reducing power. During bench-scale testing the sorbent chemical composition designation adds the suffix 1, 2, or 3 according to the simulated coal gas composition of Table 3 used in the bench-scale tests.

The oxidative regeneration was carried out between 1000 °F (538°C) and 1250 °F (677 °C) and 1-21% oxygen during the early phases of regeneration, and at 1400 °F (760 °C) during the final phase simulating the temperature rise of the sorbent bed (triggered by the exothermic oxidation reaction) in the large-scale system.

2.2.4 Chemical Composition

Chemical composition analyses were conducted on both fresh sorbents and sorbents extracted from the bench-scale reactor system after multicycle testing. Analyses concentrated on the determination of the elemental composition, solid crystalline phase composition, microstructure, and elemental distribution across the pellet cross section.

The crystalline phase composition of the sorbent was determined using x-ray diffraction (XRD). The instrument used for analysis is a Rigaku θ/θ automated diffractometer with a 43-position sample changer. The lower detection limit for most constituents is of the order of 1%. Sometimes a Laue camera was used to obtain x-ray diffractograms over a 24-hr period, especially when the diffraction reflections were weak.

Microstructure and qualitative elemental distribution of elements (such as zinc, titanium, sulfur, and molybdenum) across the pellet cross section (i.e., elemental maps) were determined by scanning electron microscopy (SEM) coupled to energy dispersive x-ray analysis (EDX), respectively. Semiquantitative analysis for zinc, titanium, molybdenum, and sulfur at various locations within a pellet was performed using electron microprobe analysis (EMA). SEM/EDX and SEM/EMA allowed us to determine the extent of chemical inhomogeneities in the cross section of a pellet caused by exposure to simulated coal gases at high temperature. Quantitative average elemental analysis of whole pellets was determined by inductively-coupled plasma (ICP) atomic emission spectroscopy or proton-induced x-ray emission (PIXE) spectroscopy; qualitative and quantitative elemental analyses for whole pellets was determined by x-ray fluorescence (XRF) spectrometry. The average content of total carbon and total sulfur in single pellets was determined by total carbon and total sulfur analyses by Commercial Testing and Engineering, Co. (South Holland, Illinois) using a LECO induction furnace analyzer.

2.2.5 Mechanical Strength

The mechanical strength of sorbents, crush strength, and attrition resistance, was measured by GE Environmental Services, Inc. (GEESI). Crush strength (i.e., deadweight load) was measured by subjecting single pellets to an increasing load until breakage occurred, and the measured force was averaged over a minimum of 20 pellets. Attrition tests were performed at ambient temperature and at 1000 °F in a rotating cylinder, and the weight loss of sorbent on attrition was measured according to a modified ASTM D4058-81 method, "Attrition and Abrasion of Catalysts and Catalysts Carriers." Modifications of the test apparatus to withstand high temperature have been described previously (Ayala, 1991, Ayala and Gal, 1991). In this study, attrition resistance is defined as 100% minus the percent loss on attrition. Percent loss on attrition is defined in the above ASTM D4058-81 method by calculating the percent difference in measured weight of the sample retained in a No. 20 (850 μ m) ASTM sieve before and after rotating the cylinder at 60 rpm for 30 minutes. Attrition rate is defined as the rate of change of loss on attrition with respect to time.

2.2.6 Physical Morphology

2.2.6.1 Pore Size Distribution by Mercury Porosimetry

Pore size distributions, including the calculation of median pore diameter (MPD) (i.e., diameter at 50% intrusion) and specific pore volume (SPV) (i.e., pore or void volume per unit mass of sorbent) were determined by RTI using a Micromeritics (Model AutoPore 9220II) mercury porosimeter (Woods et al., 1989).

2.2.6.2 Sieving

Sieving was performed using ASTM standard sieves in order to determine the size distribution of solids before and after attrition tests. Pellet size classification was divided into three categories: whole pellets, pellet pieces or aggregates (i.e., those particles or pellet pieces larger than 20 mesh but smaller than whole pellets), and fines (i.e., powder material below 850 μm , or 20 mesh). This classification allowed us to quantify the degree of degradation that whole pellets had experienced by fracture or other means even if not resulting in the formation of fines as defined by the ASTM D4058-81 test.

SECTION 3 RESULTS AND DISCUSSION

3.1 CHARACTERIZATION AND TESTING OF CYLINDRICAL EXTRUDATES

3.1.1 Fresh Cylindrical Extrudate Formulations

Nineteen zinc titanate formulations were prepared as cylindrical extrudates in the first phase of the Option 2 program. Tables 4 and 5 show the results obtained during characterization of the fresh cylindrical formulations. Formulation L-3140, the baseline formulation, was previously prepared by UCI for DOE and was selected by DOE to assess the relative performance among new formulations. Formulations are presented in order of increasing Zn:Ti molar ratio, concentration of bentonite binder, concentration of molybdenum oxide additive, and calcination temperature used. For all formulations, the calcination time was held constant at 2 hours. Formulations presented between any two consecutive horizontal bars have the same chemical composition prior to calcination.

3.1.2 Chemical Composition

Table 4 shows the chemical composition and calcination conditions used in the fabrication of cylindrical extrudates. Formulations containing a 0.8 Zn:Ti ratio produced mixtures of several stoichiometric titanates: $\text{Zn}_2\text{Ti}_3\text{O}_8$, ZnTiO_3 , and Zn_2TiO_4 , with the relative amount of each depending on temperature. Formulations containing a 2.0 Zn:Ti ratio exhibited exclusively the Zn_2TiO_4 structure. The advantage of using higher Zn:Ti ratios is, of course, the higher sulfur capacity per unit mass of sorbent.

Except for formulation L-3721C, having a low Zn:Ti ratio and calcined at low temperature, the crystalline form of the MoO_3 additive was absent after calcination, even at 10% additive. These observations suggest that, given enough time/temperature during calcination, Mo either dissolves within the zinc titanate structure forming zinc-molybdenum compounds (e.g., ZnMoO_3) or, alternatively, becomes an amorphous phase to x-ray diffraction.

XRF quantitative analyses of molybdenum were performed on powdered formulations (without extrusion) before and after calcination where the formulation initially contained 10% MoO_3 (melting point 795 °C) at 0.8 and 2.0 Zn:Ti molar ratio. After calcination at high temperature (1750-1800 °F), the molybdenum content decreased from 10.0 to 7.7%, as a result of vaporization of unreacted MoO_3 , while at the lower temperature (1400-1550 °F), the molybdenum concentration remained constant in the range 10.0-10.8% (i.e.,

within experimental error). Standard XRD analysis showed no matching patterns corresponding to zinc molybdates.

Table 4. Chemical Properties of Fresh Cylindrical Extrudates

Formulation	Zn:Ti Molar Ratio	% Bentonite	% MoO ₃	Temp °F	Zinc Titanate XRD Major Phase	Other Phases
L-3720A	0.8	2	0	1600	Zn ₂ Ti ₃ O ₈ (67%) ZnTiO ₃ (33%)	TiO ₂ , ZnO
L-3720B	0.8	2	0	1800	ZnTiO ₃ (91%) Zn ₂ TiO ₄ (?)	TiO ₂
L-3721C	0.8	2	10	1450	ZnTiO ₃ , Zn ₂ Ti ₃ O ₈	TiO ₂ , MoO ₃
L-3721A	0.8	2	10	1600	Zn ₂ TiO ₄ , ZnTiO ₃ (?)	TiO ₂
L-3721B	0.8	2	10	1800	Zn ₂ TiO ₄	TiO ₂
L-3140	1.5	3.0	0	1550	Zn ₂ TiO ₄ , Zn ₂ Ti ₃ O ₈	
L-3722A	2	3	0	1600	Zn ₂ TiO ₄ , ZnTiO ₃ (?)	TiO ₂
L-3722B	2	3	0	1800	Zn ₂ TiO ₄	
L-3767A	2	3	0	1400	Zn ₂ TiO ₄	TiO ₂ , ZnO
L-3767B	2	3	0	1800	Zn ₂ TiO ₄	
L-3766A	2	3	1.2	1400	Zn ₂ TiO ₄	
L-3766B	2	3	1.2	1600	Zn ₂ TiO ₄	
L-3766C	2	3	1.2	1800	Zn ₂ TiO ₄	
L-3765A	2	3	2.5	1400	Zn ₂ TiO ₄	
L-3765B	2	3	2.5	1600	Zn ₂ TiO ₄	
L-3764A	2	3	5	1400	Zn ₂ TiO ₄	
L-3764B	2	3	5	1600	Zn ₂ TiO ₄	
L-3723C	2	3	10	1450	Zn ₂ TiO ₄	Trace ZnO, TiO ₂
L-3723A	2	3	10	1600	Zn ₂ TiO ₄ ZnTiO ₃ (?)	
L-3723B	2	3	10	1800	Zn ₂ TiO ₄	Trace ZnO, TiO ₂

Table 5. Mechanical and Physical Properties of Fresh Zinc Titanate Cylindrical Extrudates

Formulation	% MoO ₃ / Calc. Temp. %/°F	Bed Bulk Density lb/ft ³	SPV* cc/g	MPD* Å	Crush Strength lb/mm	Attrition Resistance %
L-3140	0/1550	57.5	0.39	5800	4.0	
L-3720A	0/1600	73.5	0.32	2700	15.5	
L-3720B	0/1800	88	0.23	2920	16.0	
L-3721C	10/1450	102	0.13	4600	19.0	
L-3721A	10/1600	118.2	0.15	2900	11.3	
L-3721B	10/1800	123	0.08	7000	15.2	
L-3722A	0/1600	70	0.36	5000	7.5	
L-3722B	0/1800	70.5	0.30	6500	7.5	
L-3767A	0/1400	83	0.30	2920	8.4	94.5
L-3767B	0/1800	84	0.31	3500	8.4	95.0
L-3766A	1.2/1400	83	0.34	5000	5.6	94.0
L-3766B	1.2/1600	84	0.34	5000	7.3	94.5
L-3766C	1.2/1800	95	0.29	7000	7.3	95.0
L-3765A	2.5/1400	96	0.29	5000	8.0	96.0
L-3765B	2.5/1600	133	0.15	9500	10.4	93.5
L-3764A	5/1400	117	0.25	4375	13.2	94.5
L-3764B	5/1600	148	0.10	6360	10.7	96.0
L-3723C	10/1450	116	0.10	5650	12.5	
L-3723A	10/1600	129.5	0.07	1900	12.6	
L-3723B	10/1800	132	0.08	6500	13.5	

* SPV = specific pore volume; MPD = median pore diameter

3.1.3 Physical Morphology

The physical morphology of cylindrical extrudates is shown in Table 5. The presence of Mo modified the pore structure of the pellet for all temperatures: Mo-containing formulations exhibited higher median pore diameter, MPD (5000-7000 Å vs. 3000-3500 Å), and higher bed bulk density (102-148 vs. 70-85 lb/ft³). Crush strength and specific pore volume, SPV, were functions primarily of calcination temperature rather than of Mo content. In view of this increase in MPD, the addition of molybdenum was beneficial because larger pore sizes allow for accommodation of higher molar volume sulfides in the oxide crystal structure while reducing pellet internal stresses and breakage.

The higher calcination temperature of 1800 °F (982 °C) significantly reduced the porosity necessary for satisfactory chemical reactivity, while the lower calcination temperature of 1400 °F (760 °C) produced, in some cases, formulations with traces of residual unreacted zinc oxide and anatase titanium dioxide, as previously shown in Table 4. The reduction in porosity during calcination was accompanied by a reduction in the cylindrical extrudate diameter and, as would be expected, was directly related to calcination temperatures and MoO₃ concentration (Table 6).

Table 6. Reduction in Cylindrical Extrudate Diameter for Selected Formulations

Formulation	% MoO ₃	Calcination Temperature, °F	% Reduction in Diameter
L-3767A	0.0	1400	1.6
L-3767B	0.0	1600	1.6
L-3766A	1.2	1400	3.7
L-3766B	1.2	1600	3.7
L-3766C	1.2	1800	5.3
L-3765A	2.5	1400	1.6
L-3765B	2.5	1600	15.0
L-3764A	5.0	1400	9.1
L-3764B	5.0	1600	19.8

3.1.4 Single-Pellet Kinetic Performance

Figure 1 presents the results of TGA chemical reactivity of cylindrical extrudates during a 1.5 cycle test (i.e., sulfidation-regeneration-sulfidation). The first 30 minutes correspond to the reductive regeneration, where the pellet is exposed to simulated coal gases without H₂S to condition the pellet and to obtain a baseline initial weight. Reductive regeneration is followed by sulfidation for an additional 150-minute period, where 3% H₂S is introduced in the gas and the pellet increases in weight as a result of sulfur absorption. After sulfidation the pellet is regenerated under diluted air and decreases in weight. The test continues with another 30-minute reductive regeneration followed by a final second sulfidation.

Formulation L-3140, the baseline formulation, has a high porosity (Table 5) and, hence, exhibits a high reactivity during sulfidation (i.e., weight gain) and regeneration (i.e., weight loss) (Figure 1). Formulation L-3765A (2.5% MoO₃) loses weight immediately after the start of the reductive regeneration, where the Mo species is believed to be reduced (from MoO₃ to MoO₂, or from ZnMoO₄ to ZnMoO₃). The true nature of the molybdenum species is not known because its low concentration is below the detectability limit for XRD. During regeneration, L-3765A does not return to its original weight;

rather, some residual weight remains, perhaps a result of formation of small amounts of MoS_2 or ZnS arising from the reduction of sulfates.

Finally, formulations L-3721A (0.8 Zn:Ti ratio; 10% MoO_3) and L-3723C (2.0 Zn:Ti ratio; 10% MoO_3) do not have the porosity necessary for significant sulfur absorption (Table 5) and suffer from premature pore plugging since pore sizes are known to decrease during sulfidation. The result is low reactivity for both sulfidation and regeneration. The presence of Mo certainly modifies the pore structure of the zinc titanates by increasing the pore size in the fresh pellet, which is beneficial to accommodate the sulfur absorbed, but decreases the pellet reactivity by decreasing the specific pore volume. The use of 10% MoO_3 was found to produce unacceptably low reactivities; on the other hand, the use of 2.5% MoO_3 produces formulations with acceptable reactivities and, consequently, was considered for further testing in the second phase of this program (i.e., testing of rounded pellets).

Figure 1. TGA chemical reactivity of fresh cylindrical extrudates

3.1.5 Mechanical Performance

Measurements of mechanical strength (i.e., crush strength and attrition resistance) were also performed on cylindrical extrudates even though the initial purpose of preparing cylindrical extrudate formulations was not to optimize the mechanical strength but, rather,

to study chemical and morphological properties. The mechanical performance of cylindrical extrudates is also shown in Table 5. Crush strength was higher for the 0.8 Zn:Ti ratio formulations than for those with a 2.0 ratio and also higher for the 2.0 Zn:Ti ratio formulations as the molybdenum content increased. For a given formulation, calcination at higher temperatures did not result in an increase in crush strength, in spite of the increase in bulk density caused by the presence of molybdenum in some cases.

Comparison of formulations L-3722 and L-3767, both without Mo and calcined at various temperatures, shows the reproducibility of the crush strength at two different times starting with identical chemical compositions. Note that the reproducibility of the crush strength in a formulation is about ± 1 lb/mm. Attrition resistance was fairly insensitive to the presence of molybdenum and mildly dependent on calcination temperature: as the calcination temperatures increased from 1400 °F to 1800 °F, the attrition resistance generally increased from 94.0 to 96%. However, the porosity decreased dramatically at 1800 °F.

Summary of Results for Cylindrical Extrudates.

Formulations with a 2.0 Zn:Ti ratio containing around 2.5% MoO₃ (1.7% Mo) additive and calcined between 1400 °F and 1600 °F appear to be the most promising because of the balance of reactivity, mechanical strength, and pore structure. The 2.0 Zn:Ti ratio is the optimum ratio for the formation of the stoichiometric zinc titanate, Zn₂TiO₄, crystalline structure which has the highest sulfur capacity. The 0.8 Zn:Ti formulations produced two zinc titanate crystalline structures and sometimes unreacted zinc and titanium oxides. It is believed that the presence of multiple phases is not desirable because of differences in thermal expansion that may result in stresses and pellet mechanical degradation. The Mo additives were known to modify the pore structure of the pellet by increasing the MPD, a result thought to be favorable for the accommodation of the product zinc sulfide (of higher molar volume than zinc oxide) in the zinc titanate structure thus minimizing pellet internal stresses induced during reaction.

3.2 CHARACTERIZATION AND TESTING OF ROUNDED PELLETS

3.2.1 Fresh Rounded Sorbent Formulations

The chemical compositions previously prepared as cylindrical extrudates in Section 3.1 and considered to be the most promising were subsequently rounded for bench-scale cyclic testing. Table 7 shows the chemical and morphological properties of rounded spherical zinc titanate formulations. As a comparison, two cylindrical extrudates (L-3767A and L-3765A) are also included in the table. Because of the laboratory-size rounding apparatus used, the size distribution of rounded pellets was very narrow with more than 95% of the pellets in the range of 5 to 6 mm in diameter and an aspect ratio of 1.0. Since chemical composition is more useful than formulation identification in order to understand the

differences in sorbent performance, a chemical composition code is given first followed by the manufacturer's formulation identification in parenthesis. Thus a chemical composition code will have: 1) the Zn:Ti ratio; 2) the amount of molybdenum additive, if any, preceded by the prefix A; 3) the letter designating shape as cylindrical extrudate (C), modified sphere by rounding (M), or larger size sphere (S); and 5) the gas composition number used during the bench-scale testing. For all "M" formulations, pellet size distribution was very narrow with more than 95% of the pellets in the range 5-6 mm in diameter with an aspect ratio of 1.0. Only one formulation designated as "S" was fabricated in a larger diameter (8.3 mm). The chemical composition code will be used in the remainder of the report to designate all rounded formulations.

For any type of pelletized porous material, the observed or measured reactivity for sulfur capture is an overall rate determined by any of three controlling mechanisms: i) H_2S mass transfer from the gas phase to the pellet surface, ii) H_2S diffusion through the pores of the pellet, and iii) the intrinsic rate of reaction between H_2S and the metal oxides. It has been shown before (Ayala and Marsh, 1991) that pore diffusion, primarily, and gas phase mass transfer, secondarily, are the controlling mechanisms for desulfurization of coal gases at 1000 °F by pelletized mixed-metal oxides. Then, given a constant gas-phase mass transfer rate, differences in measured overall absorption rate are a result of differences in pore diffusion rates which are a strong function of pore structure.

Figure 2 shows a comparison of TGA chemical reactivity between cylindrical and rounded formulations fabricated with and without molybdenum. The slope of the curve of pellet weight versus time is proportional to the rate of sulfur absorption. Cylindrical extrudates (2C and 2A1.7C) have higher reactivity than rounded pellets (2M and 2A1.7M), whether or not the formulation contains molybdenum. This result suggests that the presence of molybdenum does not measurably affect the intrinsic rate of H_2S absorption; rather, the major differences in reactivity are a result of modifications in the pore structure, primarily by rounding the pellets (i.e., decreasing the SPV) or, to a much lesser extent, by adding molybdenum (i.e., increasing MPD). Further comparison between formulation 2A1.7M and formulation 2A1.7M* (both identical in preparation procedure except for the absence of 5% organic burnout in the latter) shows that the organic burnout additive is necessary to preserve porosity ($SPV > 0.20$ cc/g) and, hence, acceptable reactivity.

Formulations L-200M and L-500M were provided by RTI and found to have a high TGA chemical reactivity comparable to that of formulation 2C. As will be shown in Section 3.2.3, formulations L-200M, L-500M, and cylindrical extrudates are generally much weaker in attrition resistance than UCI rounded pellets because of higher SPV and lower MPD.

Table 7. Chemical and Morphological Properties of Rounded Zinc Titanate Pellets

Chem. Comp. Code (Formulation ID)	Zn:Ti Ratio	% wt. Additive as MoO ₃	Major Zn Titanate Phases	Bulk Density lb/ft ³	SPV cc/g	MPD Å
2C (L-3767A) ^a	2.0	0	Zn ₂ TiO ₄	83	0.30	2920
2A1.7C (L-3765A) ^a	2.0	2.5	Zn ₂ TiO ₄	96	0.29	5000
0.8M (L-3773M)	0.8	0	Zn ₂ TiO ₄ , ZnTiO ₃	81	0.26	2185
1M (L-200M)	1.0	0	ZnTiO ₃ , Zn ₂ Ti ₃ O ₈	90	0.18	1165
1.5S (L-3140M)	1.5	0	Zn ₂ TiO ₄ , ZnTiO ₃	87	0.22	4710
1.5M (L-500M)	1.5	0	Zn ₂ TiO ₄ , ZnTiO ₃	90	0.19	1163
2M (L-3774M)	2.0	0	Zn ₂ TiO ₄	77	0.30	2690
2A1.7M*(L-3786M) ^b	2.0	2.5	Zn ₂ TiO ₄	113	0.18	7000
2A1.7M (L-3787M)	2.0	2.5	Zn ₂ TiO ₄	107	0.23	7000
2A3.3M (L-3785M)	2.0	5.0	Zn ₂ TiO ₄	107	0.27	7000

^a Cylindrical extrudate formulations shown for comparison.

^b Formulation 2A1.7M* did not contain any organic burnout; all others contained 5-10% wt.

Figure 2. TGA chemical reactivity of fresh cylindrical and rounded zinc titanate sorbents

In addition to TGA single sulfidation tests, several 1.5 cycle tests (i.e., sulfidation-regeneration-sulfidation) were conducted on rounded pellets. As usual, the first 30 minutes correspond to a reductive regeneration in simulated clean coal gas (i.e., no H_2S), a 2½-hour sulfidation at 550 °C in simulated oxygen-blown gasifier gas, a 3-hr regeneration at 650 °C, another 30-minute reductive regeneration followed by the second and final sulfidation.

Figure 3. TGA chemical reactivity of fresh rounded formulations

Figure 3 shows the results of the 1.5 cycle tests on rounded pellets having a 2.0 Zn:Ti ratio. One 1.5 Zn:Ti ratio formulation is included for comparison. The reactivity, or rate of reaction, is given by the slope of the weight ratio versus time. During sulfidation the weight ratio increases, whereas during regeneration the weight ratio decreases to its original value. For all the 2.0 Zn:Ti ratio formulations, the reactivity correlates well with the specific pore volume, SPV, (Table 7). Formulation 1.5S (L-3140M) has only a 1.5 Zn:Ti ratio but exhibits the highest reactivity of all, partly because it was prepared as a much larger size pellet (8.3 mm in diameter instead of the normal 5-6 mm). Because of the fixed regeneration time to which the formulations were subjected (i.e., 3 hours), those formulations that had the highest sulfur reactivity did not regenerate completely during this time, and the weight ratio did not return to the base 1.0 value after 360 minutes. The

fact that the slope of the second sulfidation was comparable to that of the first sulfidation for all formulations indicates that none suffered significant changes in pore structure that produce a loss of reactivity after the first cycle. No trends in reactivity are observable based on the presence of molybdenum or the Zn:Ti ratio.

3.2.2 Bench-Scale Reactor Testing

In the course of performing the bench-scale reactor testing, ten cycles of absorption and regeneration were carried out for each of ten runs. Figure 4 shows a sample plot of effluent H₂S concentrations from the reactor as a function of time, or breakthrough curves, for formulations 2M2 and 2A1.7M subjected to simulated coal gas composition 1 (air-blown gasifier gas) and composition 2 (i.e., simulating the highly-reducing coal gas composition of an oxygen-blown gasifier). Shown in the lower x-axis scale is the dimensionless time calculated by dividing the real time by the theoretical time required for complete saturation of the sorbent in the bed. The dimensionless time provides a measure of the relative sorbent bed utilization at any given time with respect to the total sulfur capacity at saturation. At each absorption, breakthrough is defined as the point at which the effluent H₂S concentration reached 200 parts per million by volume (ppmv). The low pre-breakthrough H₂S concentrations (less than 25 ppmv) measured in all runs are shown in Table 8 and represent excellent sulfur removal (>99%) based on the 1% H₂S inlet gas. Bed utilizations at the 200 ppmv H₂S breakthrough time are also shown in the same table and ranged from 8 to 35% of theoretical. As will be presented in the discussion of Figure 5, where the mechanical performance of these formulations is shown, higher utilizations correspond to weaker formulations. Formulation 2A1.7M, which is one of the strongest, showed an average capacity of 12% at breakthrough under gas composition 1 and of 15% under gas composition 2. In general, the lower the H₂O concentration in the inlet gas, the lower the measured pre-breakthrough H₂S concentrations. This observation is in agreement with equilibrium predictions during desulfurization according to:

where higher H₂O levels drive the equilibrium to the left toward higher H₂S concentrations in the gas phase.

In addition, it is worth noting that higher sulfur loadings have been measured during pilot plant operation than in laboratory tests, a result of differences in the scaling factor pellet-to-reactor-size ratio.

Table 8. Breakthrough Parameters during 10-Cycle Bench Testing

Bench Reactor Run	Pre-breakthrough effluent H ₂ S ppmv	Dimensionless time at breakthrough
1.5S1 (L-3140M1)	20	0.10-0.15
1M2 (L-200M2)	20	0.20-0.35
1M3 (L-200M3)	5	0.13-0.20
1.5M1 (L-500M1)	10	0.25-0.35
2M1 (L-3774M1)	15	0.15-0.24
2M2 (L-3774M2)	5	0.17-0.23
2M3 (L-3774M3)	2	0.17-0.20
2A1.7M1 (L-3787M1)	25	0.08-0.15
2A1.7M2 (L-3787M2)	15	0.08-0.20
2A3.3M1 (L-3785M1)	25	0.08-0.15

3.2.3 Mechanical Performance

Attrition resistance and crush strength were evaluated on samples extracted from the bench-scale reactor system and compared against the strength of the corresponding fresh formulations (Figure 5). Attrition resistance of fresh and cycled formulations (10th absorption and 10th regeneration), is shown in the upper diagram of Figure 5. Except for the baseline cylindrical extrudate 1.5C (UCI's L-3140) and the rounded 1.5S1, all of the rounded formulations had an acceptable initial attrition resistance above the target value of 96% for fresh sorbents. Those formulations prepared as straight zinc titanates with no molybdenum additive suffered significant losses in attrition resistance during the 10 cycles, both in the sulfided (10th absorption) and the regenerated (10th regeneration) states. Moreover, most of the straight zinc titanate formulations became broken (i.e., spalled) pellets during attrition tests and had the appearance of gravel (i.e., aggregates) and fine dust; those formulations containing molybdenum remained almost exclusively as whole pellets with small amounts of fine dust.

As mentioned earlier, cylindrical extrudates were weaker in attrition resistance than rounded pellets. The baseline formulation 1.5C (L-3140) had an attrition of 88.0%. Cylindrical extrudates fabricated in the current program had attrition resistances in the range of 93.5 to 96.0% (Table 5 and Figure 5), while fresh rounded pellets were in the range of 96.7 to 98.9% (Figure 5).

Figure 4. Breakthrough curves of 2M and 2A1.7M Bench-Scale Sorbents

Evidently, an enhancement of the mechanical durability of sorbents is obtained by adding molybdenum oxide and rounding after extrusion.

An analogous difference between straight zinc titanate formulations and Mo-doped formulations is seen during crush strength measurements (lower diagram of Figure 5); visible pellet exfoliation, and cracking of the pellet surface always accompanied low crush strengths. Since the only difference in the chemical composition of the rounded formulations is the presence or absence of molybdenum additive (when testing at constant gas composition), it can be concluded that higher attrition resistance and crush strength are a result of the presence of molybdenum.

All formulations tested under two or more gas compositions showed that the attrition losses are greater under gas composition 2 (simulating oxygen-blown, entrained flow gasifier gas) and less under gas composition 1 (simulating fixed-bed, air blown gasifier gas) with gas composition 3 falling in the middle. The crush strength followed the same general trend as the attrition test for the molybdenum-doped formulations, but the crush strength losses were more severe for gas composition 3 than gas composition 2 for bentonite-only formulations. Overall, the severity of mechanical strength losses followed the trend: gas composition 1 < gas composition 3 < gas composition 2. These conclusions imply that the total $(\text{CO} + \text{H}_2)$ concentration of a gas is more indicative of the expected severity of mechanical strength losses than the reducing power $(\text{CO} + \text{H}_2)/(\text{CO}_2 + \text{H}_2\text{O})$. Apparently, the modification of an oxygen-blown gas composition with nitrogen had a beneficial effect on the sorbent mechanical properties.

Figure 5. Attrition resistance (top) and crush strength (bottom) after bench-scale tests

3.2.4 Physical Morphology

Having observed and measured significant differences in mechanical strength between chemically identical formulations differing only by the presence or absence of molybdenum oxide additive (2M vs. 2A1.7M), the physical properties of the formulations (e.g., external appearance and internal pore structure) were studied. Pellets extracted from the bench-scale reactor after the 10th regeneration using gas composition 1 are shown in Figure 6. The 2M pellets show heavy signs of deterioration, as seen by the loss of fragments from the pellet surface, where the desulfurization reaction took place. This loss of material occurring by fragmentation of surface layers, or spalling, is of major concern for the long-term durability of sorbents. In contrast, formulation 2A1.7M does not exhibit any of these signs.

Figure 6. Photograph of pellets of formulations 2M1 and 2A1.7M1 after the 10th regeneration in bench-scale tests

Figure 7. Photograph of pellets of formulations 2M2 and 2A1.7M2 as fresh sorbent, after the 10th absorption, and after the 10th regeneration in bench-scale tests

Figure 7 shows the same trend of spalling for the same formulations (2M and 2A1.7M) exposed to gas composition 2. Again, 2M2 pellets show deterioration in the 10th absorption and 10th regeneration states while pellets of 2A1.7M2 do not. A light tan color was observed on both formulations of Figure 7, and is most likely a result of the gas composition used (i.e., gas composition 2 with a high CO and H₂ concentration); this color was not observed on pellets exposed to gas compositions 1 or 3 (as in Figure 6)

Figure 8 shows a comparison of pore size distribution by mercury intrusion porosimetry for a weak (2M) and for a strong (2A1.7M) formulation. The weak formulation (2M) decreased in SPV from 0.30 to 0.26 cc/g, and the peak intensity of the most-likely pore size decreased in half. A number of micropores (i.e., pores less than 200 Å) centered at 0.004 μm (40 Å) and macropores centered at 20 μm developed in the structure. On the other hand, the strong formulation (2A1.7M) retained its SPV at 0.20 cc/g, and the peak intensity of the most-likely pore size even increased slightly. Essentially, no micropores below 0.01 μm were found, and only a few macropores at 20 μm were detected.

The correlation between pellet physical deterioration and pore size distribution can be rationalized in the following manner: when a 2.0 zinc titanate undergoes full sulfidation, the product solid increases in molar volume by 50% at the expense of a reduction in pore void volume. If pores are narrow (low MPD) and many (large SPV), it is believed that the thin pore walls collapse from the density changes of sulfidation/oxidation, resulting in collapsing of the walls and the appearance of a weaker structure; if pores are wide (high MPD) and fewer (low SPV) the thicker walls between pores may be able to withstand the internal stresses due to reaction, the result being that deterioration of the pellet structure is less. The presence of Mo does not directly affect the chemistry of desulfurization as long as there is enough surface oxide available for reaction. The effect apparently occurs indirectly through the modification of the pellet pore structure. At this point it is believed that the SPV determines the sulfur loading of the pellet, while the MPD determines both the chemical reactivity of the pellet (larger pores present less pore diffusion resistance to gaseous reactants) and durability of the pellet throughout extended cyclic testing. The available Mo provides a solid structure during calcination mobile enough to remove the micropores in the pellet. In turn, the absence of micropores reduces the weakness in the pellet which causes cracking and spalling.

Figure 8. Pore size distribution of weak (2M) and strong (2A1.7M) sorbents after bench-scale tests

3.2.5 Single-Pellet Kinetic Performance After Bench Testing

The reactivity of the pellets removed from the reactor after the 10th regeneration is shown in Figure 9. The rate of sulfur absorption is given by the slope of the weight ratio versus time plot. Prior to reaction, the pellets are subjected to the usual initial 30-minute period of reductive regeneration where the pellet is exposed to simulated coal gas without hydrogen sulfide so that a horizontal baseline weight is obtained. The rate of sulfur capture of 2M2 after 10 cycles was similar to that of the fresh material for all times. The rate of 2A1.7M2 after 10 cycles was lower than that of the fresh pellet during the first 120 minutes but was the same as that of the fresh material thereafter, with no signs of premature reaction die-off or pore plugging.

3.2.6 Chemical Composition

Chemical analyses were conducted on samples removed from the reactor at three bed locations (gas inlet, middle, and gas outlet) after the 10th absorption and the 10th regeneration. Only results for the gas inlet location (i.e., the most heavily sulfided location) are presented since this location has the harshest or most severe environment to which the sorbent was exposed.

Figure 9. TGA chemical reactivity of 2M and 2A1.7M bench-scale sorbents (fresh and 10th regeneration gas inlet)

Zero or low levels of residual carbon are desirable in cycled sorbents since carbon is a deposition product of carbonaceous species in the coal gas that will prevent

desulfurization. A high total sulfur in absorption and a low sulfate content in regeneration are also desirable to maximize sulfur removal performance. Sulfate formation is undesirable because it induces internal stresses in the pellet that promote degradation and deterioration of the mechanical properties of the sorbent.

Table 9 presents the measurements of total carbon, and sulfur species. The levels of carbon in the samples (<0.7%) and the amount of sulfate found in regenerated samples (<0.3%) are very small and considered insignificant in their effect on the desulfurization performance of the sorbents. These levels of sulfate were measured after having exposed the sorbent to 1400 °F during regeneration. Analysis of sulfate sulfur was conducted on a few regeneration samples immediately before the exposure to the final stage of regeneration at 1400 °F where sulfate is expected to be greatest. Residual sulfate sulfur at that point in time was approximately 0.24% for samples 2M3 and 0.22% or less for 1M3; this result suggests that the regeneration scheme used did not result in significant amounts of residual sulfate. In some cases, the level of residual carbon in regenerator samples was higher than in the corresponding absorber samples. This result is the combined effect of the reproducibility of the technique at low levels of carbon and the variations from pellet to pellet. A similar result occurs in low-level sulfate analyses.

Table 9. Chemical Analyses of Cycled Samples from the Bench Reactor

Sample*	% Carbon	% Total Sulfur	% Sulfate Sulfur
1M2 10th Absorption	0.09	6.52	0.22
1M2 10th Regeneration	0.07	0.11	0.07
1M3 10th Absorption	0.01	5.46	0.02
1M3 10th Regeneration	<0.01	0.11	0.02
1.5S1 10th Absorption	0.05	6.23	0.60
1.5S1 10th Regeneration	0.14	0.13	0.10
1.5M1 10th Absorption	0.30	11.50	0.01
1.5M1 10th Regeneration	0.19	0.13	0.01
2M1 10th Absorption	0.30	5.60	0.07
2M1 10th Regeneration	0.11	0.37	0.02
2M2 10th Absorption	0.10	6.98	0.01
2M2 10th Regeneration	0.71	0.30	0.26
2M3 10th Absorption	0.02	5.09	0.02
2M3 10th Regeneration	0.02	0.24	0.13
2A1.7M1 10th Absorption	0.39	3.34	0.02
2A1.7M1 10th Regeneration	0.30	0.30	0.02
2A1.7M2 10th Absorption	0.08	5.20	0.76
2A1.7M2 10th Regeneration	0.08	0.16	0.11
2A3.4M1 10th Absorption	0.15	3.38	0.39
2A3.4M1 10th Regeneration	0.16	0.16	0.16

*All samples are for the gas inlet location.

The regeneration scheme used, with a final temperature rise to 1400 °F (760 °C), was successful at minimizing the formation of zinc sulfate and oxidizing any carbon previously formed. The amount of total sulfur in the absorption samples (3-7% wt.) corresponds to 15-31% of the total theoretical sulfur capacity of the sorbent and is considered satisfactory for moving-bed systems.

In addition to carbon and sulfur analyses, elemental analyses of zinc and molybdenum by ICP were performed and the results are shown in Table 10. No significant losses in zinc were measured within the experimental error of the technique (5% relative error), since the absorption temperatures were only near 1000 °F (538 °C). It should be emphasized that the absence of zinc sublimation for the 2.0 Zn:Ti zinc titanates during the absorption test conditions used here may not hold if the desulfurization is carried out at higher temperatures (e.g., >1300 °F, 704 °C) where zinc metal sublimation is known to be significant. Similarly, no losses of molybdenum were detected above the experimental error of ICP (also 5% rel. error) when the molybdenum concentration was 1.7% wt.

Table 10. Elemental Analysis by Inductively-Coupled Plasma (ICP)

Sample	% Zn	% Exp. Error	% Mo	% Exp. Error
2M Fresh	52.4	2.6	0	n/a
2M2 10th Regeneration	52.2	2.6	0	n/a
2A1.7M Fresh	52.9	2.6	1.66-1.71	±0.08
2A1.7M 10th Regeneration	51.2	2.6	1.61-1.68	±0.08
2A3.3M Fresh	n/m	n/a	3.52	±0.18
2A3.3M1 10th Regeneration	n/m	n/a	3.23	±0.16

n/m = not measured; n/a = not applicable.

On the other hand, Mo losses were measured for 3.3% and higher Mo levels where, presumably, the vapor pressure of unreacted molybdenum oxide MoO_3 (melting point : 1463 °F, 795 °C) is significant. It is inferred from these results that the use of Mo as a porosity modifier in zinc titanate is an asset as long as the reactant MoO_3 is completely incorporated into the zinc titanate structure (by proper calcination) and the properties of bulk MoO_3 are no longer applicable. Other molybdenum compounds, such as MoS_2 , have much higher melting points and do not represent a concern for Mo vaporization.

Based on the differences observed in the mechanical strength of formulations with and without molybdenum, it was decided to do a side-by-side comparison between formulation 2M and 2A1.7M. SEM/EDX photomicrographs of fresh 2A1.7M sorbent showed that

molybdenum is dispersed into the zinc titanate structure in clusters less than 20 μm in size. In addition, SEM/EMA measurements of elemental distribution of Zn and Mo along the pellet radii were obtained. Figure 10 shows typical results of the Zn:Ti ratio distribution along the pellet diameter for formulations 2M and 2A1.7M. Within the accuracy associated with doing EMA analysis of porous pellets, the results showed that there were no significant gradients in the radial distribution of zinc from which it could be inferred that measurable evaporation had taken place during the 10-cycle bench testing. EMA of porous materials requires a careful selection of the pellet areas under examination, since the presence of voids or pores produces erroneous results on the intensities of the elements under analysis.

Figure 10. SEM/EMA Zn:Ti molar ratio distributions along the pellet diameter (from the outer region, Ro, to the pellet center, Rc) of 2M and 2A1.7M sorbents in the fresh state and after the 10th regeneration

In spite of these encouraging results of the lack of zinc and molybdenum evaporation, it is important to recognize that these conclusions apply only to the conditions simulating a GE moving-bed system to which the sorbent was exposed during testing. Other test conditions of higher temperatures/higher coal gas reducing properties may yield different results.

Another major difference between 2M and 2A1.7M formulations was observed in the distribution of sulfur across the pellet diameter. Figure 11 shows the SEM/EDX qualitative maps and the SEM/EMA sulfur-to-titanium molar ratio, S:Ti ratio, for pellets extracted from the same samples.

Figure 11. SEM/EDX sulfur distribution and SEM/EMA S:Zn ratio along the pellet diameter (from the outer region, Ro, to the pellet center, Rc) of 2M and 2A1.7M sorbents after the 10th absorption.

Note that the 2M formulation has the sulfur present on the periphery of the pellet, following the unreacted core model with a sharp boundary between sulfided and fresh oxide layers. On the other hand, 2A1.7M shows a more diffuse boundary and the sulfur gradient is less steep. This observation, coupled to the pore size distribution of both pellets, led us to ascribe the pellet deterioration observed in formulation 2M to the internal stresses generated from a high sulfur gradient and subsequent spalling on the periphery of the pellet.

Summary of Results for Rounded Spherical Pellets.

The modification of the pellet shape by rounding into spherical pellets resulted in an increase in attrition resistance from 88.0 to 96.0% for cylindrical extrudates to 91.7 to 98.9% for rounded spherical pellets. All the rounded 2.0 zinc titanate formulations had higher attrition resistance than those with lower zinc-to-titanium ratios. The addition of up to 10% organic burnout was necessary in the Mo-doped formulations to maintain the SPV above the desired 0.20 cc/g for satisfactory chemical reactivity. The presence of organic burnout material did not affect the MPD of the formulations.

Spalling and pellet physical degradation during bench testing was found to be inhibited by the addition of molybdenum oxide attributed to the resulting modification of the pore structure. Straight zinc titanate pellets, with a Zn:Ti ratio in the range 1.0-2.0, showed heavy spalling while those containing molybdenum oxide showed very little or no spalling.

During bench-scale testing, pre-breakthrough H_2S concentrations were below 20-25 ppmv at 1% H_2S in the inlet gas, regardless of the concentration of Mo additive in the sorbent. This desulfurization level corresponds to 99.8% H_2S removal from the gas stream. Sulfur loading in the gas inlet samples removed at the 200 ppm H_2S breakthrough ranged from 8% to 35% of the theoretical value for zinc titanates, with a bed average value of approximately 12% to 14% for the Mo-doped formulations. Levels of carbon, residual sulfur, and sulfate sulfur were low enough after the 10th regeneration in the bench reactor and did not represent a concern during scaleup, provided similar test conditions are maintained.

From the overall analysis of differences in pore structures, sulfur distribution, mechanical strength, and chemical reactivity, formulations containing a 2.0 Zn:Ti ratio and 2.5% molybdenum oxide as an additive have shown a better balance of overall properties suitable for moving-bed systems.

SECTION 4 CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

The following conclusions can be drawn from the characterization of cylindrical formulations:

- Formulations with a 0.8 Zn:Ti ratio contained mixtures of several stoichiometric titanates: $\text{Zn}_2\text{Ti}_3\text{O}_8$, ZnTiO_3 , and Zn_2TiO_4 , the relative amount of each depending on calcination temperature. Formulations with a 2.0 Zn:Ti ratio contained only the Zn_2TiO_4 structure which is more desirable because of its higher sulfur capacity.
- The higher calcination temperature of 1800 °F (982 °C) significantly reduced the sorbent porosity in Mo-doped formulations, while the lower calcination temperature of 1400°F (760 °C) produced, in some cases, sorbents with traces of residual unreacted zinc oxide and anatase titanium dioxide. The optimum calcination temperature range was found to be 1400-1550 °F for Mo-doped formulations and up to 1800 °F for straight zinc titanates.
- The crystalline form of the MoO_3 additive was absent after calcination, even at a 10% concentration, suggesting that Mo dissolves into the zinc titanate structure forming zinc molybdates.
- Addition of molybdenum oxide modifies the pore structure of the pellet: Mo-containing formulations exhibited higher MPD (5000-7000 Å vs. 3000-3500 Å), and higher bed bulk density (1.63-2.37 vs. 1.12-1.36 g/cc). This modification of the pore structure is considered to be beneficial for desulfurization. Crush strength and specific pore volume, SPV, were functions primarily of calcination temperature rather than of Mo content.

The following conclusions can be drawn from the characterization of rounded pellets:

- Modification of the extrudate shape by further rounding into spherical pellets prior to calcination resulted in an increase in attrition resistance from 88.0-96.0% for cylindrical extrudates to 91.7-98.9% for rounded

spherical pellets. All rounded 2.0 zinc titanate formulations had attrition resistances in the range 96.7-98.9%, which is higher than those with lower zinc-to-titanium ratios.

- Addition of up to 10% organic burnout material was necessary in the Mo-doped formulations in order to maintain the SPV above the desired 0.20 cc/g after calcination, while maintaining satisfactory chemical reactivity. The presence of organic burnout material did not affect the median pore diameter, MPD, of the formulations.
- Differences in chemical reactivity between cylindrical extrudates and rounded spherical pellets during single-pellet TGA tests were attributed to differences in SPV, rather than to differences in the presence or absence of molybdenum.
- Differences in mechanical durability of rounded spherical pellets during bench-scale tests were explained by the presence or absence of molybdenum. Spalling and pellet physical degradation during bench-scale testing were inhibited by the addition of molybdenum oxide and attributed to the modification of the pore structure and sulfur distribution profile within the pellet. Straight zinc titanate pellets, having only bentonite as a binder, exhibited heavy spalling while those with added molybdenum oxide showed very little or no spalling over the whole range of Zn:Ti ratios (1.0-2.0) and after 10 cycles of testing.
- During bench-scale testing, pre-breakthrough H_2S concentrations were below 20-25 ppmv at 1% H_2S in the inlet gas, regardless of the concentration of Mo additive. This desulfurization level corresponds to 99.8% H_2S removal from the gas stream. Sulfur loadings in the sorbents at the gas inlet ranged from 8 to 35% of the theoretical value for all the zinc titanates, with an average value of approximately 12-14% for the Mo-doped formulations.
- Levels of carbon, residual sulfur, and sulfate sulfur were low enough after the 10th regeneration in the bench reactor so as not to present a concern during scaleup, provided similar conditions are maintained.

The overall conclusion of the Option 2 program work is that the more promising formulations were those with a 2:1 Zn:Ti ratio containing molybdenum oxide additive. Formulation 2A1.7M (UCI formulation L-3787M), containing 2.5% MoO_3 (1.7% Mo) additive was the best performer in the family of sorbents tested because of a good balance of chemical reactivity, mechanical strength, and pore structure. The 2:1 zinc-to-titanium ratio is the optimum ratio for the yielding of the stoichiometric zinc titanate, Zn_2TiO_4 , with the highest sulfur capacity. The molybdenum concentration was not optimized over

the range 0-10% MoO_3 and, hence, a lower molybdenum concentration (<1.7% Mo reported here) may be optimum for desulfurization sorbents. The Mo additives were found to modify the pore structure of the pellet by increasing the MPD, a result thought to be favorable for the accommodation of the products zinc sulfide or zinc sulfate (of higher molar volumes than zinc oxide) in the zinc oxide structure, thus minimizing pellet internal stresses induced during reaction. Mo also reacts with hydrogen sulfide forming Mo sulfide, MoS_2 , which in turn is well known for being catalytically active in hydrodesulfurization and hydrodenitritication reactions in the petroleum industry (Sittig, 1978) and may be advantageous in absorbing sulfur from tars in the gas stream.

4.2 RECOMMENDATIONS

Based on the overall conclusions presented in the previous section, it is shown that the presence of molybdenum oxide enhances the desired properties for moving-bed sorbents. However, a careful choice of molybdenum concentration is necessary to achieve the optimum performance of Mo-doped formulations. Since Mo concentrations were tested at discrete points in the range 0-10% MoO_3 (0.8-6.7% Mo) under the Option 2 program, more work is needed to optimize the sorbent properties with respect to molybdenum concentrations. It is recommended that this work be performed using molybdenum concentrations between 0 and 2.5% MoO_3 . Also, an alternate modifier may be found or sought.

The addition of molybdenum oxide prior to calcination up to 1600 °F was found to be useful in modifying the pellet pore structure. Bench-scale testing was restricted to temperatures up to 1400 °F. Routine regeneration operation above 1500 °F during regeneration would require further evaluation of the sorbent for potential molybdenum evaporation, excessive pellet sintering, or appearance of pellet cohesiveness (i.e., stickiness) because of formation of low-temperature eutectic phases at the contact points. The use of structural promoters to stabilize the molybdenum phase after calcination may further increase the temperature window of operation of Mo-doped zinc titanate above 1500-1600 °F. Further study in this area is recommended.

A second approach to altering the pore structure and the mechanical properties of sorbents is to use substrate modifiers. During desulfurization with zinc titanate, the TiO_2 phase acts as an inert microscopic support that keeps the pellet structure in place while the ZnO is undergoing phase changes and forming sulfides and/or sulfates. The use of materials that will increase the strength of TiO_2 is thought to be worth considering for future sorbent preparation. Close work with sorbent manufacturers is very critical in the evaluation of other avenues of sorbent fabrication and in keeping manufacturing costs at reasonable levels.

In summary, it was found during the course of performance of the Option 2 program that the use of additives for the modification of the pore structure of zinc titanate was

beneficial within the range of calcination temperatures (1400-1600 °F) and Mo concentrations (0-2.5% MoO₃). Further work is recommended to optimize this new family of Mo-containing sorbent materials or to explore other additives that perform the same functions of pore modification and mechanical strengthening.

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