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Moving-Bed Sorbents

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Moving-Bed Sorbents

CONTRACT INFORMATION

Contract Number	DE-AC21-88MC25003
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METC Project Manager	Daniel Cicero
Period of Performance	September 21, 1988 to June 30, 1995

Schedule and Milestones

FY95 Program Schedule

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

OBJECTIVES

The objective of the option 3 program within this contract is to develop chemically reactive and mechanically durable mixed-metal oxide sorbent formulations that are suitable for moving-bed, high-temperature, desulfurization of coal gas. One optimum formulation is to be evaluated in a pressurized 50-cycle bench-scale test. Work on zinc ferrite formulations was performed under the base program (Ayala, 1991). Work on zinc titanate formulations was initiated under the option 2 program (Ayala, 1993) and is continued under the present option 3 program along with testing of other mixed-metal oxides.

BACKGROUND INFORMATION

GE is developing a moving-bed, high-temperature desulfurization system for integrated gasification combined-cycle (IGCC) power systems in which zinc-based regenerable sorbents are currently being used as desulfurization sorbents (Bevan et al., 1994). Zinc titanate and other zinc-based oxides are being considered as sorbents for use in the Clean

Coal Technology Demonstration Program at Tampa Electric Co.'s Polk Power Station. A key to success in the development of high-temperature desulfurization systems is the matching of sorbent properties for the selected process operating conditions, namely, sustainable desulfurization kinetics, sulfur capacity, and mechanical durability over multiple cycles.

Mixed-metal oxide sorbents have been studied quite extensively in the past, including various types of zinc titanates (e.g., Zn_2TiO_4 and $Zn_2Ti_3O_8$) (Ayala et al., 1994; Gangwal and Gupta, 1993) or as combinations of other metal oxides such as nickel, copper, manganese, cobalt, tin, and others; see for instance (Gasper-Galvin et al., 1994; Hepworth, 1994; Karpuk, 1994). Proprietary zinc-based sorbents, such as Phillips Petroleum Company's Z-Sorb™ III sorbent and METC sorbents, have also been tested (Everitt, 1994; Gangwal et al., 1994; Siriwardane et al., 1994). The reactions occurring during desulfurization of coal gases and regeneration of the sulfided sorbents have been described before in many sources; see for instance, (Gangwal and Gupta, 1993).

PROJECT DESCRIPTION

Program participants are: GE Corporate Research and Development (GE-CRD, prime contractor), GE Environmental Systems, Inc., (GEESI, subcontractor), and Research Triangle Institute (RTI, subcontractor). United Catalysts, Inc. (UCI) and Phillips Petroleum Company (PPC), acting as vendors, provided the sorbent samples for testing.

As mentioned in previous papers (Ayala et al., 1994; Ayala et al., 1993), sorbents developed for moving-bed systems must comply with a minimum of chemical and mechanical durability performance characteristics in order to be considered acceptable for long-term operation. Among the desired properties, a sorbent must have:

- High chemical reactivity, as measured by the global rate of sulfur absorption (including gas-phase mass transfer, pore diffusion, and intrinsic reaction rates) [Westerterp, 1984] and the total sulfur loading on the sorbent.
- High mechanical strength, as measured by the pellet crush strength and the attrition resistance.
- Suitable pellet morphology, as given by pellet size and shape to promote good bulk flowability and reasonable porosity to increase reactivity.

RESULTS

During the current reporting year ('94-'95), the bench-scale reactor system at GE-CRD was upgraded to conduct tests of sorbents at pressure (up to 10 atm). Previously, the system operated only at 1 atm in both absorption and regeneration modes. Both Z-Sorb™ III sorbent and zinc titanate have been considered in laboratory testing in the past 12 months. A 50-cycle bench test was planned using Z-Sorb™ III sorbent given that it had been shown to be more attrition resistant during side-by-side (1 atm) tests against zinc titanate sorbents (Ayala et al., 1994). Tests on zinc titanate have focused on understanding regeneration schemes during pressurized operation and making zinc titanate more attrition resistant when sulfates are present.

Z-Sorb™ Sorbent Results

Preparation methods for Z-Sorb™ sorbent formulations are considered proprietary

to PPC, and only analyses that describe performance in hot gas desulfurization will be presented here.

Table 1 shows the properties of the Z-Sorb™ III sorbent formulation used in this study. These properties correspond to the GE designation "Z-Sorb E", which distinguishes it among various Z-Sorb™ III sorbent formulations provided in previous years that differed primarily in pellet size and reactivity (see, for instance, Ayala et al., 1994).

Table 1.- Physical Properties of Z-Sorb™ III Sorbent

	Z-SORB E
Pellet Length, mm	6.4
Pellet Diam., mm	4.3
Pellet Mass, mg	114
Crush Strength, lb/pellet	10.2
(ASTM) Attrition Loss*, %	1.6
Bulk Density, lb/ft^3	~60

* Attrition losses of the fresh sorbent at the GE-CRD Pilot Plant are typically a factor of 10 lower.

Samples of Z-Sorb™ III sorbent, prepared as 4-mm ellipsoidal pellets by PPC, were used for the bench tests using wet regeneration (2% H_2O) and dry regeneration procedures. Wet regeneration tests were terminated early (after 12 cycles) due to loss of sorbent capacity that was assumed to be a combination of steam regeneration and sulfate formation effects arising from use of 20% oxygen in the final step of the second regeneration. This regeneration step was abandoned thereafter; hence the data did not allow proper analysis of each process parameter separately. Only results corresponding to the dry regeneration tests will be presented here.

During dry regeneration multicycle tests, absorption was conducted in an 800 ml sorbent bed at 5 atm and 538 °C (1000 °F), with a simplified gas composition similar to that of an oxygen-blown gasifier with high H_2S (39% CO, 10% CO_2, 30% H_2, 20% H_2O, 1% H_2S). Space velocity was 1000 scc/cc•hr (25 °C, 1 atm). Regeneration was conducted also at 5 atm, 538 °C (1000 °F), maintaining the peak bed temperature below 732 °C (1350 °F); gas composition was 0-4% O_2 in nitrogen. A final step in regeneration included depressurization of the reactor to 1 atm under nitrogen at 732 °C (1350 °F) to decompose zinc sulfates formed during regeneration. No SO_2 was added to the regeneration gas (which would have simulated recycled SO_2 in pilot plant operation). The direction of flow of gases was the same in both absorption and regeneration.

Figure 1 shows the results of ten cycles of bench testing of Z-Sorb™ sorbent at the GE-CRD reactor unit using a dry regeneration scheme. The first cycle shows a higher sulfur bed capacity than cycles two to seven. This is a result of the sulfidation of nickel during the first cycle that increases the overall sulfur capacity of the bed. After nickel is sulfided, the bed desulfurization capacity is a result of zinc-only desulfurization. Cycle ten shows a loss in bed capacity with respect to cycles two to five, which would be a concern if a stable operation is to be maintained.

Small samples were taken from the reactor bed after 5 cycles to conduct single-pellet TGA chemical reactivity tests. Figure 2 shows the thermogravimetric analyzer (TGA) chemical reactivity of pellets after the fifth and tenth cycles. The weight gained by the pellet is proportional to the sulfur loading in the pellet. The first forty minutes are exposure to pure nitrogen (30 minutes) and clean (i.e., no H_2S) simulated coal gas (10 minutes). H_2S is introduced 40 minutes after start. Pellet weights are stable under N_2, and a small weight loss is observed when clean simulated coal gas is introduced, suggesting decomposition of small amounts of sulfate. Fresh pellets did not exhibit this weight loss upon exposure to coal gas. These reactivity tests were performed under a standard GE procedure using a simulated coal gas having 3% H_2S at 538 °C (1000 °F). The high H_2S concentration is used to expedite the testing, such that pellet saturation with sulfur occurs in two to three hours. Full sulfidation of Z-Sorb™ III sorbent pellets corresponds to a weight gain of approximately 10%. For the samples after the fifth cycle, the results suggest that the samples that were sulfided heavily at each cycle (i.e., the gas inlet location) did not suffer loss in reactivity (given by the slope of the curve) and capacity (given by the final weight of the pellet), while those at the gas outlet location, where the pellets are partially sulfided, did. These results follow similar trends observed in pilot plant tests. For the gas outlet samples, reactivity is higher very early in the test (during the external sulfidation of the pellets), but decreases with time; capacity after two hours of sulfidation was about 60 to 65% of that of fresh pellets.

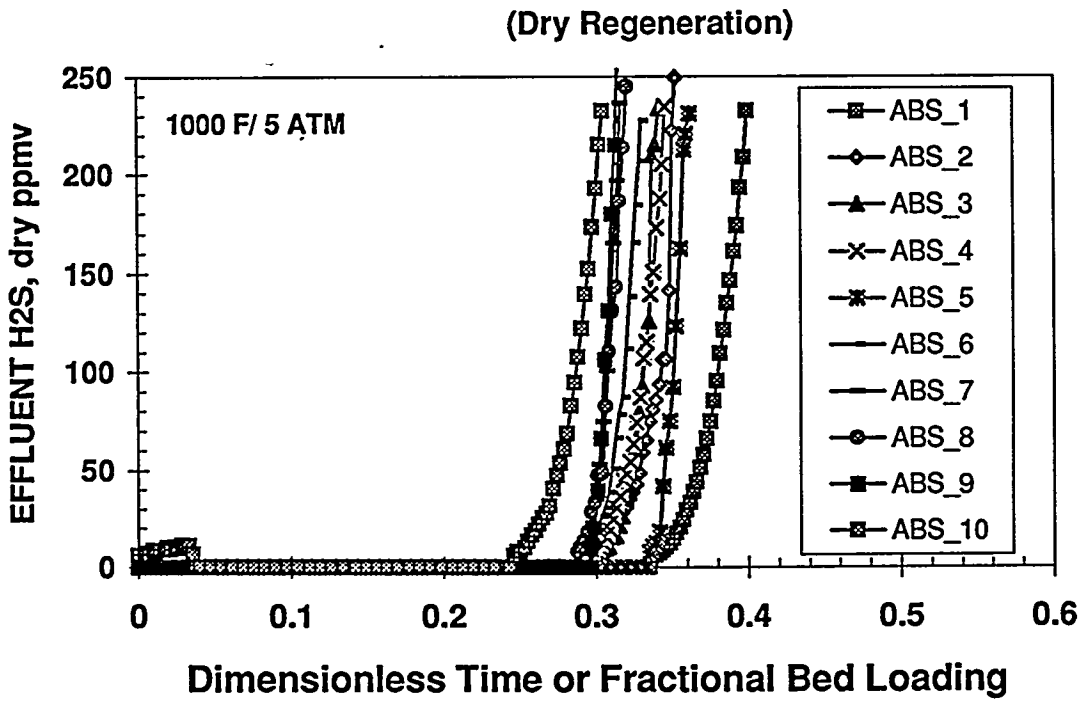

Figure 1 .- Absorption Breakthrough Curves for Z-Sorb™ III Sorbent

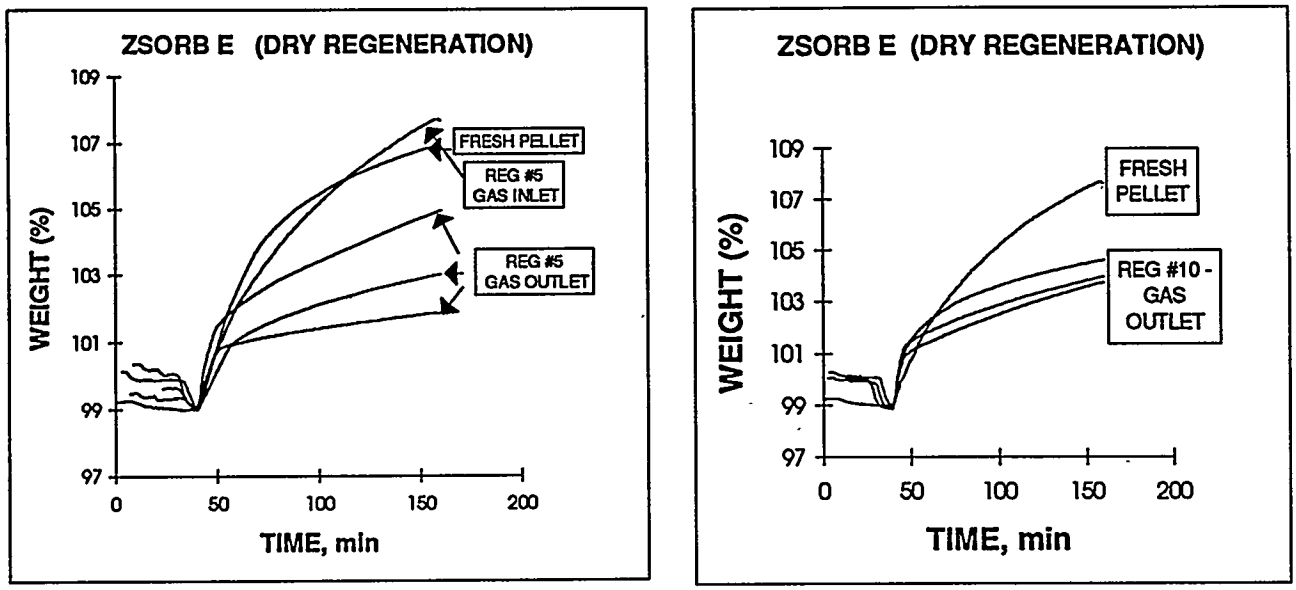

Figure 2.- TGA chemical reactivity of Z-Sorb™ III sorbent samples after 5 and 10 cycles

Design conditions for sorbent performance at Tampa Electric Co.'s moving-bed system require a sulfur loading of 6 lb/ft^3 on any sorbent. For Z-Sorb™ III sorbent, this requirement translates into 50% of theoretical sulfur loading or 5% weight gain under TGA testing. There is loss in reactivity and capacity in the gas outlet samples, as indicated by TGA tests, when exposed to laboratory conditions of simulated coal gases (no steam during regeneration, no tars during absorption, and no exposure to sodium-containing halogen-removal sorbents, as in pilot plant tests).

Further tests are needed to isolate the major cause of degradation and determine whether the problems encountered are surmountable. Currently, Phillips Petroleum Co. is working on a more resistant Z-Sorb IV sorbent formulation which will be available in the near future for testing.

Another operating scheme tested in the laboratory was the feasibility of decomposing sulfates during regeneration. Figure 3 shows the last step in the regeneration sequence where the sorbent is at 1350 °F under nitrogen at 5 atm. Some SO_2 is evolved as a result of sulfate decomposition. By depressurizing the reactor to 1 atm, still under N_2, the sulfate decomposition is further accelerated, as given by the sudden burst of additional SO_2 evolved. This step is beneficial because less residual sulfate in the sorbent is carried to the absorption step, where it converts to SO_2 and H_2S, thus resulting in lower overall desulfurization efficiency.

The effect of sulfate decomposition and subsequent SO_2 evolution can be explained from thermodynamic principles. Figure 4 shows the phase stability diagram for the ternary system Zn-S-O at two temperatures 550 °C (1022 °F) and 732 °C (1350 °F). A typical regeneration gas composition at 550 °C and 1-7 atm of pressure in the presence of O_2 and SO_2 is shown by the point marked X. This point falls in the region of stable formation of $ZnO{\bullet}2ZnSO_4$ (zinc oxysulfate). As the temperature is increased to 732 °C, the pressure reduced to 1 atm, and the gas composition changed to N_2 only, the system moves to point O, where the zinc oxysulfate is

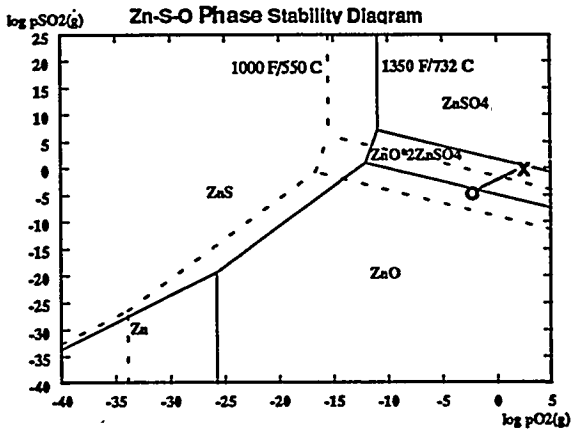

Figure 4.- Phase stability diagram for the system Zn-S-O at 550 °C and 732 °C

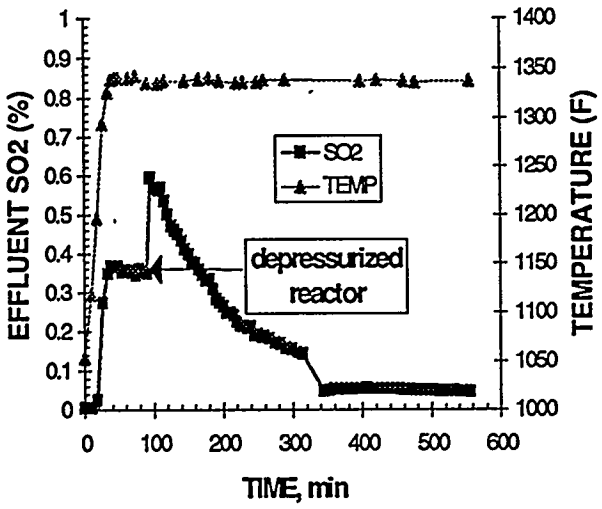

Figure 3.- SO_2 evolution during regeneration at 5 atm and 1 atm

unstable and decomposes into zinc oxide. This operation mode is achieved during lockhopper operation in the moving-bed process, thus preventing carryover of sulfate into the absorption step.

Zinc Titanate Sorbent Results

Zinc titanate sorbent formulations were also tested at pressure in the laboratory as an alternate sorbent; the objective of the zinc titanate testing is to characterize the sulfate formation kinetics during pressurized regeneration and be able to strengthen the pellet structure against sulfate-induced attrition. Tests at pressure are designed to provide additional data on the sorbent performance at conditions similar to those to be encountered at the Tampa Electric Co.'s Polk Station, where regeneration will be conducted at up to 7 atmospheres of pressure.

Table 2 shows the physical properties of T-2535M zinc titanate sorbent prepared by UCI. Preparation methods for UCI's zinc titanate sorbents have been described before (Ayala, 1993).T-2535M2 zinc titanate is the GE designation for second batch of formulation T-2535M having approximately 2.5% MoO_3 as pore modifier and 3% bentonite binder. It was produced in 1993 as a large batch (6,000 lb) for use in the GE moving-bed pilot plant in Schenectady, New York.

Table 2.- Physical Properties of Zinc Titanate Sorbent

	T-2535M2
Pellet Length, mm	6.1
Pellet Diam., mm	4.9
Pellet Mass, mg	214
Crush Strength, lb/pellet	17.1
ASTM Attrition Resistance, %	98.5
Bulk Density, lb/ft^3	~100

Bench-scale reactor tests on T-2535M zinc titanate have been re-initiated to determine its performance under pressurized regeneration in the laboratory. Figure 5 shows the breakthrough curve for T-2535M as a function of dimensionless time, or average bed sulfur loading. The outlet H_2S prior to breakthrough was measured at less than 10 ppmv. For the size

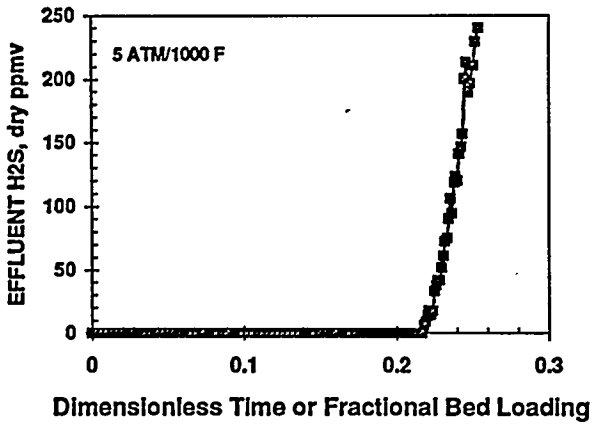

Figure 5.- Bench reactor testing of T-2535M zinc titanate

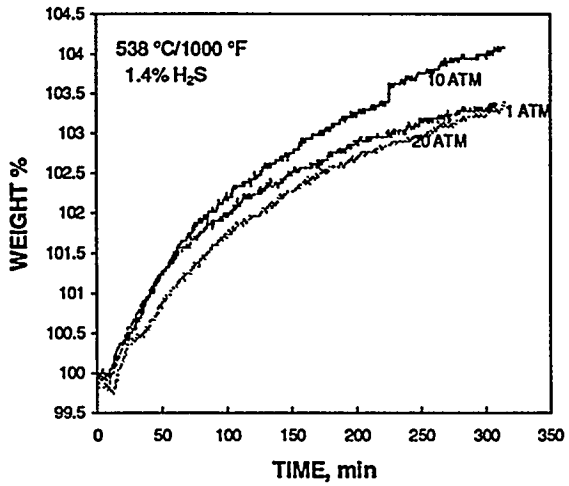

Figure 6.- TGA reactivity of T-2535M2 zinc titanate as a function of sulfidation pressure

of bed used (800 ml), the dimensionless time at breakthrough is about 0.25 of the theoretical, or 25% average sulfur loading on the bed, which is the design target (i.e., 6 lb sulfur/ft^3 of bed) for pilot plant and large scale operation.

TGA reactivity tests at pressure on zinc titanate were conducted at RTI. Figure 6 shows the pellet performance as a function of pressure at constant 1.4% H_2S in the feed gas. Note that this H_2S concentration is less than the concentration used in standard screening at GE under atmospheric conditions. If the curves are adjusted to the same starting point in the vertical axis, there is no significant difference in performance between 1 atm and 20 atm; furthermore, performance for all three pressures falls within the variation in reactivity from pellet to pellet. Hence, no significant trends from pressure effects are seen in this sorbent.

For regeneration, two additional TGA reactivity tests were performed. One in which sulfate was allowed to form during regeneration at 5 atm pressure, and the other in which sulfate was inhibited from forming, also at pressure. In Figure 7 (left), fresh pellets were sulfided during the first 300 minutes according to the procedure shown in Figure 6. Then, by switching between regeneration condition *A* (10% SO_2, 2% O_2, 88% N_2 at 650 °C) and regeneration condition *B* (100% N_2 at 730 °C), zinc sulfate was allowed to form and decompose, as given by the weight gain/loss during transition from *A* to *B* to *A* condition. In Figure 7 (right), the same process was performed, except that condition *A* did not contain any O_2. The result is a lack of sulfate formation. This experiment demonstrates that the conditions that control the level of sulfate formation and decomposition during regeneration can be adjusted to prevent pellet decrepitation.

CONCLUSIONS

Tests performed on Z-Sorb™ III sorbent showed that the sorbent is capable of reducing H_2S levels below a target of 20 ppm during desulfurization of simulated coal gases meeting the requirements for desulfurization in commercial operation. During regeneration, sulfate can be decomposed by adjusting the process conditions that lead to thermodynamic instability and thermal decomposition of zinc sulfates. However, the ability to maintain desulfurization of Z-Sorb™ III sorbent under cyclic operation is a concern in view of the losses in reactivity and capacity observed in the gas outlet location under dry regeneration conditions in the laboratory. Future evaluation is necessary.

Zinc titanate operation was reinitiated with a bench test also at pressurized conditions in the laboratory. Desulfurization below 20 ppmv was also achieved. Evaluation of regeneration conditions that lead to minimization of sulfate formation and maximization of sulfate decomposition (and hence leading to low

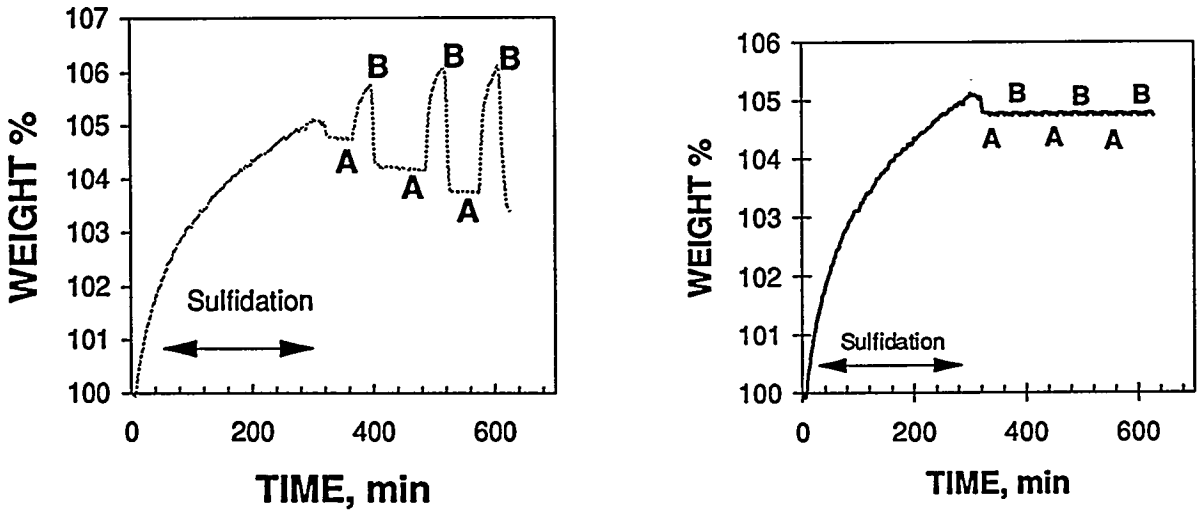

Figure 7.- TGA regeneration of T-2535M2 in the presence (left) or absence (right)of O_2

attrition losses) were evaluated.

FUTURE WORK

The results of the cyclic testing of sorbents are being summarized in a topical report to be submitted to DOE in the near future. Many of the ideas under consideration for future testing will be pursued under another current contract with DOE, Advanced Sorbent Development (Contract DE-AC21-94MC31089).

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