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Enhanced Durability of High-Temperature Deulfurization Sorbents for Moving-Bed Applications

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Enhanced Durability of High-Temperature Desulfurization Sorbents for Moving-Bed Applications

CONTRACT INFORMATION

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Period of Performance	September 21, 1988 to December 31, 1992

Schedule and Milestones

FY92 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A	S
Sorbent Preparation	—												
Bench-Scale Testing		—	—										
Bench-Scale Analysis			—	—									
Topical Report				—									

OBJECTIVES

The objective of this project is to develop chemically reactive and mechanically durable zinc ferrite and zinc titanate sorbent formulations that are suitable for moving-bed, high-temperature, coal gas desulfurization processes. Zinc ferrite formulations were studied under the Base program; novel mixed-metal oxide formulations, particularly zinc titanates, are being studied in the current Option 2 program.

BACKGROUND INFORMATION

GE is developing a moving-bed, high-temperature desulfurization system for IGCC power systems in which zinc ferrite and zinc titanate 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 also being considered as 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.

Mixed-metal oxide sorbents have been studied in the past, both as straight zinc titanates, (e.g., Zn_2TiO_4 and $Zn_2Ti_3O_8$) (Woods et al., 1989) or as combinations of oxides of vanadium, copper, manganese, cobalt, and others; see for instance (Flytzani-Stephanopoulos et al., 1987). Although the feasibility of removing H_2S to very low levels (e.g., < 50 ppmv) from coal gases has been shown to be viable in most studies of mixed-metal oxides, the major limitation for large scale use of mixed-metal oxides other than zinc titanates is the lack of chemical and mechanical stability under reducing gas atmospheres or the difficulty of regeneration over many cycles. From an evaluation of predictions and experimental studies of metal oxide sorbents, zinc titanates are considered very promising sorbent materials for high-temperature desulfurization.

PROJECT DESCRIPTION

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 formulations for chemical performance in desulfurization. The rounded pellets were prepared to achieve a desired balance of mechanical properties (crush strength and attrition resistance) and chemical properties. The rounding procedure, 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, 1991).

Formulation L-3140 (a cylindrical extrudate of zinc titanate containing a 1.5 Zn:Ti molar ratio and 3% bentonite binder) 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 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 (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 can withstand in compression prior to fracture; attrition resistance is defined as 100% minus the percent attrition loss when measured according to the ASTM D4058-81 method. Mechanical strength was measured at GE Environmental Services, Inc. (GEESI). 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 measured at Research Triangle Institute (RTI).

When calcining mixtures of ZnO and TiO_2 powders at high temperature, three crystalline structures of zinc titanate may form depending of the ratio of zinc to titanium: $ZnTiO_3$, $Zn_2Ti_3O_8$, or Zn_2TiO_4.The highest zinc-to-titanium molar ratio zinc titanate, Zn_2TiO_4, would be the most desired crystalline phase because of its higher sulfur capacity. For this case, the overall reactions occuring during H_2S absorption from coal gases and regeneration with diluted air are as follows:

Absorption:

$$Zn_2TiO_4 + 2H_2S \Rightarrow 2ZnS + TiO_2 + 2H_2O$$

Regeneration:

$$2ZnS + TiO_2 + 3O_2 \Rightarrow Zn_2TiO_4 + 2SO_2$$

In addition to absorption and regeneration reactions, zinc sulfate formation may occur during regeneration, below 1200 °F and at high O_2 and SO_2 concentrations. Zinc sulfate formation is undesired because the sulfate occupies more volume than the sulfides in the pores (producing more internal pellet stresses) and decomposes during subsequent absorption releasing SO_2. Hence, a regeneration scheme where the temperature is above 1250 °F at the end of regeneration is necessary.

Chemical reactivity was determined at GE-CRD by measuring sorbent sulfur loading (defined as grams of sulfur absorbed per 100 g of fresh sorbent) in fresh and in cycled samples from a 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 the bench-scale reactor system. Details of the bench-scale reactor and procedures 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 to which the sorbent would be exposed in a typical cycle of the full-scale moving-bed system. Absorption was carried out at 1000 °F using any of three gas compositions, all having a deliberately high H_2S concentration (1%) to accelerate testing. The oxidative regeneration was carried out between 1000 and 1250 °F and 1-21% oxygen during the early phases of regeneration, and at 1400 °F during the final phase simulating the temperature rise of the sorbent bed (triggered by the exothermic oxidation reaction) in the large-scale system.

RESULTS

Fresh Sorbent Preparation and Characterization

Sixteen zinc titanate formulations were prepared as cylindrical extrudates in the first phase of the Option 2 program. Variables investigated during fabrication are shown in Table 1. For all formulations, the calcination time was held constant at 2 hours.

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

The following results were obtained during characterization of cylindrical formulations:

- Formulations containing a 0.8 Zn:Ti ratio produced mixtures of several stoichiometric titanates: $Zn_2Ti_3O_8$, $ZnTiO_3$, 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 higher calcination temperature of 1800 °F significantly reduced the porosity available for chemical reactivity, while the lower calcination temperature of 1400 °F produced, in some cases, formulations with traces of residual unreacted zinc oxide and anatase titanium dioxide.

- The crystalline form of the MoO_3 additive was absent after calcination, even at 10% additive, suggesting that Mo dissolves within the zinc titanate structure or, alternatively, becomes an amorphous phase to x-ray diffraction.

- The presence of Mo modified the pore structure of the pellet: Mo-containing formulations exhibited higher MPD (5000-7000 Å vs. 3000-3500 Å), and higher bulk density (102-148 vs 70-85 to lb/ft^3). Crush strength and SPV were functions primarily of calcination temperature rather than of Mo content.

The more promising formulations were those with a 2:1 Zn:Ti ratio containing around 2.5% MoO_3 (1.7% Mo) additive. This zinc-to-titanium ratio is the optimum ratio for the formation of the stoichiometric zinc titanate, Zn_2TiO_4, crystalline structure with the highest sulfur capacity. 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 zinc sulfide (of higher molar volume than zinc oxide) in the 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 hydrodenitrification reactions in the petroleum industry.

The most promising chemical compositions were subsequently rounded for bench-scale cyclic testing. Table 2 shows the fabrication properties of several zinc titanate formulations. Since chemical composition is more useful than formulation ID to understand the differences in performance, the manufacturers' formulation ID has been replaced by a code describing the chemical composition and test conditions. Thus a chemical composition code will have: 1) the Zn:Ti ratio; 2) the amount of molybdenum additive, if any, followed by the prefix A; 3) the letter designating shape as cylindrical extrudate (C), modified by rounding (M), or as sphere (S); and (after bench-scale testing) 5) the gas composition number used during the test. 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 comparison of TGA chemical reactivity between cylindrical and rounded formulations fabricated with or without molybdenum is shown in Figure 1, where the weight ratio (i.e., weight gained) by the pellet is proportional to the cumulative amount of sulfur absorbed. Cylindrical extrudates (2C and 2A1.7C) have higher reactivity than rounded pellets (2M, 2A1.7M), whether the formulation contains molybdenum or not. This result suggests that the presence of molybdenum does not directly affect the mechanism of H_2S capture, except for the modification of the pore structure. In general,

Table 2. Chemical Composition of Zinc Titanate Formulations

Chem. Comp. Code (Formulation ID)	Zn:Ti Ratio	% wt. MoO_3 Additive	Major Zn Titanate Phases	Density lb/cu. ft	SPV cc/g	MPD Å
2C (L-3767A)	2.0	0	Zn_2TiO_4	83	0.30	2920
2A1.7C (L-3765A)	2.0	1.7	Zn_2TiO_4	96	0.29	5000
0.8M (L-3773M)	0.8	0	Zn_2TiO_4, $ZnTiO_3$	80	0.26	2185
1.5S (L-3140M)	1.5	0	Zn_2TiO_4, $ZnTiO_3$	87	0.22	4710
1M (L-200M)	1.0	0	$ZnTiO_3$, $Zn_2Ti_3O_8$	90	0.18	1165
1.5M (L-500M)	1.5	0	Zn_2TiO_4, $ZnTiO_3$	90	0.19	1163
2M (L-3774M)	2.0	0	Zn_2TiO_4	77	0.30	2690
2A1.7M*(L-3786M)[a]	2.0	2.5	Zn_2TiO_4	113	0.18	7000
2A1.7M (L-3787M)	2.0	2.5	Zn_2TiO_4	107	0.23	7000
2A3.3M (L-3785M)	2.0	5.0	Zn_2TiO_4	107	0.27	7000

[a] Did not contain any organic burnout; all others contained 5-10% wt.

cylindrical extrudates are much weaker than rounded pellets because of higher SPV. Further comparison between formulation 2A1.7M and formulation 2A1.7M* (both identical in preparation procedure but differing by the absence of 10% 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.

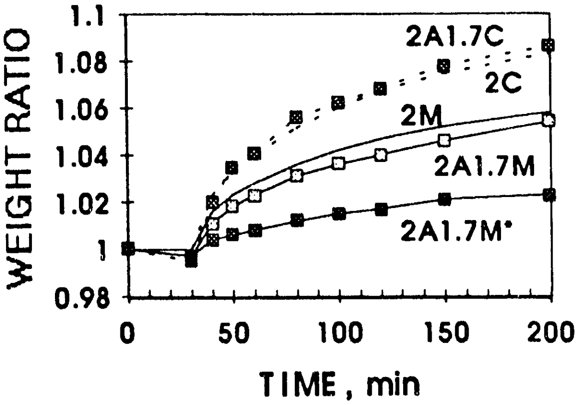


Figure 1. TGA Chemical Reactivity of cylindrical and rounded zinc titanate sorbents

Bench-Scale Reactor Testing

Three simulated coal gas compositions were selected for bench-scale reactor testing (Table 3) to approximate gasifier gas compositions and provide a means to screen the effect of: (1) reducing power (CO+ H_2)/(CO_2 + H_2O), (2) total concentration of (CO + H_2), and (3) steam concentration on the performance of zinc titanate sorbents.

Composition 1 is a high-steam, low-CO, low-H_2 gas composition, typical of a Lurgi fixed-bed gasifier. Composition 2 is a simulated oxygen-blown composition with high CO and high H_2 concentrations, but intermediate reducing power. Composition 3 is a high-CO, low-H_2 , low-CO_2 composition that has nitrogen included to decrease the total (CO+H_2) concentration below that of gas composition 2 and yet with increased reducing power. During bench-scale testing, the sorbent chemical composition code shown in Table 2 was modified by adding the suffix 1, 2, or 3 according to the simulated coal gas composition in used to perform the bench-scale tests.

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

Component	# 1 (%)	# 2 (%)	# 3 (%)
CO	8	39	33
CO_2	11	10	0.4
H_2	16	30	16
H_2O	30	20	10
H_2S	1	1	1
N_2	34	0	39.6
Reducing Power†	0.61	2.33	4.70
(CO + H_2)%	24	69	49

† Defined as (CO+H_2)/(CO_2+H_2O)

Ten bench-scale reactor runs were conducted. Only results for the gas-inlet location of one straight 2.0 zinc titanate, 2M, and one Mo-doped zinc titanate, 2A1.7M, will be presented. Figure 2 shows a sample plot of reactor effluent H_2S concentrations as a function of time, or breakthrough curves, and TGA chemical reactivity under simulated coal gas composition 2. Ten cycles of absorption and regeneration were carried out for each of ten runs. At each absorption, breakthrough is defined as the point at which the effluent H_2S concentration reached 200 parts per million by volume (ppmv). The low pre-breakthrough H_2S concentrations measured in all runs (typically less than 15 ppmv) represent excellent sulfur removal, ~99.9% based on the 1% H_2S inlet gas. Shown in the lower X-axis scale is the dimensionless time, which provides a measure of overall sorbent bed utilization relative to the theoretical calculated time for saturation. In most cases, bed utilization at the 200 ppmv H_2S breakthrough time ranged between 15-25% of theoretical, with weaker formulations exhibiting higher utilizations. Formulation 2A1.7M, being one of the strongest, showed an average capacity of 15% at the 200 ppmv breakthrough. As a comparison, sulfur capacities of previous zinc ferrite sorbents have been measured to be 50% higher during pilot plant operation than during laboratory evaluation since scale-up improves desulfurization performance because of higher pellet-to-reactor diameter ratio.

Characterization of Bench Reactor Samples

Chemical Composition. Chemical analyses were conducted on samples extracted from three reactor bed locations (gas inlet, middle, and gas outlet) after the 10th absorption and the 10th. regeneration. The gas inlet location (i.e., the most heavily sulfided location) has the most severe environment to which the sorbent is exposed. Zero or low levels of residual carbon are desired 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 samples and a low sulfate content in regeneration samples are also desired to maximize sulfur removal performance by the sorbent. Sulfate formation is also undesirable because it induces internal stresses in the pellet

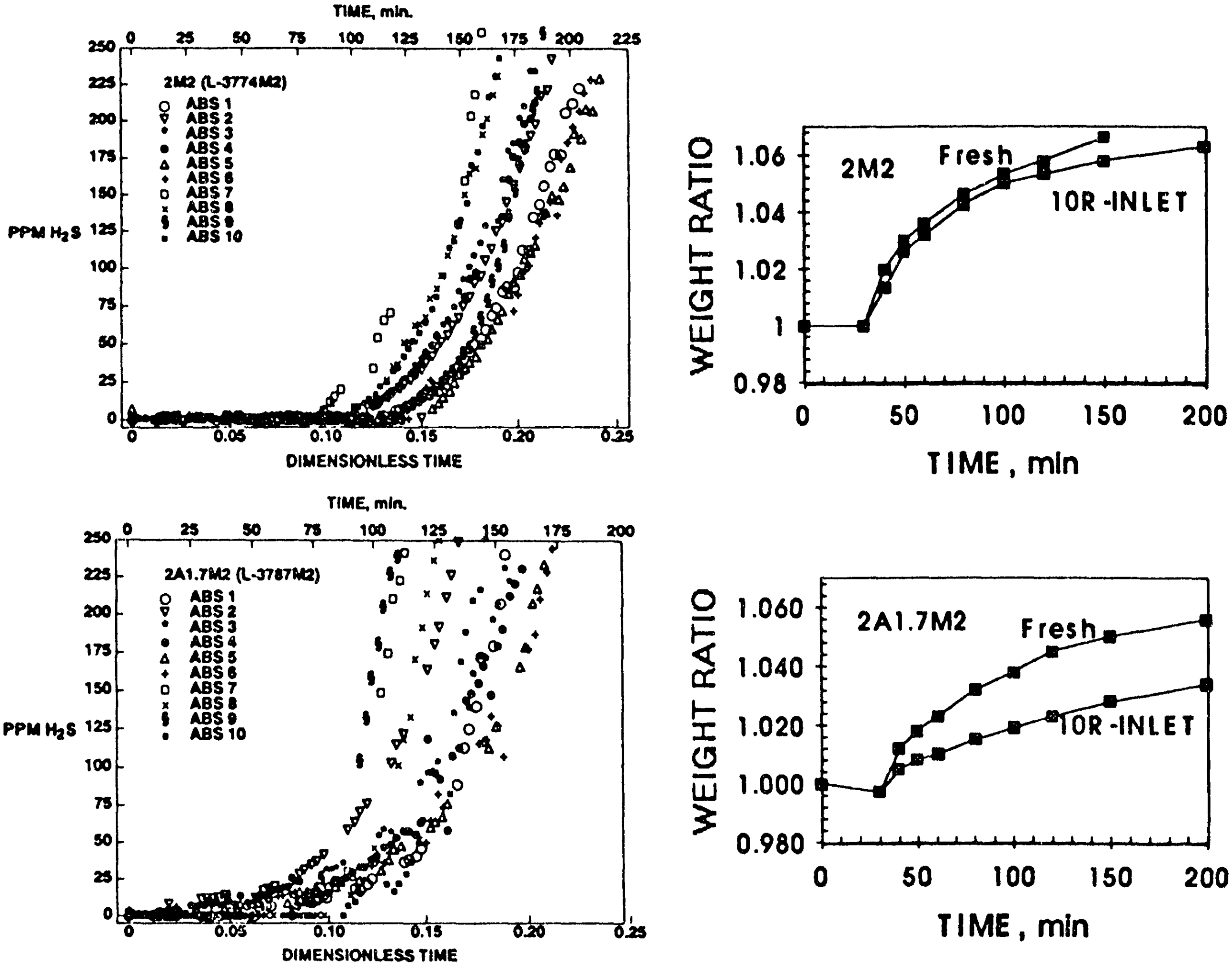


Figure 2. Breakthrough curves and TGA Chemical Reactivity of Bench-Scale Sorbents

that promote degradation and deterioration of the mechanical properties of the sorbent.

The levels of carbon in absorption samples (< 0.5% wt) and the amount of sulfate found in regenerated samples (<0.3%) are considered too small to have a significant adverse effect on the desulfurization performance of the sorbents. The regeneration scheme used, with a final temperature rise to 1400 °F, 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.) correspond to 15-31% of the total theoretical sulfur capacity of the sorbent and is considered satisfactory for moving-bed systems.

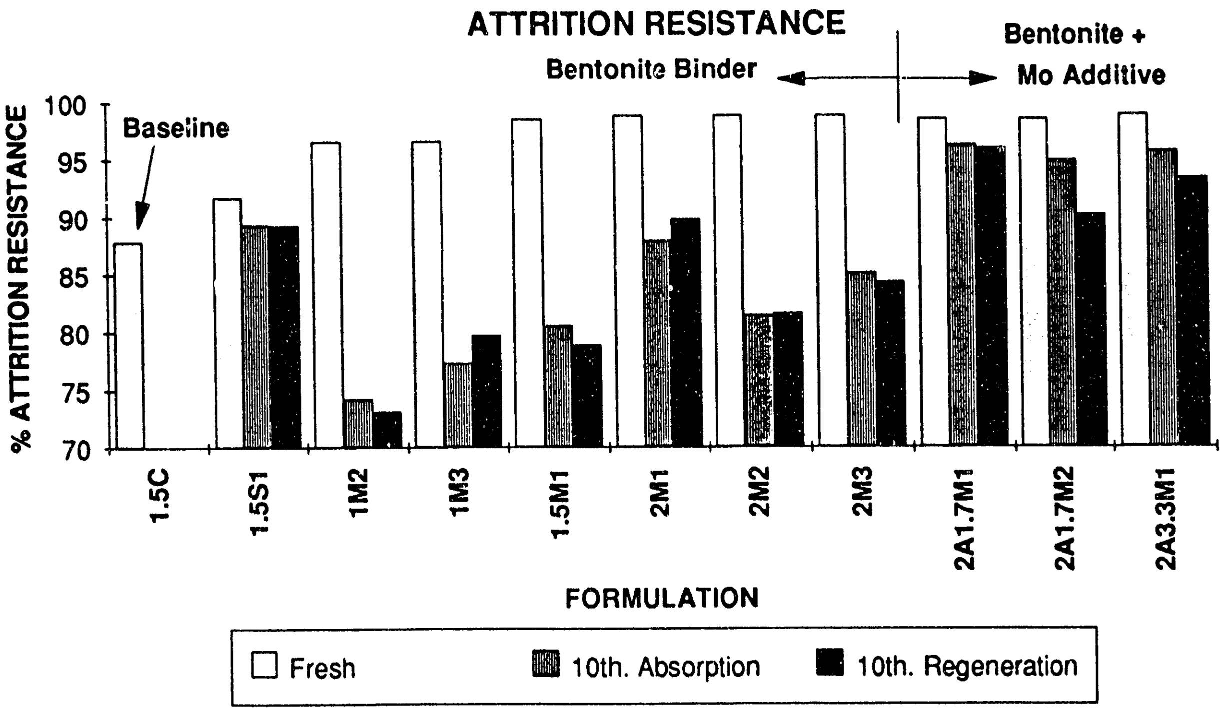
In addition to carbon and sulfur analyses, elemental analyses of zinc and molybdenum by ICP were performed and the results are shown in Table 4. No significant losses in zinc were measured, within the experimental error of the technique (5% relative error) at absorption temperatures of 1000 °F. It should be emphasized that the absence of zinc sublimation for the 2:1 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) 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. On the other hand, Mo losses were measured at 3.3% and higher Mo levels where, presumably, the vapor pressure of unreacted molybdenum oxide MoO_3 (melting point : 795 °C, 1463 °F) was 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. SEM/EMA photomicrographs of 2A1.7M sorbent showed that molybdenum is dispersed into the zinc titanate structure in small clusters less than 20 µm in size for the 2A1.7M formulation.

Table 4. 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.

Mechanical Strength. 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 3). Those formulations prepared as straight zinc titanates suffered significant physical deterioration and losses in attrition resistance during the 10 cycles. An identical observation is seen in crush strengths (lower diagram of Figure 3).



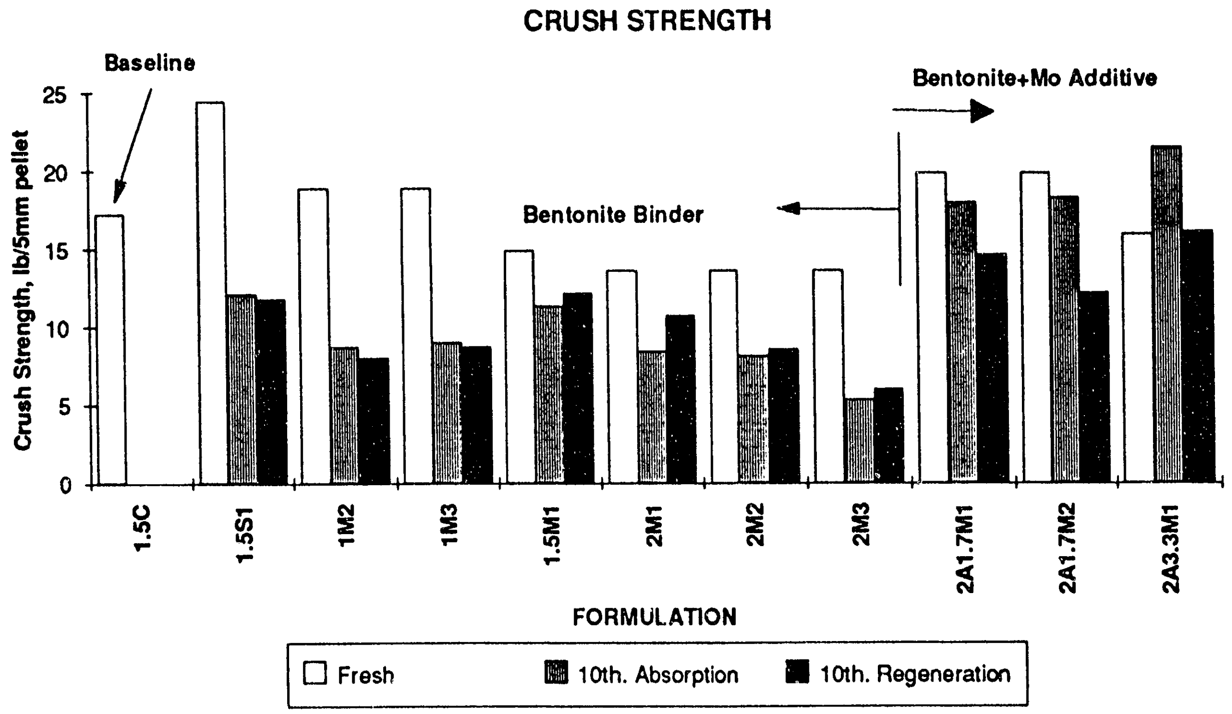


Figure 3. Attrition Resistance and Crush Strength after Bench-Scale Testing

Attrition resistance of fresh and cycled formulations (10th. absorption and 10th. regeneration), is shown in the upper diagram of Figure 3. Except for the baseline cylindrical extrudate 1.5C (UCI's L-3140) and the rounded 1.5M1, all of the rounded formulations had an acceptable initial attrition resistance above 96%.

Those formulations prepared as straight zinc titanates suffered significant physical deterioration and losses in attrition resistance during the 10 cycles. An identical observation is seen in crush strengths (lower diagram of Figure 3); physically, pellets with low crush strengths exhibited exfoliation and cracking of the surface that weakened the pellet. 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 is concluded that the better performance in strength is a result of the presence of molybdenum.

In addition, all formulations tested under two or more gas compositions showed that the attrition losses are greater under gas composition 2 and less when tested under gas composition 1 with gas composition 3 falling in the middle. The crush strength followed the same trend as the attrition test except for formulation 2M. 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 ($CO + H_2$) concentration of a gas is more indicative of the expected severity of mechanical strength losses than the reducing power $(CO + H_2)/(CO_2 + H_2O)$.

Figure 4 shows a comparison of pore size distribution by mercury intrusion porosimetry for a

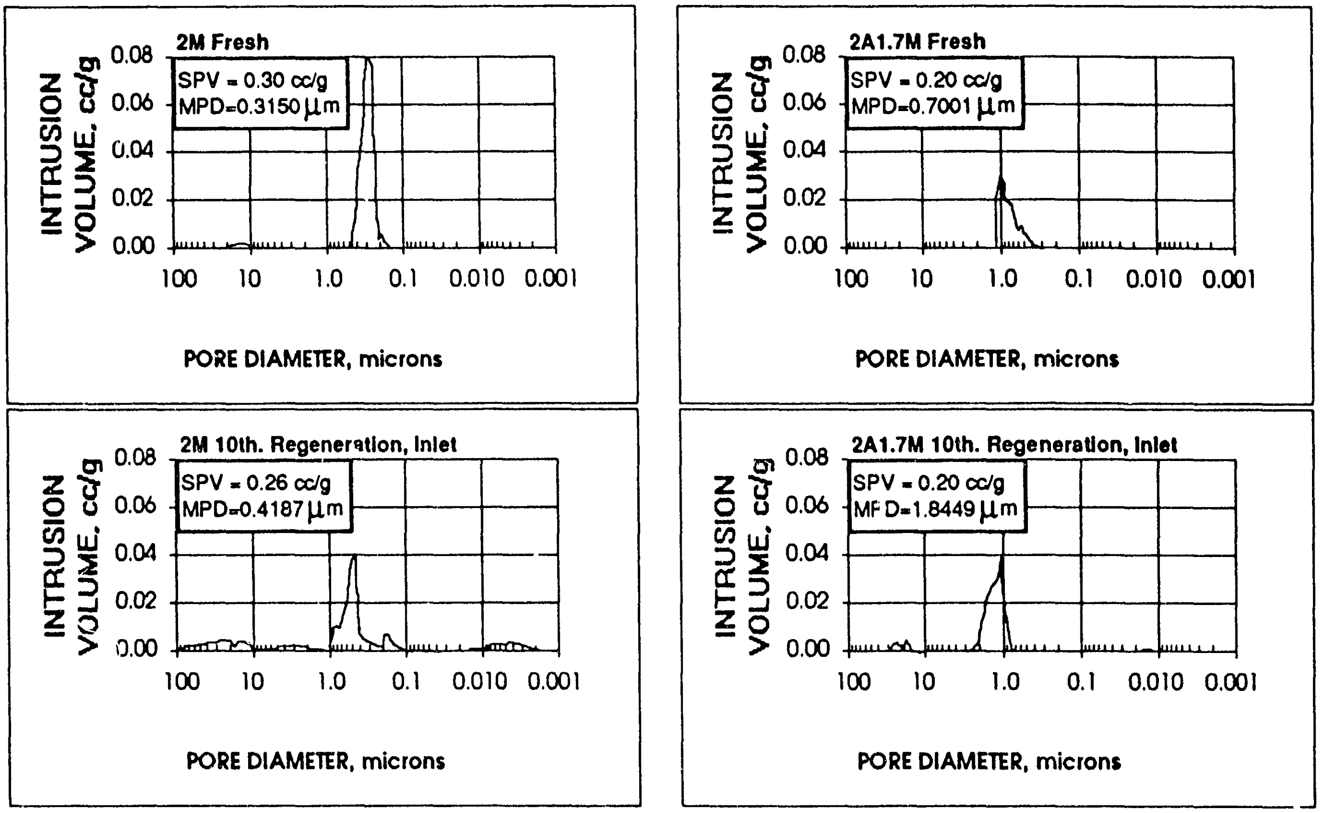


Figure 4. Pore Size Distribution of Weak (2M) and Strong (2A1.7M) Sorbents after Bench-Scale Testing

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 centered at 0.004 µm 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.

It is believed that the lower MPD of the 2M formulation is responsible for its loss of strength: when a 2.0 zinc titanate undergoes full sulfidation, the molar volume increases by 50% at the expense of a reduction in pore void volume; on the other hand, if pores are narrow (low MPD) and many (large SPV), the thin pore walls can collapse from the molar volume changes of sulfidation/regeneration; if pores are wide (high MPD) and fewer (low SPV) the thicker walls between pores are able to withstand the internal stresses due to reaction, with the result that deterioration of the pellet structure is minimal as in 2A1.7M. The presence of Mo oxide in 2A1.7M may provide a mobile enough solid structure during calcination to remove the micropores (i.e., pores < 100 Å) in the pellet and result in a more durable pellet.

FUTURE WORK

Results presented in this paper correspond to the performance of the Option 2 program. Based on the results and conclusions reached, additional zinc titanate sorbents will be prepared under the Option 3 program in order to optimize the mechanical durability of current formulations and understand the chemistry of desulfurization for moving-bed systems.

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