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Multicycle Testing of METC10-M Sorbent

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Disclaimer

INTRODUCTION

This report describes the results of testing the METC10-M sorbent in the Research Triangle Institute's (RTI's) high-temperature, high-pressure (HTHP) sorbent test facility. The objective of this testing was to determine optimum operating conditions for achieving target performance of the METC10-M sorbent and to assess its compatibility for use in the Tampa Electric Company's (TECo's) Hot Gas Cleanup Unit hardware as it currently exists.

The minimum criteria for consideration as sorbent candidates for TECo's evaluation were established in November 1996. In relation to bench-scale testing, these requirements include:

a. The H_2S leakage (prebreakthrough level) prior to target sulfur loading of 6.7 lb/ft^3 (at gas inlet) must be below 100 parts per million by volume (ppmv).

b. The sorbent must maintain a minimum of 50 percent of theoretical capacity throughout 25 cycles of testing, but never less than 6.7 lbs/ft^3.

c. The sorbent attrition determined by American Society for Testing Materials (ASTM) Standard D4058-81 must be $\leq$4 percent for the fresh material and $\leq$5 percent for the 24-Cycle regenerated material.

d. The sorbent must be regenerable at 900 to 950 °F in the presence of 8 to 10 vol% of SO_2 in the regenerator feed gas.

The METC10-M sorbent was developed by Morgantown Energy Technology Center (METC) in-house researchers. The parent version of this sorbent (METC10) was tested in General Electric's (GE's) pilot plant facility in March 1996. The current version, designated as METC10-M where "M" stands for "modified," was an improved version of the parent material. United Catalysts Inc. (UCI) prepared the current formulation under guidance from METC using equipment large enough to produce a sorbent batch with the physical and chemical characteristics that would be obtained for a commercially prepared sorbent batch. This sorbent was supplied as 3-mm ellipsoidal pellets. ASTM attrition and crush strength of the fresh pellets are shown later in Table 1.

Initial scoping tests to identify optimum operating conditions for the 25-cycle test indicated that the METC10-M sorbent could be regenerated readily at 950 °F, 3.5 vol% O_2 and a space velocity of 2,000 h^{-1}. Exposure to increasing levels of SO_2 (up to 10 vol%) during regeneration did not have any adverse effect on the ability of this sorbent to remove the desired amount of sulfur from simulated coal gas streams or to be regenerated at 900 °F. Baseline tests with this sorbent conducted in accordance with the test protocol, in which SO_2 was not added to reactor feed gas during regeneration, confirmed that the desired sulfur loading of 6.7 lb/ft^3 was easily attainable with no H_2S breakthrough. Pre-breakthrough H_2S levels in the reactor effluent were $<$20 ppmv. Regeneration was easily initiated at 900 to 950 °F with 3.5 vol% O_2 and a space velocity of 2,000 h^{-1}. No change was observed in either the sulfidation or the regeneration from cycle to cycle during this 10-cycle baseline test. Following these scoping and baseline tests, the METC10-M sorbent was subjected to the 25-cycle test using the approved test protocol provided by the U.S. Department of Energy (DOE).

EXPERIMENTAL PROCEDURE

The 25-cycle test was performed in RTI's HTHP bench-scale sorbent test facility. This facility consists of a specially designed reactor system in which the sorbent is held in a quartz cage and exposed to simulated coal gas or regeneration gases at HTHP. The quartz reactor provides an inert surface that does not adsorb H_2S or catalyze reactions between coal gas components or regeneration gases. During sulfidation, a reactor effluent slipstream, from which the steam has been condensed, is analyzed by a Varian 3300 gas chromatograph (GC) for H_2S, COS, and SO_2 every 5 to 7 min. From this information, H_2S concentration as a function of time is monitored. During regeneration, reactor effluent slipstreams are fed to on-line O_2 and SO_2 analyzers. Concentration of the SO_2 in the reactor feed is continuously monitored by another on-line SO_2 analyzer. The regeneration feed gas containing 3.5% O_2 and 8% SO_2 in N_2 was generated by pumping controlled quantities of liquid SO_2, vaporizing liquid SO_2, and mixing the vaporized SO_2 into an air-nitrogen mixture generated by blending metered quantities of air and nitrogen.

The run was stopped after the 24th regeneration and the sorbent was examined. Out of the sorbent removed from the reactor, 110 g of the sorbent were kept for characterization. The remaining sorbent was loaded into the reactor and an additional sulfidation cycle was performed. This sulfidation cycle was carried out until breakthrough. To account for the reduced sorbent charge in the reactor, the total gas flow was reduced to maintain the same space velocity. At the end of this sulfidation, the reactor was opened and the sorbent was removed.

SULFIDATION RESULTS

Hydrogen sulfide concentration in the reactor effluent is shown as a function of time in Figure 1. As can be seen, H_2S concentration in the reactor effluent remains <20 ppmv during the 125 min sulfidation for the first 24 cycles. No change in this prebreakthrough H_2S level was observed over 24 cycles. Figure 2 shows an envelope of H_2S concentration observed at 125 min as a function of cycle number. As can be seen, this number is below 20 ppmv as would be expected from thermodynamic calculations.

The breakthrough behavior of the sorbent was also confirmed by the estimated sulfur loading calculated based on the mass balance for sulfur around the reactor system as shown in Figure 3. A horizontal line at 20.7 g of sulfur loaded indicates that the desired sulfur loading (6.7 lb/ft^3 at gas inlet) was achieved prior to H_2S breakthrough. The breakthrough curve generated during the 25th sulfidation shows a sulfur loading capacity of approximately 17 wt% after 25 cycles of testing and being exposed to high SO_2 concentrations during regeneration.

REGENERATION RESULTS

Figures 4 through 9 show the temperature profiles for Cycles 1, 2, 3, 4, 12, and 24. These results clearly indicate that sorbent ignites nicely at 950 °F with 3.5% O_2 at a space velocity of 2,000 h^{-1}, both with and without the presence of SO_2 in the regeneration feed gas. The peak temperature of the sorbent bed during the regeneration was between 1,150 and 1,200 °F with temperature wave moving from the bottom of the bed to the top section. Furnace settings were maintained at 950 °F during the entire regeneration.

Figures 10 through 15 show inlet SO_2, outlet SO_2 and O_2 concentrations for Cycles 1, 2, 3, 4, 12, and 24. Results from the first three cycles (Figures 10 to 12) show the sorbent performance during increasing SO_2 concentrations (0, 0.5, and 3.5 percent in Cycles 1, 2, and 3, respectively). The remaining figures (Figures 13 to 15) indicate the consistency of sorbent cycle-to-cycle regeneration performance. After 24 cycles, the sorbent had essentially the same performance during regeneration as it had after four cycles.

POST-TEST CHARACTERIZATION

Table 1 compares various physical and chemical properties of fresh and reacted sorbent removed at various stages.

As can be seen, the sulfur loading at breakthrough was 17 percent after the 10-cycle baseline as well

Table 1. Physical and Chemical Properties of Fresh and Reacted METC10-M Sorbent

Property	Fresh	After 10th sulfidation (baseline test)	After 24th regeneration	After 25th sulfidation
Sulfur loading at gas inlet (wt%)[a]	NA	17	NA	17
ASTM attrition (wt%)	0.6	1.2	1.8	1.8
Crush strength (lb/pellet)	6	22	13	18
Sulfate sulfur (wt%)[a]	NA	0	0.8	0

[a]Analyzed by Commercial Testing and Engineering Company.
NA = Not applicable.

as the 25-cycle test with SO_2 regeneration, indicating that the presence of SO_2 had no effect on the sorbent performance. The ASTM attrition of the fresh material was 0.6 percent and it increased to 1.2 percent after 10 cycles of baseline testing and 1.8 percent after 25 cycles. The crush strength of the 25-cycle sulfided material was 18 lb/pellet compared to 6 lb/pellet for the fresh material. The thermogravimetric analysis (TGA) reactivity tests were not applicable for this material because the weight change in TGA did not correspond to the extent of sulfidation or regeneration.

SUMMARY AND CONCLUSIONS

Based on scoping, baseline and 25-cycle testing of the METC10-M sorbent, the following conclusions can be made:

- The sorbent is capable of absorbing 6.7 lb/ft^3 of sulfur (at gas inlet) without H_2S breakthrough.

- The prebreakthrough H_2S concentration was below 20 ppmv over 25 cycles.

- No change in sulfur capacity was observed over 25 cycles of testing.
- This sorbent can be easily regenerated at 900 to 950 °F with 3.5% O_2 at a space velocity of 2,000 h^{-1}.
- Presence of up to 8 percent SO_2 in the regeneration feed gas did not have any adverse effect on the sorbent performance.
- Sorbent was able to maintain its mechanical strength over 25 cycles of testing. The crush strength of the pellets increased from 6 lb/pellet for the fresh to 18 lb/pellet for the 25-cycle sulfided material while the ASTM attrition increased from 0.6 to 1.8 percent.
- The METC10-M sorbent had a sulfur loading of 17 wt% and attrition of 1.8 wt% at the end of 25 cycles. The required sulfur loading and attrition for TECo operation (6.7 lb/ft^3 and $\leq$5 wt%) were both met and exceeded throughout the bench-scale testing.

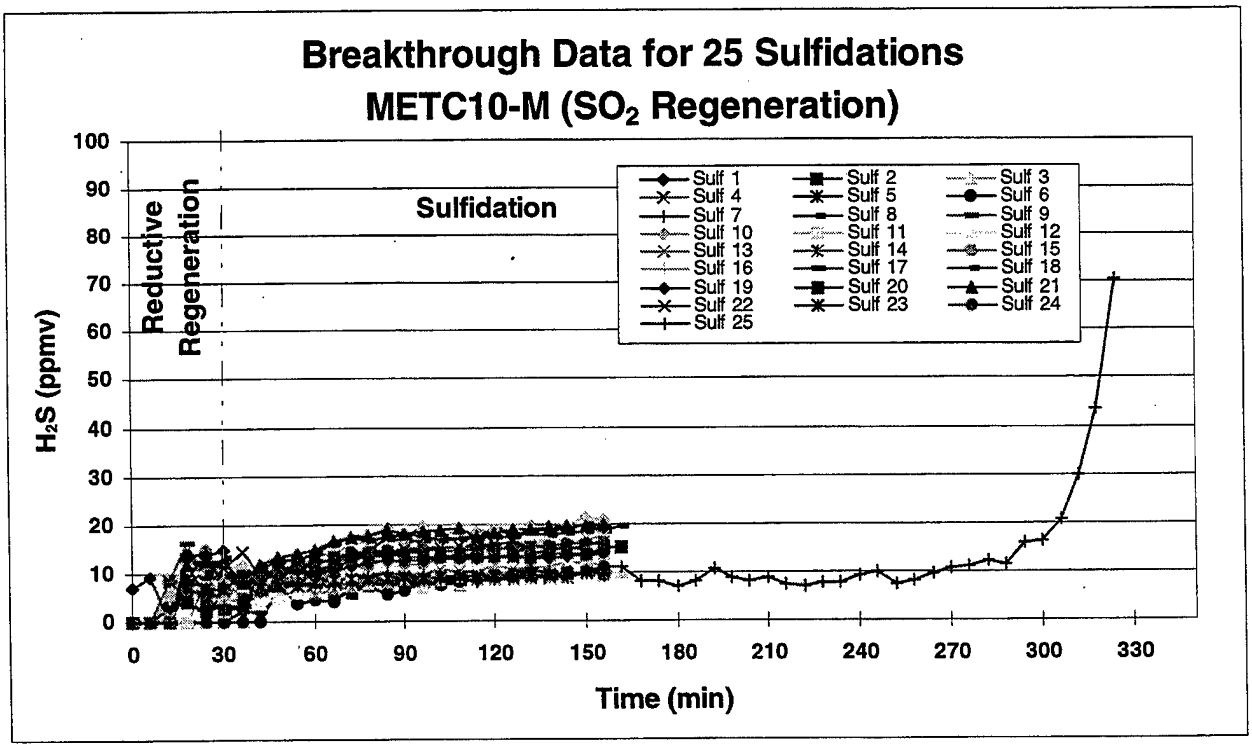


Figure 1

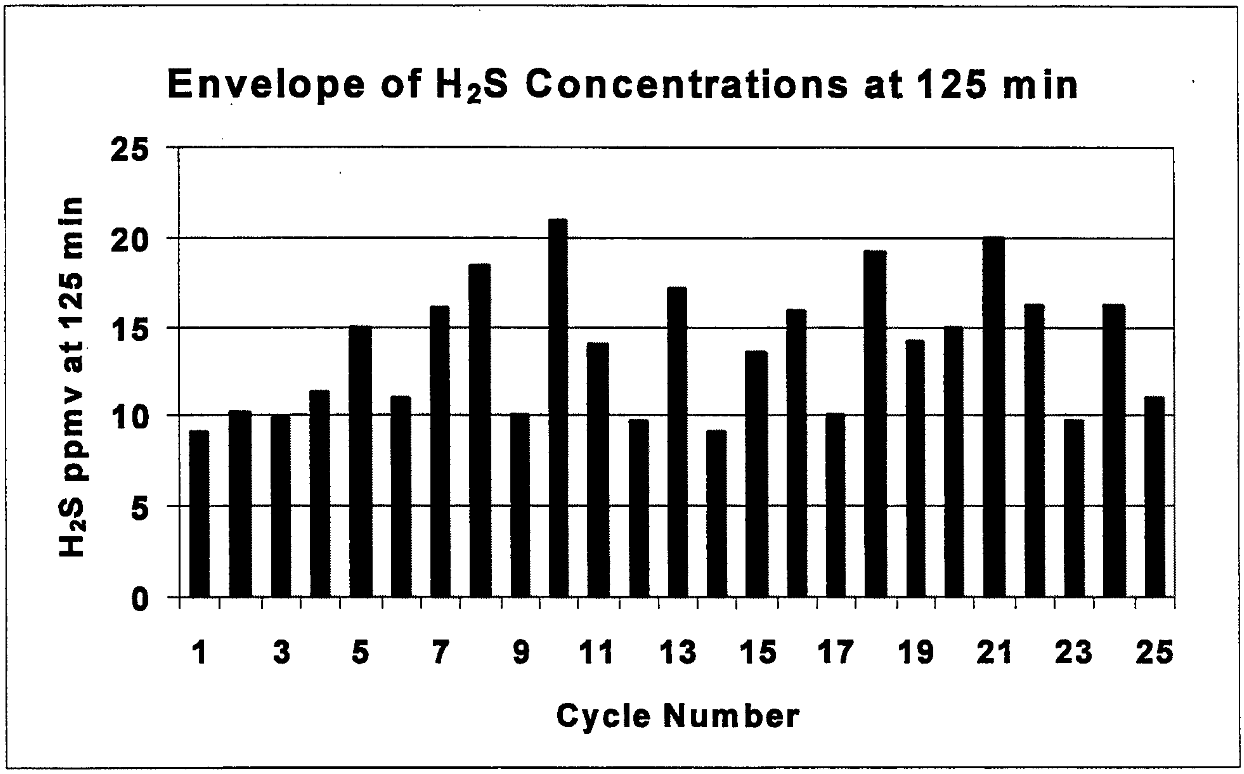
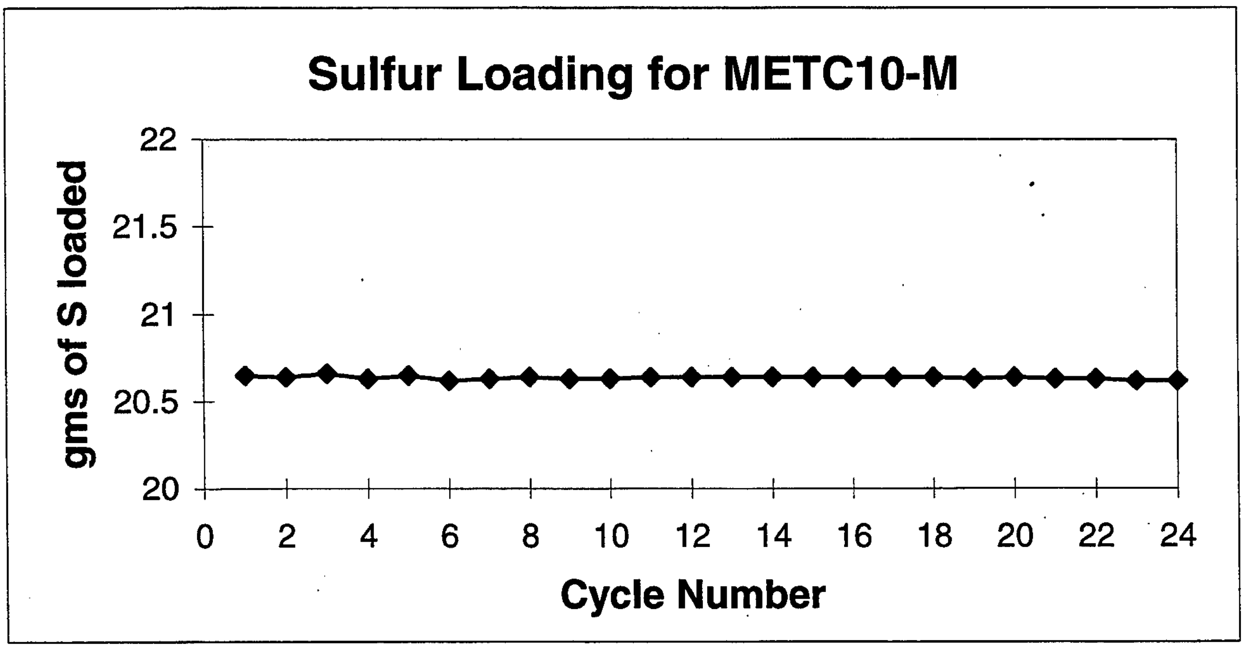


Figure 2



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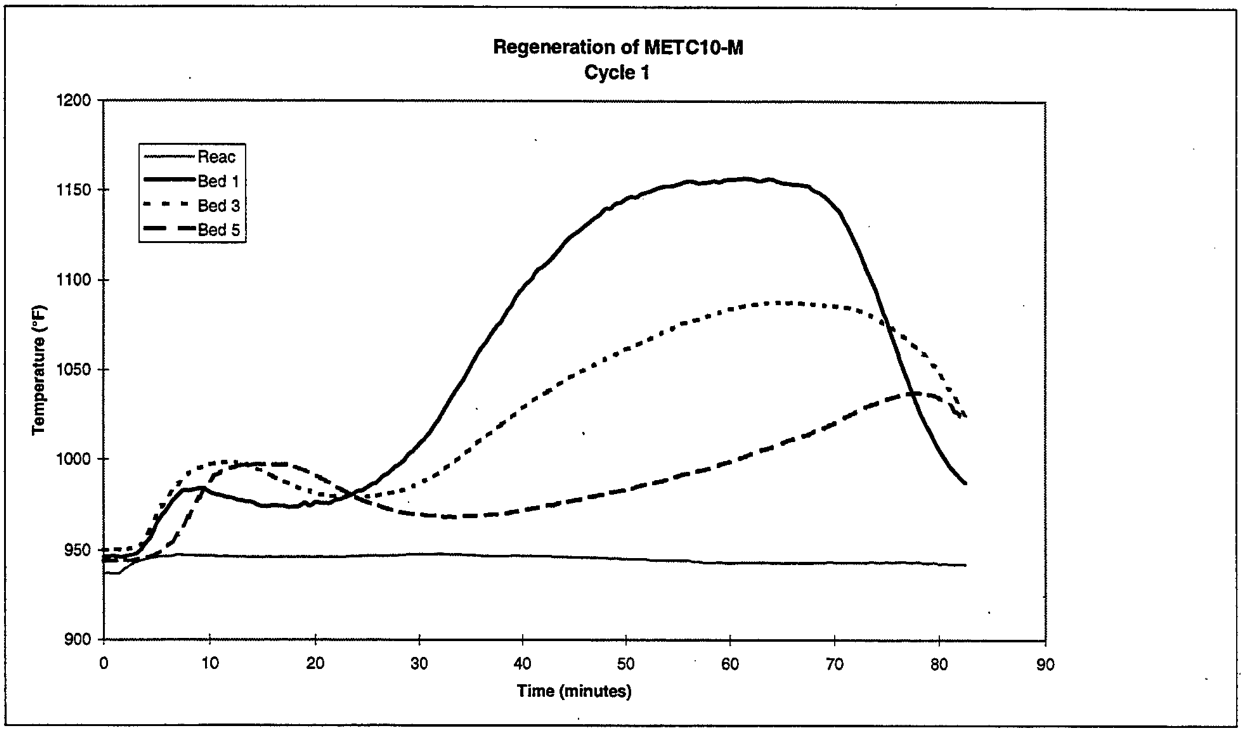

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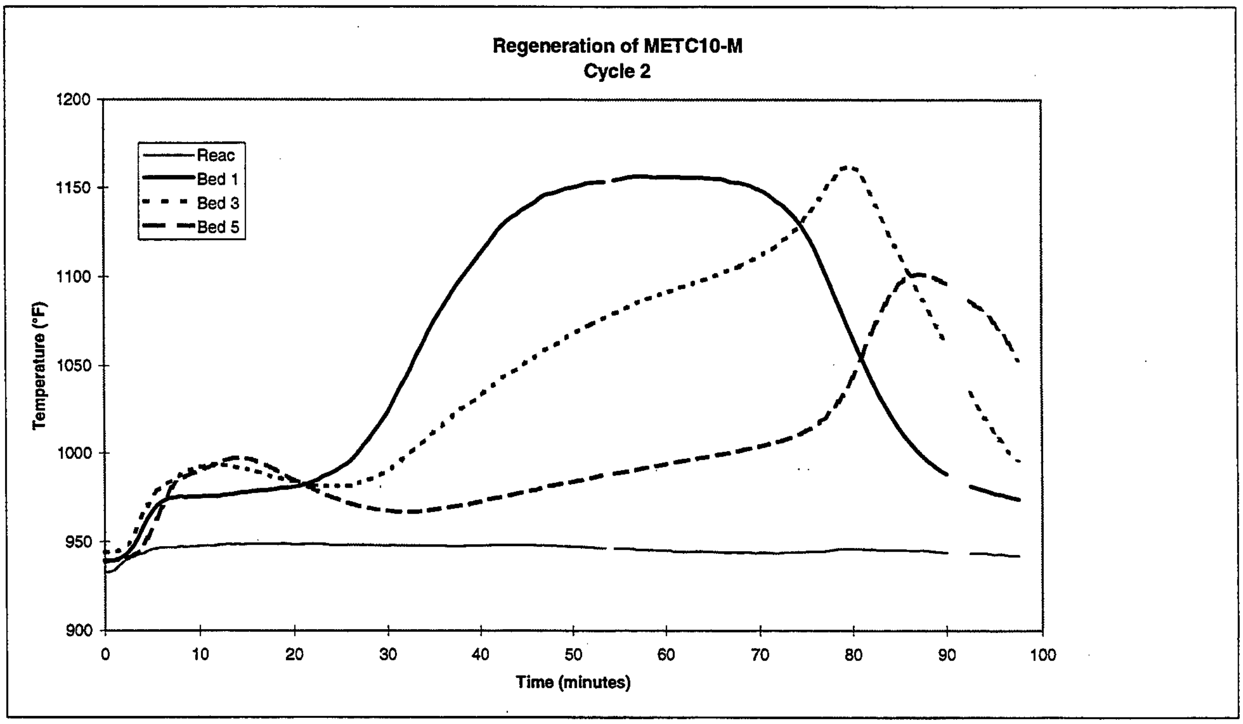

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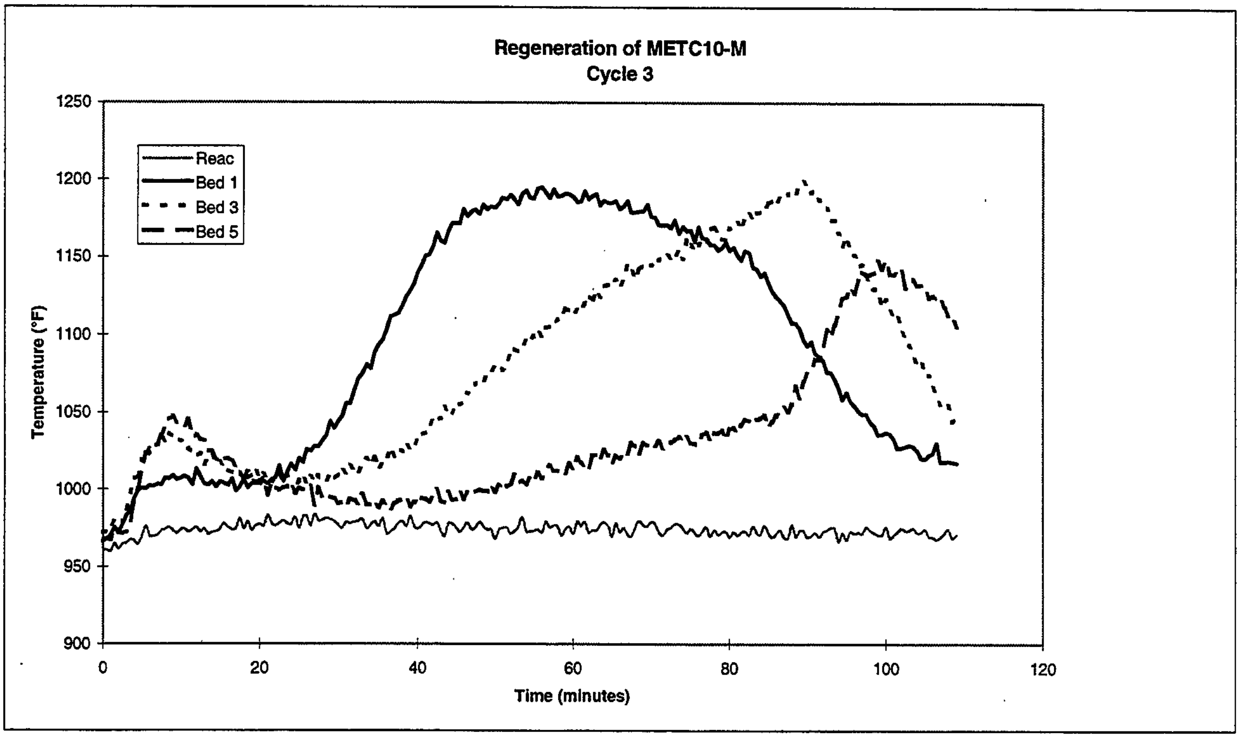

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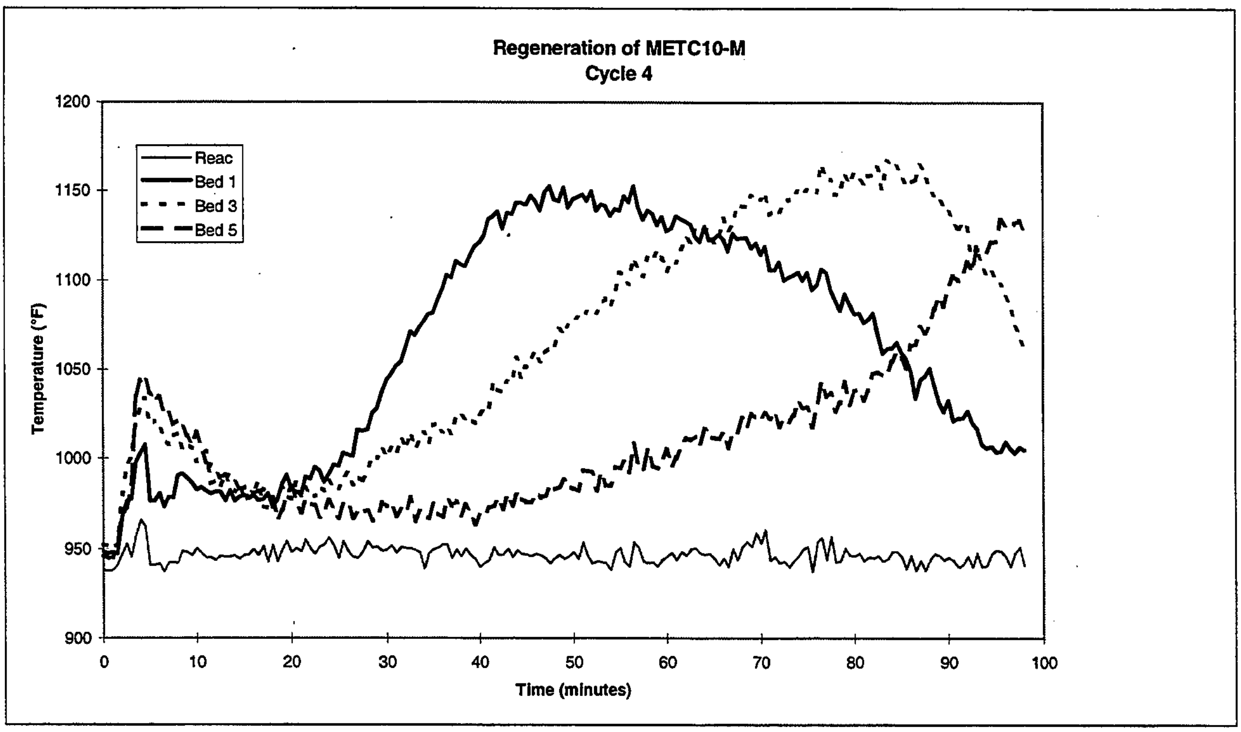

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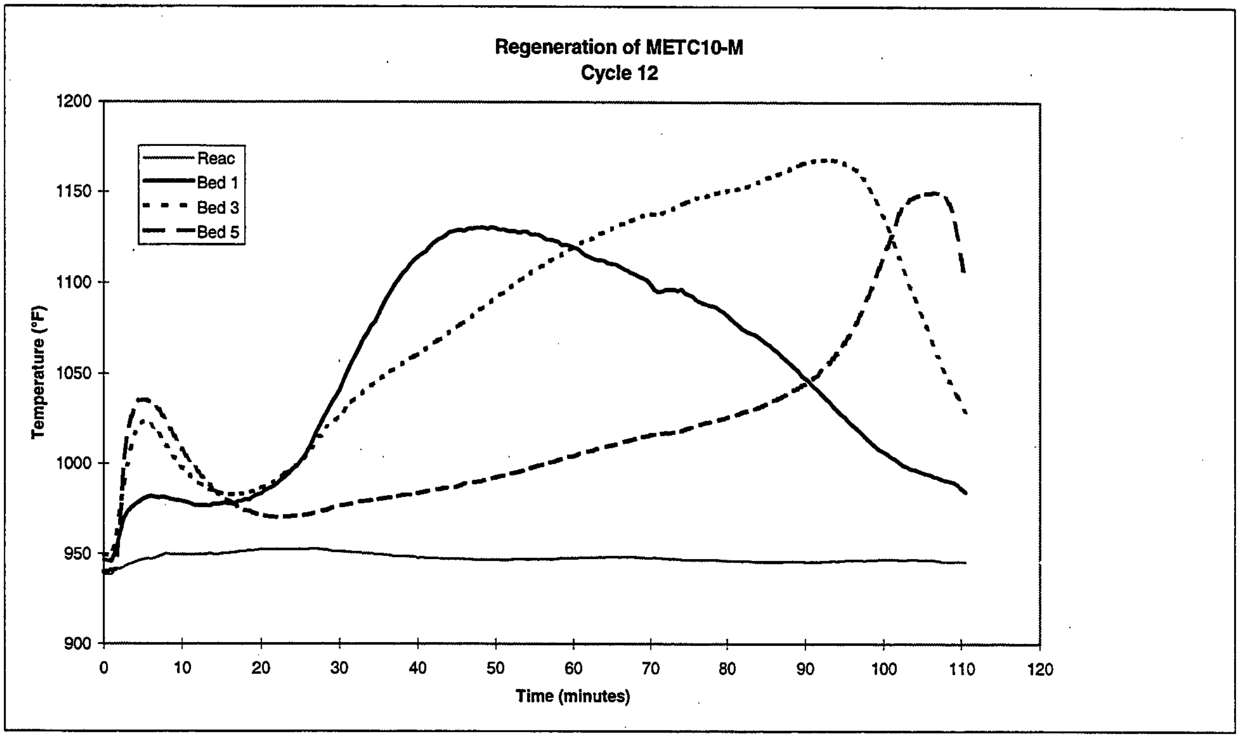

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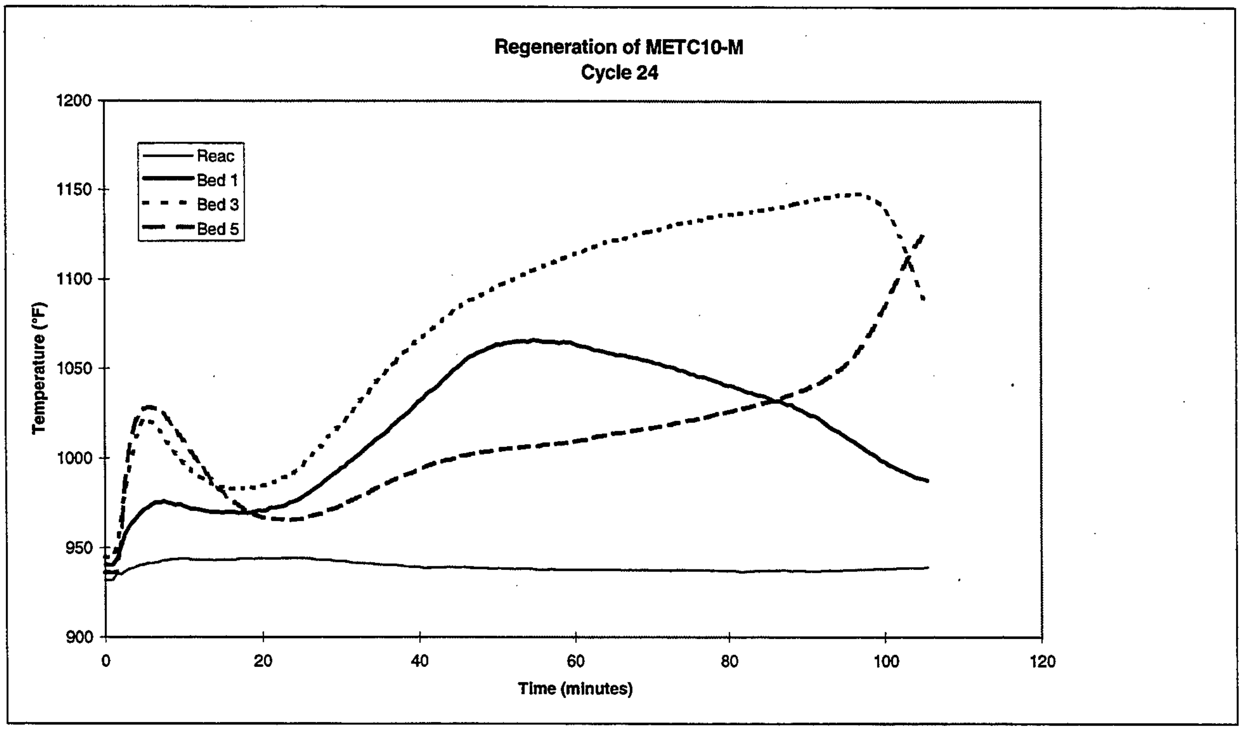

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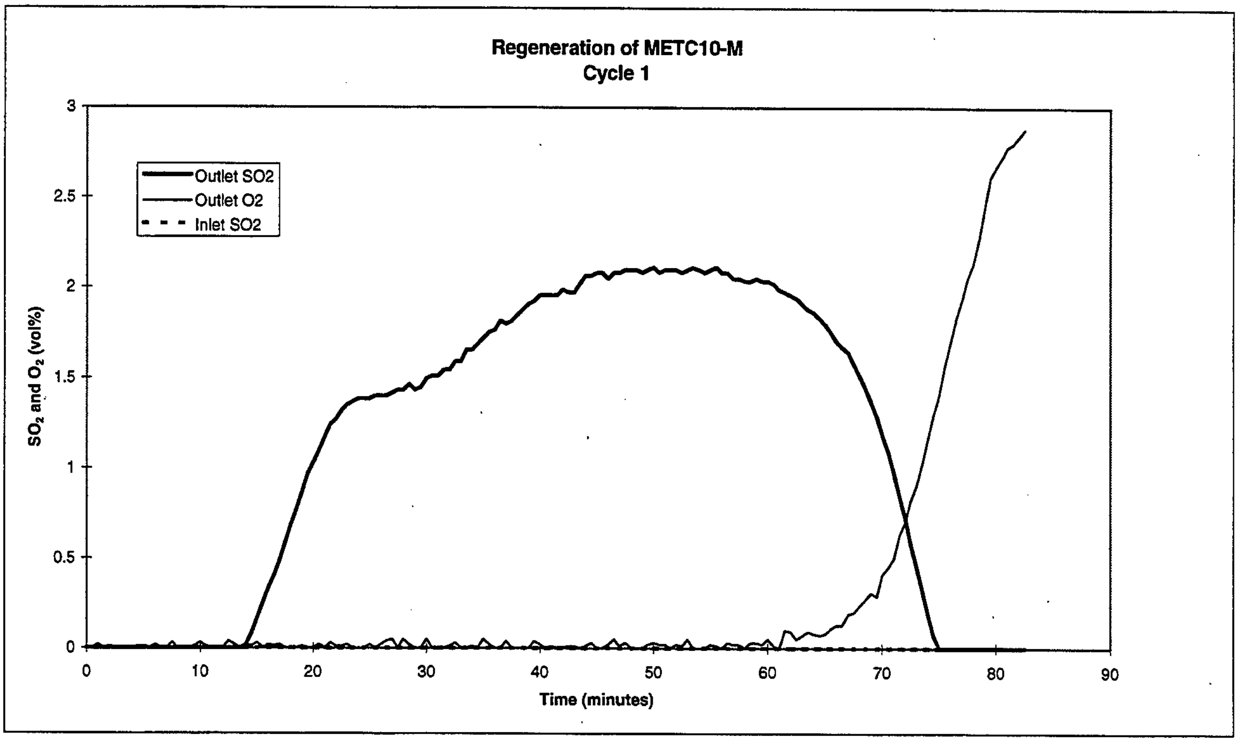

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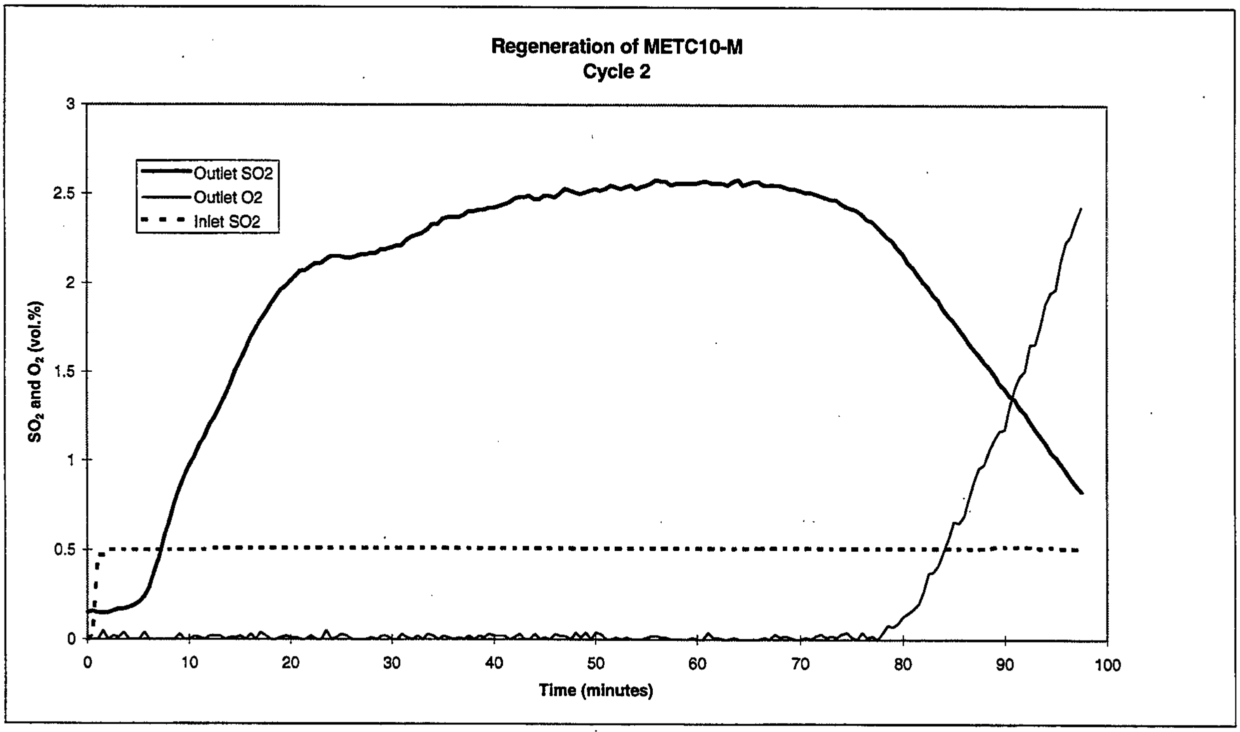

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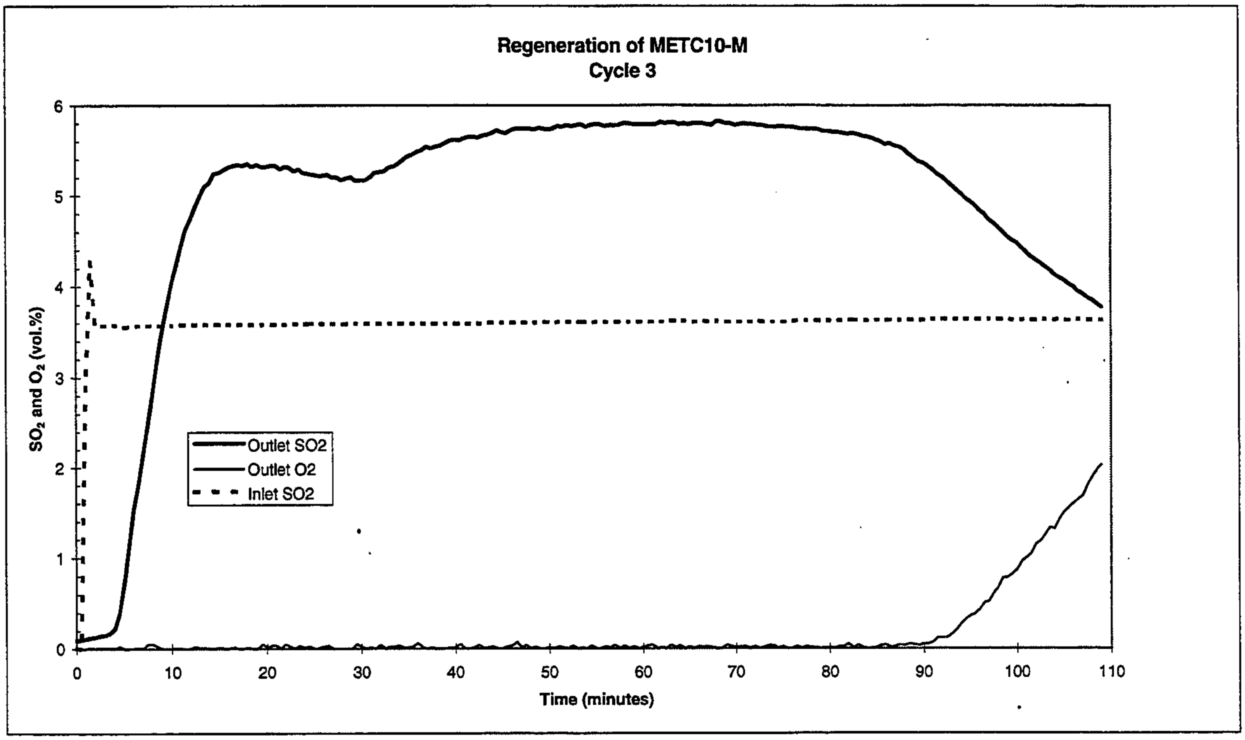

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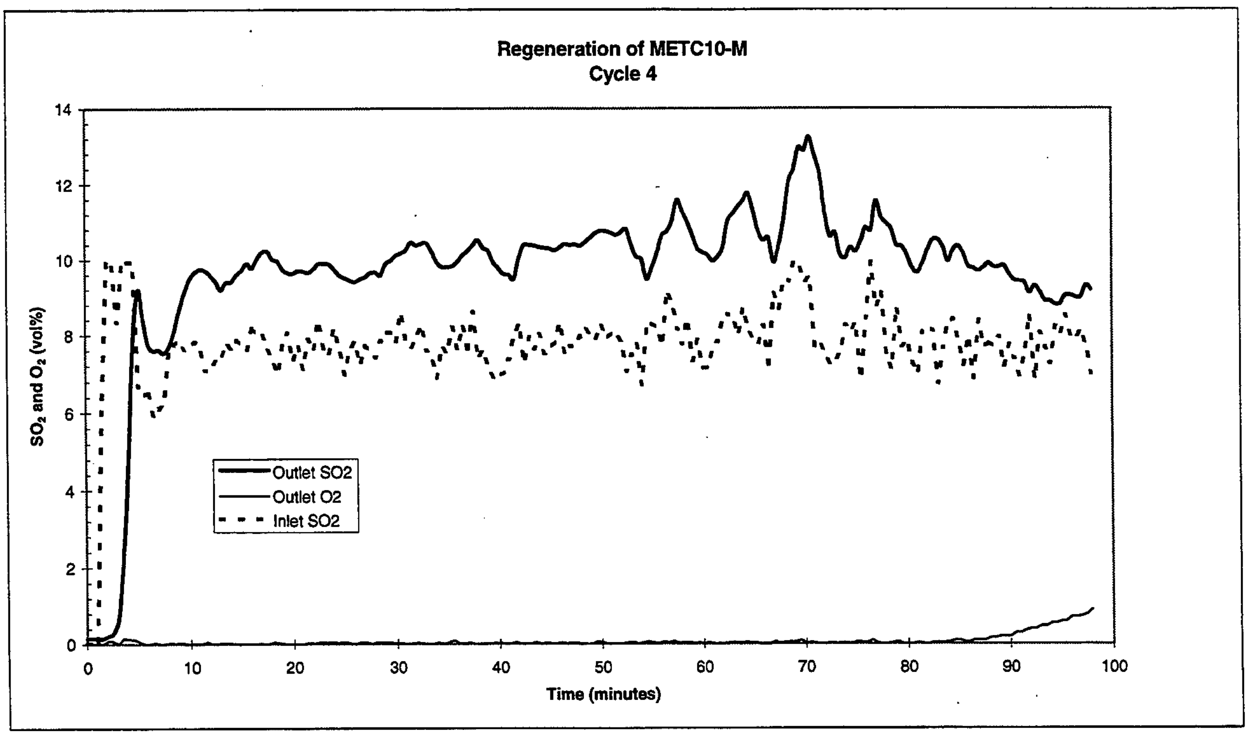

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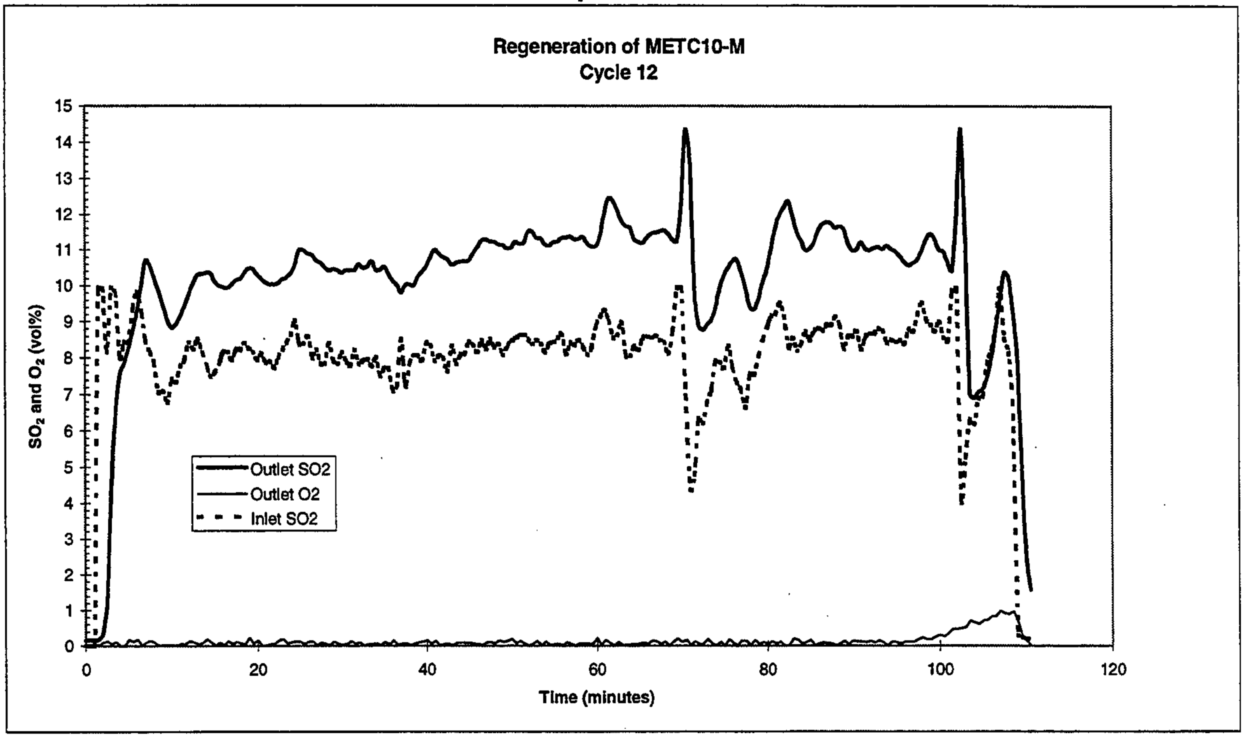

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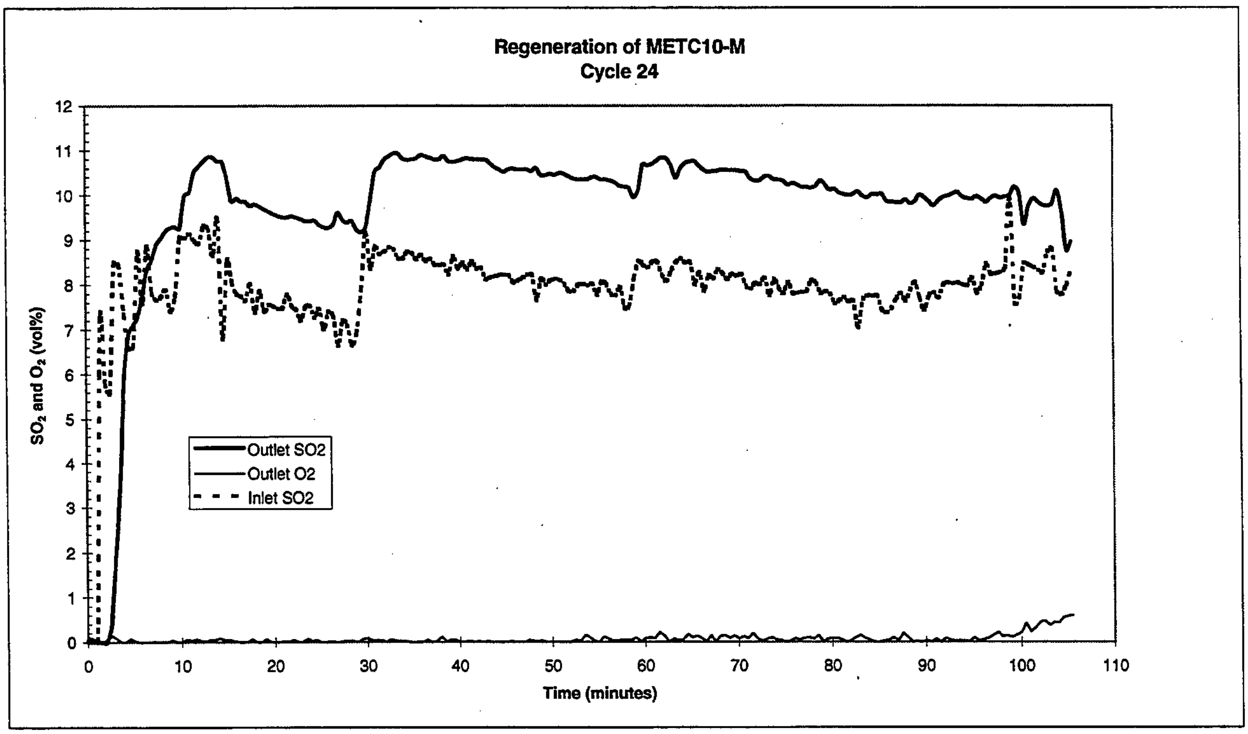

Figure 15

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