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Development of Advanced Hot-Gas Desulfurization Sorbents

Final Report
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EXECUTIVE SUMMARY

This report describes the project, " Development of Advanced Hot-Gas Desulfurization Sorbents" sponsored by U.S. Department of Energy, Federal Energy Technology Center under Grant No. DE-FG-22-94MC31393. The work was performed by Hampton University (prime contractor) with support by Research Triangle Institute as subcontractor.

Hot-Gas Desufurization (HGD) of fuel gas in integrated gasification combined cycle (IGCC) power systems has received a great deal of attention over the past two decades due to the potential for high thermal efficiency (up to 47%) and low environmental impact of these advanced power systems using HGD. In an IGCC system coal is gasified at elevated pressures, typically 20 to 30 atm, to produce a low-volume fuel gas which is desulfurized prior to burning in a combustion turbine to produce electricity. Higher efficiency and lower cost are achieved by efficient integration of modular designs of the gasification, hot-gas cleanup, and turbine subsystems. Gas cleaning primarily involves removal of particulates and sulfur compounds —mostly H_2S and some carbonyl sulfide (COS). Sorbents based on zinc oxide, currently the leading candidates, can effectively reduce the H_2S in coal gas to around 10 ppm levels and can be regenerated for multicycle operation. However, all current first-generation leading sorbents undergo significant loss of sulfidation reactivity and capacity with cycling, as much as 50% or greater loss in only 25-50 cycles. Stability of the hot-gas desulfurization sorbents over one hundred cycles is essential for improved IGCC economics over conventional power plants.

The objective of this study was to develop advanced attrition-resistant hot-gas desufurization sorbents would maintain stability and high sulfidation reactivity and capacity at 343°C (650°F) to 538°C (1000°F). Further, the sorbents would also regenerable at lower

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temperatures than leading first generation sorbents.

Fifty sorbents were synthesized using a coprecipitation technique. The preparation technique and the formulations are proprietary and pending a patent application. Thus no details regarding the technique are divulged in this report. Sulfidations were conducted with a simulated gas containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, and balance N_2 in the temperature range of 343-538°C. Regenerations were conducted at temperatures in the range of 400-600°C with air-N_2 mixtures. To prevent sulfation, catalyst additives were investigated, which promote a lower regeneration temperature. Characterization were performed for fresh, sulfided and regenerated sorbents.

A superior zinc-based sorbent (designated MCRH-25) was tested for 100 cycles in a laboratory -scale reactor. The 100-cycle test clearly demonstrated that the MCRH-25 sorbent does not chemically deactivate. In fact, the capacity at breakthrough increased between cycles 1 to 25 from 22.5 to 27.7 gS/100 g sorbent and remained stable thereafter. TGA and physical property data confirmed the breakthrough data. This is in contrast to existing leading sorbents such as Z-sorb and ZT-4 that deactivated significantly, as much as 50 % in 50 to 100 cycles. Furthermore, the MCRH-25 sorbent regenerated at temperatures as low as 475°C, in contrast to current zinc-based sorbents that require 600°C or higher.

Following the successful preparation of MCRH-25, attention was shifted to preparing the MCRH-25 recipe with binders to provide attrition-resistance suitable for a transport reactor. An attrition-resistant form of MCRH-25, namely MCRH-61 was tested for 50 cycles of sulfidation in the lab-scale reactor at 482°C. Regeneration between cycles was conducted with 2 volume percent O_2 in N_2 at 550°C. The gas hourly space velocity for the 50-cycle test was about

2500 h^{-1} during both sulfidation and regeneration. MCRH-61 sorbent showed excellent sulfidation behavior. The pre-breakthrough H$_2$S level was less than 100 ppm and the breakthrough conversion was 100%. There was no deactivation in 50 cycles in this fixed bed study. This promising test results indicates that an optimized MCRH-61 should be a good candidate sorbent for Sierra-Pacific clean coal project or similar project involving transport reactor.

ACKNOWLEDGMENTS

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1.0 INTRODUCTION

Advanced integrated gasification combined cycle (IGCC) power plants are being developed to produce electricity from coal due to their potential for superior environmental performance, economics, and efficiency in comparison to conventional coal-based power plants. The U.S. Department of Energy (DOE), Federal Energy Technology Center (FETC) Clean Coal Technology program has led to the successful construction of two such advanced plants--Sierra Pacific and Tampa Electric Company (TECO), with shakedown and commissioning currently in progress. A key component of these advanced IGCC plants is a hot-gas desulfurization (HGD) process that employs efficient regenerable zinc-based mixed-metal oxide sorbents. These sorbents can remove the hydrogen sulfide (H_2S) in coal gas to <20 ppmv and that can be regenerated with air for multi-cycle operation as shown below for zinc oxide:

$$ZnO + H_2S \rightarrow ZnS + H_2O \qquad \text{(Sulfidation)}$$

$$ZnS + (3/2)O_2 \rightarrow ZnO + SO_2 \qquad \text{(Regeneration)}$$
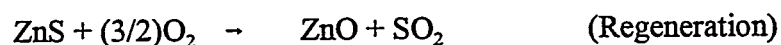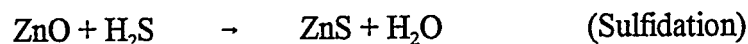
For economic reasons, the sorbent must be able to maintain an acceptable level of reactivity over one hundred absorption (sulfidation)-regeneration cycles.

High temperature sulfur removal techniques are based on the reaction of H_2S with solid sorbents to form solid sulfur compounds. Metal oxide sorbents can be classified as disposable or regenerable. Disposable sorbents are typically calcium based and are generally employed in situ, but they can also be employed externally in a once-through process. Fundamental studies on calcium-based sorbents by Michel et al. (1996) and Heesink and VanSwaaij (1996) provide an excellent review of the research on the $CaO-H_2S$ reaction at 700 to 1,000°C. The problem with these sorbents is disposal following sulfidation. When employed in situ, the intent is to convert

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CaS to stable $CaSO_4$; however, pore plugging limits this phenomenon. Also, these sorbents cannot typically achieve more than 80% sulfur removal. Finally disposable in landfills is becoming more and more difficult due to scarcity of land in many parts of the world. Past studies have attempted to regenerate calcium sulfide back to calcium oxide but with very limited success (Curran et al., 1977; O'Brien et al., 1976). Calcium-based sorbents are presently employed in situ in two gasifiers—U-gas and KRW (Kellogg). IGCC systems employing these gasifiers require an external regenerable sulfur polishing sorbent to achieve a high degree of sulfur removal.

Regenerable sorbents can be employed in the polishing mode to remove essentially all of the H_2S and COS for IGCC systems such as Shell, Destec, or Texaco gasifiers that do not use in-bed desulfurization. The principle requirement during air regeneration is that the sorbent should predominantly revert back to its oxide ($MS + 3/2\ O_2 \rightarrow MO + SO_2$) rather than to sulfate ($MO + SO_2 + \frac{1}{2}\ O_2 \rightarrow MSO_4$). Air regeneration is highly exothermic and requires tight temperature control using large quantities of diluent (N_2) or other means to prevent sorbent sintering and sulfate formation.

A number of metal oxides have been and/or are currently being evaluated as regenerable sorbents (Gangwal et al., 1995). These include oxides of copper, cerium, manganese, cobalt, tin, iron, and zinc, both individually and in combinations. The chemistry associated with the use of these sorbents is generally similar with a few exceptions. These metal oxide or mixed-metal oxide sorbents have been investigated with and without a secondary oxide such as silica, alumina, titania, and chromia. These secondary oxide act as supports for strengthening mechanical structure, stabilizers against reduction of the metal oxide to metal in a reducing environment, and modifiers of thermodynamic properties of the metallic oxide (by forming a perovskite type

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structure) to enhance elemental sulfur formation during regeneration.

The bulk of research on regenerable sorbents has been on zinc-based sorbents because sorbents based on zinc oxide appear to have the fewest technical problems among all sorbents. Zinc oxide has highly attractive thermodynamics for H_2S adsorption and can reduce the H_2S to parts-per-million levels over a very wide temperature range. Iron oxide appears to be the next most popular sorbent; however, the thermodynamics for iron is not very attractive. Also iron oxide can readily undergo reduction ($Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$) depending on the reducing power of coal gas. This can consume valuable fuel gas and cause sorbent deterioration. Iron oxide can also catalyze carbon formation if sufficient steam is not present in the fuel gas.

In contrast to calcium-based sorbents, which can operate up to 900 to 1,000°C, zinc and iron sorbents operate at lower temperatures. A temperature of 480°C appears to be the limit of iron-based sorbents due to iron's reduction potential. A combined zinc oxide (ZnO)-iron oxide (Fe_2O_3) sorbent, namely, zinc ferrite ($ZnFe_2O_4$), was developed by Grindley and Steinfeld (1981) to combine the advantages of ZnO and Fe_2O_3 and to extend the upper temperature limit to around 600°C. A temperature range of 550 to 750°C received the major research emphasis in the United States during the 1980s and early 1990s. Because of zinc oxide's potential for reduction (ZnO + $H_2 \rightarrow Zn + H_2O$) at >600°C followed by evaporation, a zinc oxide-titanium oxide sorbent, namely zinc titanate sorbent, was developed and tested at high temperature and high pressure (Gangwal et al., 1988; Jothimurugesan and Harrison, 1990; Stephanpoulos and Jothimurugesan, 1990; Woods et al., 1990;1991). Zinc titanate is currently one of the leading sorbents. However, all current first-regeneration leading sorbents undergo significant loss of reactivity with cycling, as much as 50% or greater loss in only 25-50 cycles. Stability of the hot-gas desulfurization sorbent

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over one hundred cycles is essential for improved IGCC economics over conventional power plants.

Air regeneration, a highly exothermic process, leads to a dilute SO_2 tail gas that must be disposed. In this context, Kellogg's transport reactor technology for HGD that is to be used at Sierra-Pacific represents one of the most significant recent developments in HGD because it allows the use of neat air for regeneration by using fast sorbent circulation to soak up the heat generated. This results in a relatively small volume SO_2 tail gas containing around 14 vol% SO_2. Converting to a salable product—sulfuric acid or elemental sulfur is an attractive option as opposed to lime absorption leading to a waste. Elemental sulfur is particularly attractive because it is the smallest volume sulfur product and because it can be stored easily, transported over long distances, readily disposed, or sold. A promising process called Direct Sulfur Recovery Process (DSRP) (Portzer et al., 1996) is currently in an advanced development stage to treat the SO_2 tail gas. In this process the SO_2 is catalytically reduced to elemental sulfur at the pressure and temperature condition of the tail gas using a slipstream of the fuel gas:

$$SO_2 + 2\ H_2\ (\text{or CO}) \rightarrow \tfrac{1}{2}\ S_2 + 2\ H_2O\ (\text{or 2 CO}_2)$$
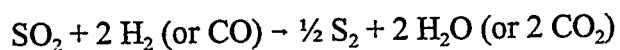
The process is undergoing testing with actual coal gas from a gasifier and is being scaled up to a small pilot-scale stage. As seen above, the problematic SO_2 tail gas produced by air regeneration not only needs disposal but also consumes 2 mol of valuable reducing components in fuel gas for every mole of sulfur dioxide treated if elemental sulfur is to be produced. Novel regeneration processes that could lead to elemental sulfur without use of fuel gas or with limited use of fuel gas are being developed (Harrison et al. 1996; Gangwal et al., 1996). RTI (Gangwal, 1996) has been testing a novel zinc-iron sorbent that could be regenerated using SO_2 to directly produce

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elemental sulfur.

During recent years, research emphasis has shifted toward lower temperatures (350 to 550 °C) based on a study in the Netherlands (NOVEM, 1991). According to this study, the thermal efficiency of a 800 MWe IGCC plant increased from 42.75% using cold-gas cleanup to 45.14% using HGD at 350°C and to 45.46% using HGD at 600°C. The small efficiency increase from 350 to 600°C suggested that the temperature severity of the hot-gas cleanup devices can be somewhat reduced without significant loss of thermal efficiency. An important reason for development of sorbents in the temperature range suggested above is the reduction of the operating temperature of the upstream ceramic candle filter which have not provided reliable long-term operation at high temperatures. Reduction in the hot-gas cleanup temperature would also result in reduction in semi-volatile contaminants (e.g. alkali vapors), which may be particularly damaging to ceramic filters. Another important reason to reduce hot-gas cleanup severity is to reduce the operating temperatures and temperature swings of on-off valves and vessels for cyclic fixed-bed desulfurization/regeneration systems, lock-hopper valves for moving-bed applications, and the turbine load control valves. Finally, the current plans in Europe (for example, slip-stream tests at the Buggenum IGCC plant) call for hot-gas desulfurization system operation at 350-600 °C. Also iron-oxide process development studies in Japan have concentrated on a temperature range of 400-600 °C. Thus development of suitable advanced sorbents in the U.S. for this temperature range is necessary for U.S. manufactures and sorbent vendors to license their products overseas.

Reduction in severity of temperature would lead to greater reliability of long-term operation of hot-gas cleanup devices and lesser stress on piping and vessels. The challenge,

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however, is to develop suitable sorbents that are sufficiently reactive and regenerable at the relatively lower temperatures of interest in this work. The rate of the sulfidation reaction of metal oxide sorbents drops exponentially as temperature is reduced. Thus in order to maintain sufficient reactivity that results in reasonable reactor size to remove H_2S down to low ppm level in large scale systems, it will be necessary to prepare highly dispersed porous mixed-metal oxide sorbents with sufficiently small and accessible metal oxide crystallites. During regeneration, unless temperature is raised sufficiently, sulfation of the metal may occur leading to incomplete regeneration and sorbent deterioration. On the other hand, if the temperature is increased to prevent sulfation, sintering of crystallites may occur leading to reduced reactivity for the subsequent cycle.

A two-reactor configuration is necessary for hot-gas desulfurization due to its cyclic nature. Early developments emphasized fixed beds. The highly exothermic regeneration led to a move away from fixed beds toward moving beds (Ayala et al., 1995; Cook et al., 1992) and fluidized beds (Gupta and Gangwal, 1992). Pelletized sorbents were developed using appropriate binders in the size range of 3 to 6 mm for fixed and moving beds. However, the binders could not hold the sorbents together over several cycles due to chemical reactions leading to expansion and /or contraction followed by spalling and cracking. Durable zinc titanate sorbent development for fluidized beds is on-going (Gupta et al., 1996). Recently a zinc oxide -nickel oxide sorbent (Z-sorb) produced by Phillips Petroleum Company for H_2S removal from Claus plant tail gas has been extensively tested for HGD (Khare et al., 1996). Several advanced version of this sorbent have been developed to incorporate special features such as resistance to sintering in high-temperature steam, low light-off temperature, and high attrition resistance.

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1.1 PROJECT OBJECTIVES

The objective of this project was to develop hot-gas desulfurization sorbent formulations for relatively lower temperature application, with emphasis on the temperature range from 343-538°C. The candidate sorbents include highly dispersed mixed metal oxides of zinc, iron, copper, cobalt, nickel and molybdenum. The specific objective was to develop suitable sorbents, that would have high and stable surface area and are sufficiently reactive and regenerable at the relatively lower temperatures of interest in this work. Stability of surface area during regeneration was achieved by adding stabilizers. To prevent sulfation, catalyst additives that promote the light-off of the regeneration reaction at lower temperature was considered.

Another objective of this study was to develop attrition-resistant advanced hot-gas desufurization sorbents which show stable and high sulfidation reactivity at 343 to 538°C and regenerabilty at lower temperatures than leading first generation sorbents.

2.0 DESCRIPTION OF PROJECT TASKS

TASK 1:   Sorbent Preparation and Characterization

The objectives of this task were to prepare and characterize various sorbents. A detailed description of sorbent preparation is given in section 3.1 of the report. Several parameters were varied in the sorbent preparation to study their effects on the physical properties and chemical phases of the sorbents. Section 3.1 also describes the various analytical techniques employed for sorbent characterization.

TASK 2:   Experimental Testing and Sorbent Evaluation

The objective of this task was to evaluate the performance of various sorbents under similar conditions in a fixed-bed microreactor. Section 3.2 describe the experimental apparatus and procedures employed throughout the project. Sorbent comparisons were to be carried out at the following operating conditions:

P=1 atm, T= 343-538°C, S.V. =2500 h^{-1}

Sulfidation Gas (vol %): 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2.

Regeneration gas (vol %): 10 air-90 N_2

At least four to five cycles of sulfidation/regeneration were run with each sorbent until stabilized performance was attained. Following these tests, the most promising sorbent was further tested over multicyles.

TASK 3:   Cyclic Testing

The objectives of this task was to determine how well the sulfidation performance of the sorbents was retained in many cycles of consecutive sulfidation/regeneration.

3.0 EXPERIMENTAL APPROACH

TASK 1:   3.1 SORBRNT PREPARATION AND CHARACTERIZATION

Sorbents were prepared by precipitation of soluble salts of appropriate metals with a basic solution. The principal novelty of the method involves incorporation of surface area stabilizers. Zinc nitrate, iron nitrate, cobalt nitrate hexahydrate, nickel nitrate hexahydrate, copper nitrate and ammonium molybdate hexahydrate (all the chemicals were obtained from Aldrich) were used as the metal salts. The precipitation was carried out by adding the raw salt solution and the basic

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solution simultaneously under vigorous mixing at room temperature. The product of the precipitation was washed, separated by filtration, dried at 150°C for 12 h, and then calcined in an air stream in the range of 600-800°C. The product thus obtained was crushed and sieved to -32+60 mesh.

A detailed physical and chemical characterization of the fresh, sulfided and regenerated sorbent materials was carried out using the following analytical techniques.

1.   X-ray powder diffraction patterns were obtained using a Phillips PW 1800 X-ray unit using CuKα radiation. Analyses were conducted using a continuous scan mode at a scan rates of 0.05° 2θ per second.

2.   The BET Surface area of the sorbents were determined by N_2 physisorption using a Micromeritics Gemini 2360 system. The samples were degassed in a Micromeritics Flow Prep 060 at 120°C for 1 h prior to each measurement.

3.   Hg-porosimetry was used for pore volume, bulk density, average pore diameter and pore size distribution determination.

4.   Atomic Absorption (AA) Spectrometry for elemental composition analysis.

5.   The SEM (Scanning Electron Microscopy) micrograph was taken using a Cambridge Stereoscan 100.

TASK 2: 3.2 APPARATUS AND PROCEDURES

The sorbent materials prepared were tested in a laboratory scale high-temperature and high- pressure (HTHP) fixed bed reactor which is shown in Figure 1. Briefly, the experimental setup consisted of a gas delivery system, a fixed bed reactor, and a gas analysis system. In the gas delivery system, a simulated fuel gas of any desired composition could be generated using the
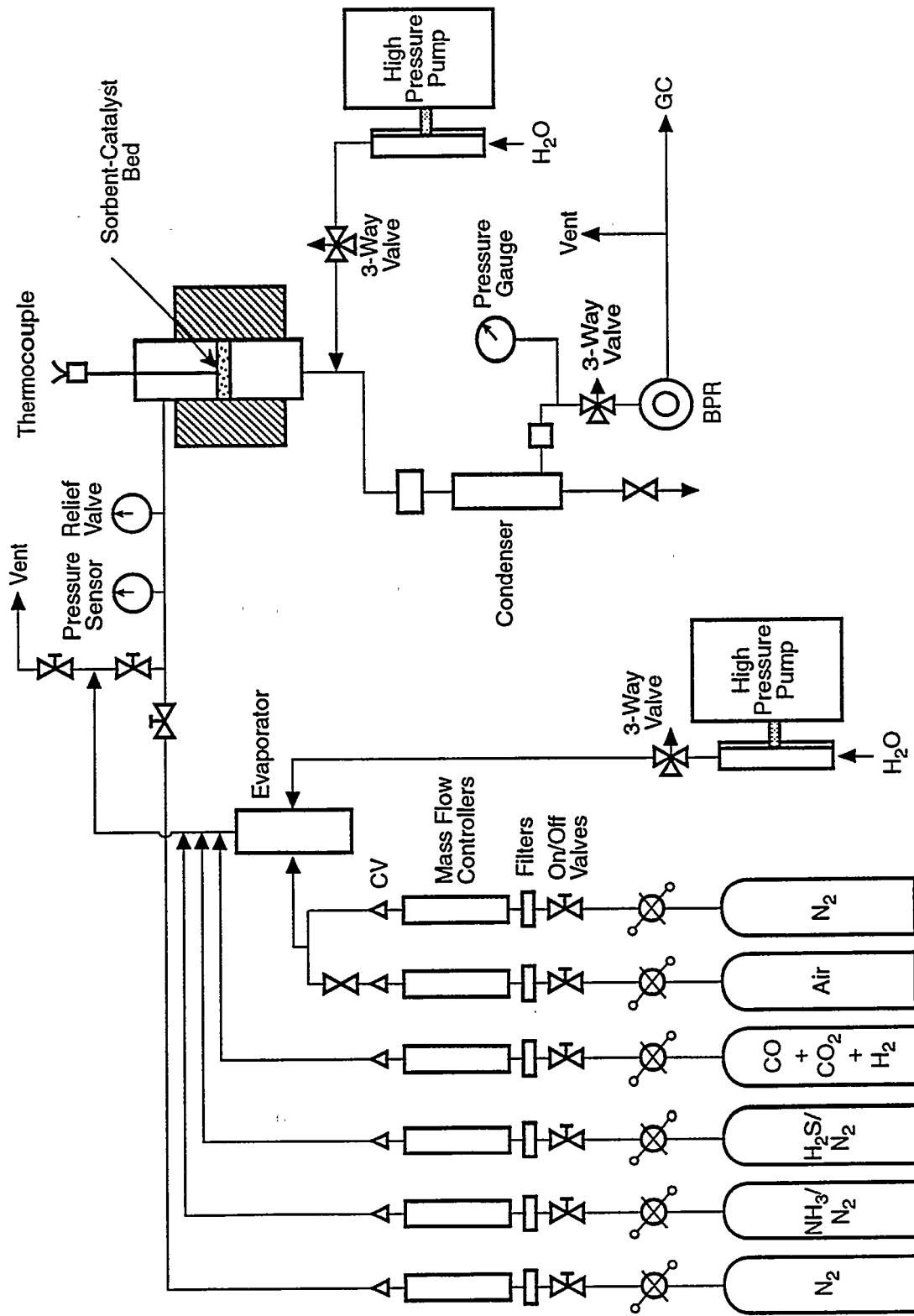
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Figure 1. HGD Laboratory-Scale Fixed-Bed Reactor System

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bottled gases, a set of mass flow controllers, and high-pressure syringe pumps. Steam was added to the mixed dry gas by vaporizing liquid water injected it into the gas stream at a controlled rate by a high pressure syringe pump. The reactor was made from a 3/4-inch stainless steel tube. Inside the 3/4-inch there was a removable 316 stainless steel 1.0 cm I.D insert with a porous alumina plate in the bottom that acted as a gas distributor. The insert was Alon-processed to prevent corrosion of stainless steel by sulfurous gases in the presence of steam. The pressure in the reactor was controlled by a back pressure regulator and measured by an electronic pressure sensor. Thermocouples were positioned to measure the temperatures of the preheated feed gas, the sorbent bed, and the product gas. The tests were conducted with a simulated gas nominally containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, and balance N_2. The outlet H_2S and SO_2 concentrations were monitored using a gas chromatograph.

A typical run consists of loading the sorbent having a particle size range of -32+ 64 mesh and heating the reactor to a desired temperature of 350-500°C with continuous flow of nitrogen. Once the desired temperature was attained, the flow of fuel gas to the reactor was started and the concentration of H_2S was measured continuously in the effluent gas. When the H_2S concentration reached 500 ppmv, the run was stopped and the system was prepared for regeneration. The regeneration of sulfided material was carried out at the desired temperature ranging between 400-550°C with 2 to 4 volume % oxygen in nitrogen. In all the runs, space velocity used was in the range of 2000-3000 h^{-1}. The regeneration of the sulfided material was carried out until the SO_2 concentration in the reactor effluent dropped below 50 ppm. These sulfidation-regeneration cycles were repeated as many times as desired. Typically each material was tested for 4 to 5 cycles to obtain meaningful data on material durability. At the end of the 4 to 5 cycle run, the

material was removed from the reactor and all physical and chemical characterizations, as listed above, were carried out on the reacted material to determine changes due to reaction.

4.0 RESULTS AND DISCUSSIONS

The summary of the experimental data for sulfidation are presented in Table 1, with t denoting real time and t* a calculated time corresponding to 100 percent metal oxide conversion. Sulfidation tests were carried out with a sulfidation gas containing (vol%) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2 for all the sorbents shown in Table 1. The temperature was chosen in the range 350-500 °C and was held fixed for the duration of the sulfidation. Sulfided sorbents were regenerated using a nitrogen-air at temperatures of 400-600°C.

Table 1. Summary of Sulfidation Tests with MCRH Sorbents

Sorbent	T_s (°C)	Pre-Break- Through H_2S (ppm)	Breakthrough Sorbent Conversion, (t/t*) at cycle-4	Sulfur Loading (gS/100g sorbent) at cycle 4
MCRH-1	427	4-6	0.82	19.49
MCRH-2	427	8-10	0.72	28.66
MCRH-10	427	50-60	0.88	21.06
MCRH-14	427	50-60	0.69	17.31
MCRH-23	427	50-60	0.31	7.81
MCRH-24	427	80-90	1.0	23.77
MCRH-25	**427**	**60-70**	**0.94**	**24.12**
MCRH-26	427	60-70	0.43	11.89
MCRH-27	427	65-75	0.97	23.73

MCRH-1 : A mixed oxide sorbent (designated MCRH-1) was prepared by coprecipitation. For the coprecipitation, the salt solutions were mixed in the proportions needed to obtain the desired molar ratio in the final sorbent and then precipitated using a basic solution. The resulting precipitate was filtered off, and washed with deionized water twice. The filtered precipitates were then dried for 16 h at 150°C. Finally it was calcined in a muffle furnace at 700°C for 2 h under a stream of air to produce the final mixed-oxide phase. The SEM morphology of the fresh MCRH-1 sorbent is depicted in Figure 2.

This material was tested for sulfidation in a laboratory scale reactor. Regeneration between cycles was conducted with 10 vol% air-90 vol% N_2 at 600°C. The gas hourly space velocity was about 2500 h^{-1}(STP) both in sulfidation and in regeneration. In tests with MCRH-1 sorbent conducted at 427°C, with a sulfidation gas containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at breakthrough was 80 percent as shown in Figure 3. In fact, the H_2S level remained at 0 ppm until 17 percent conversion and then gradually increased to ~5 ppm when conversion reached 80 percent. There was no decline in activity for 6 cycles. The sulfidation summery is summarized in Table 1.

The sulfidation performance of the MCRH-1 sorbent was examined as a function of temperature up to 538 °C. The results are shown in Figure 4. As expected, sulfidation efficiency increased at higher temperatures. The sorbent conversions at 343 and 538°C were 60 and 100 percent, respectively. Apparently this is due to faster kinetics at higher temperature and to the absence of diffusional limitations. The sulfur capacities of the MCRH-1 sorbent during cycles 1 and 6 were 19.49 and 19.49 gS/100 g of sorbent, respectively, indicating a 100 percent capacity utilization even after 6 cycles. Sulfur capacity is calculated using the concentration of H_2S in
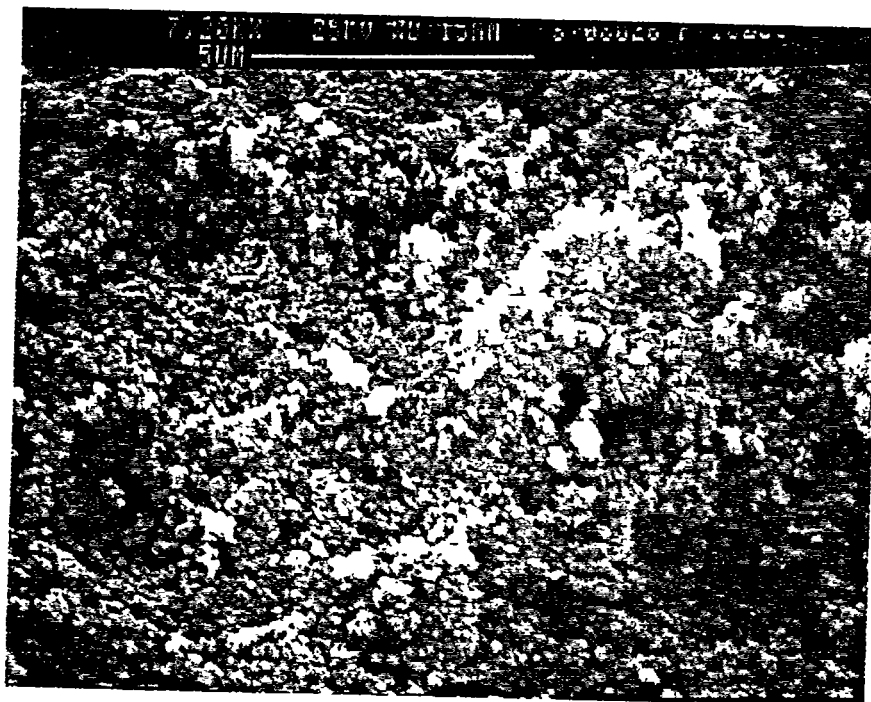
13
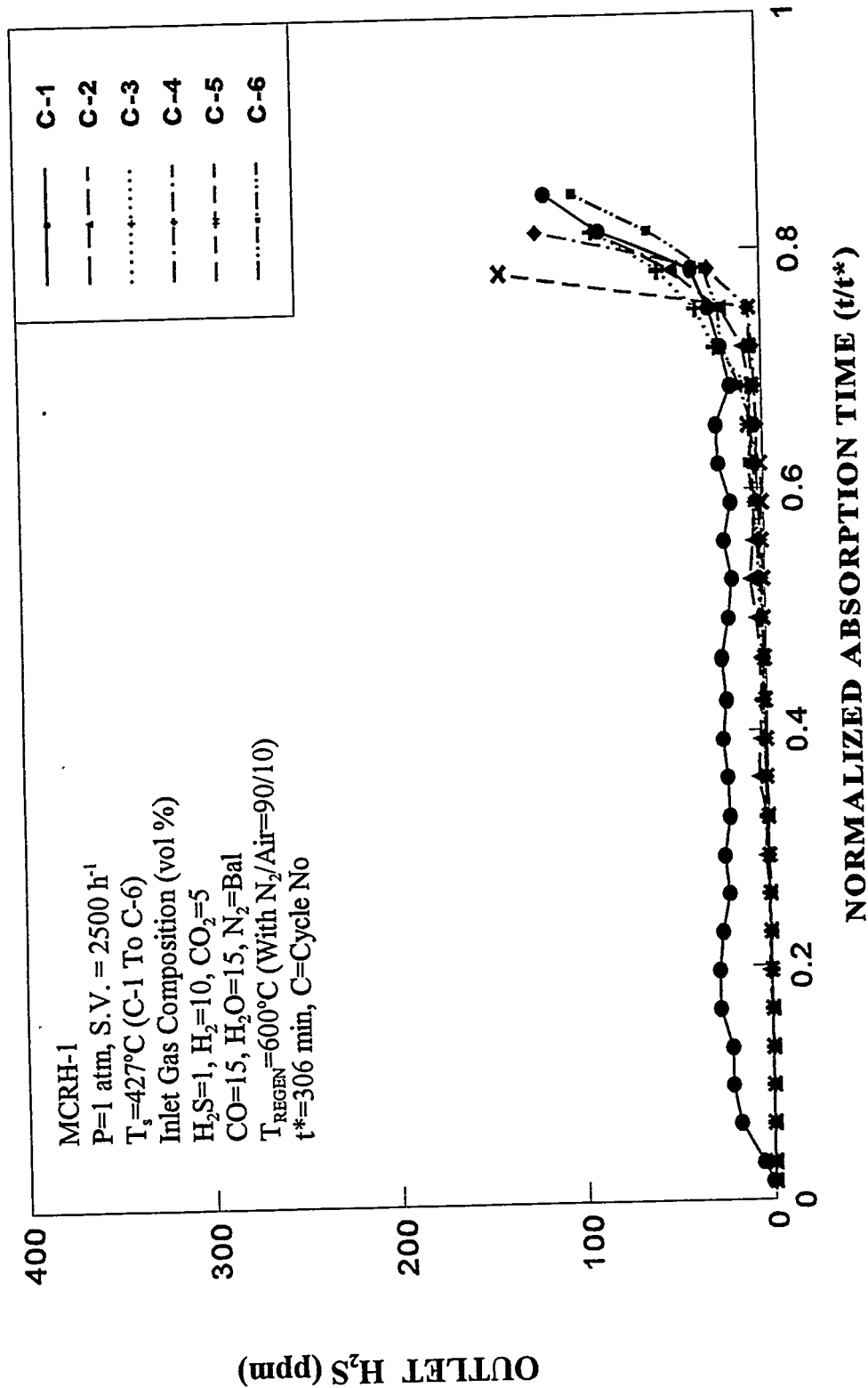
Figure 2.   SEM Micrographs of MCRH-1 Fresh Sorbents

Figure 3.   H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-1 Sorbent
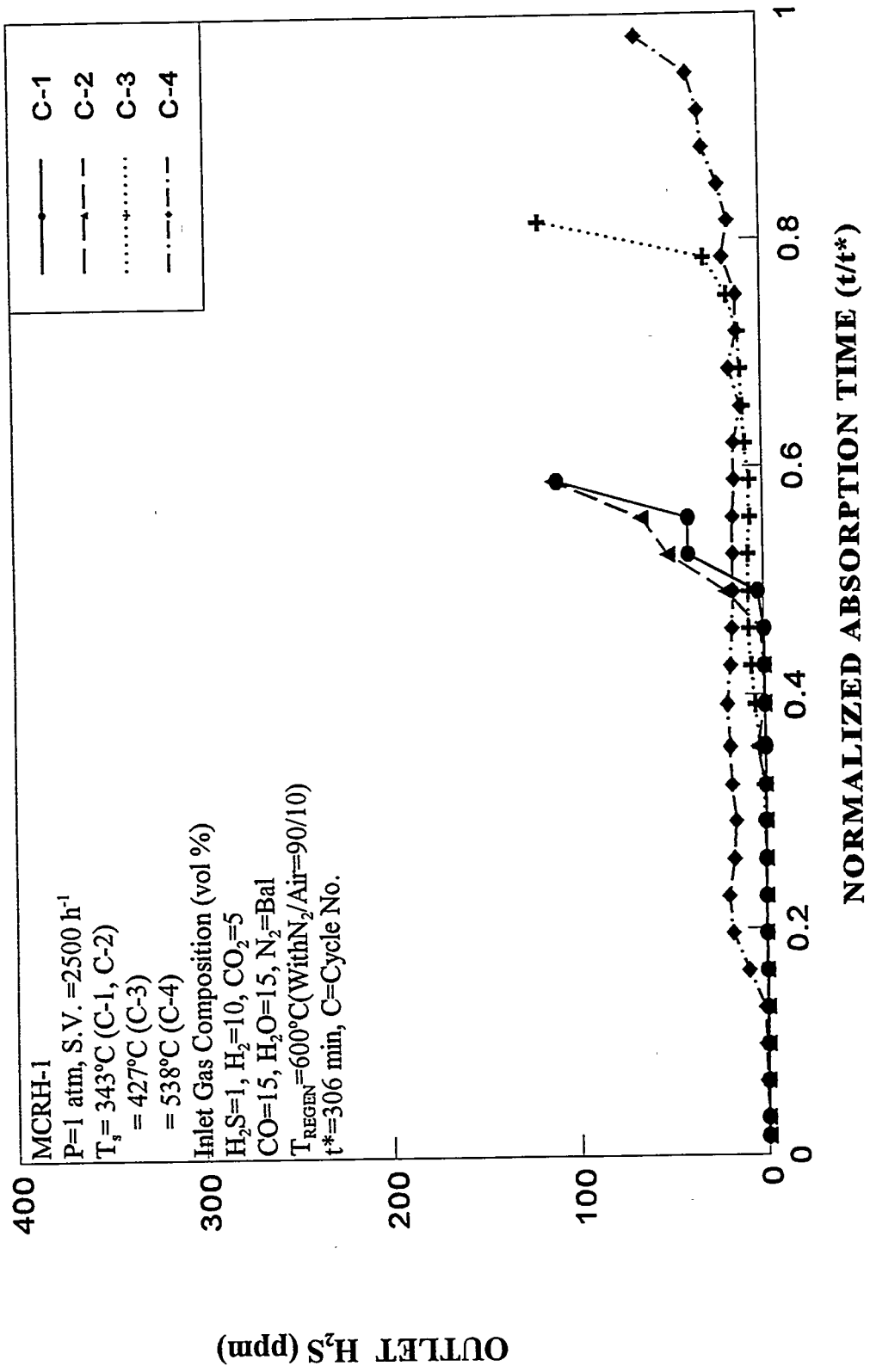
Figure 4. H_2S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-1 Sorbent

feed, breakthrough time and the amount of sorbent used.

As mentioned previously, the sorbent for the desulfurization application must have high chemical reactivity. The chemical reactivity is measured by the total sulfur loading as well as the rate of sulfur absorption. In order to measure the latter, standard 1.5 cycle TGA reactivity tests were carried out for fresh, and 6 cycle used sorbent. The TGA results (Figure 5), indicate that the rate of sulfur pickup (indicated by the slope of the sulfidation curve) remained relatively constant over six cycles of test. In the conventional sorbents, both the rate of sulfur pick-up and capacity progressively decreases with cycling. TGA results indicate that MCRH-1 has high chemical reactivity for sulfur capture even at a relatively low temperature of 427°C.

MCRH-2 : A mixed oxide sorbent (designated MCRH-2) was prepared by the same procedure as MCRH-1 in page 13. This material was tested for sulfidation in a laboratory scale reactor. Regeneration between cycles was conducted with 10 vol% air-90 vol% N_2 at 600°C. The gas hourly space velocity was about 2500 h^{-1} (STP) both in sulfidation and in regeneration. In tests with MCRH-2 sorbent conducted at 427°C, with a sulfidation gas containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at breakthrough was 60 percent or higher. As shown in Figure 6, the H_2S level remained at 0 ppm until 13 percent sorbent conversion and then gradually increased to ~20 ppm when conversion reached 60 percent. The sulfur capacities of the MCRH-2 sorbent during cycle 4 was 28.66 gS/100 g of sorbent. Sulfur capacity is calculated using the concentration of H_2S in feed, breakthrough time and the amount of sorbent used.

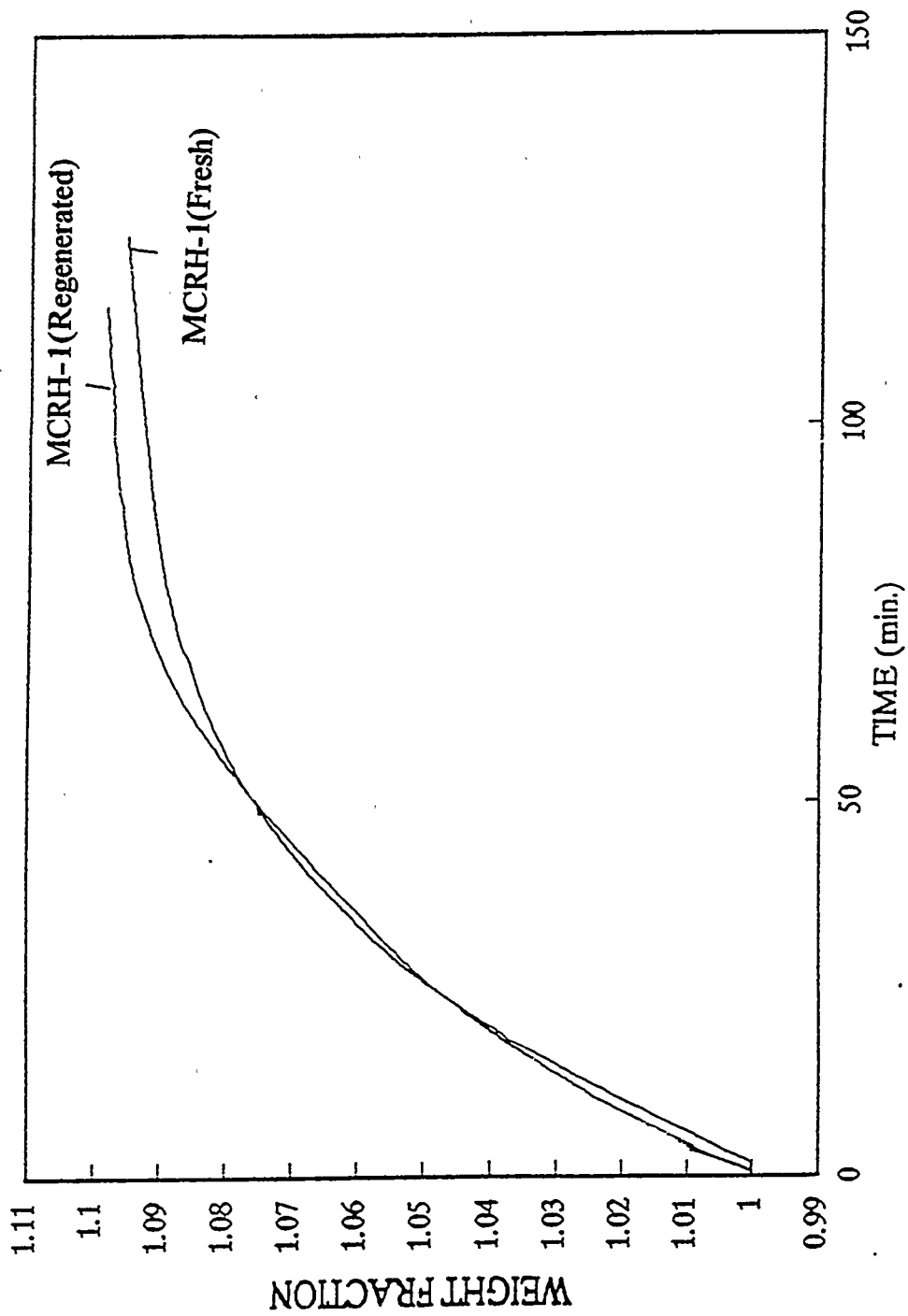**TGA Reactivities of MCRH-1(Fresh) and MCRH-(Regenerated) Sorbents**

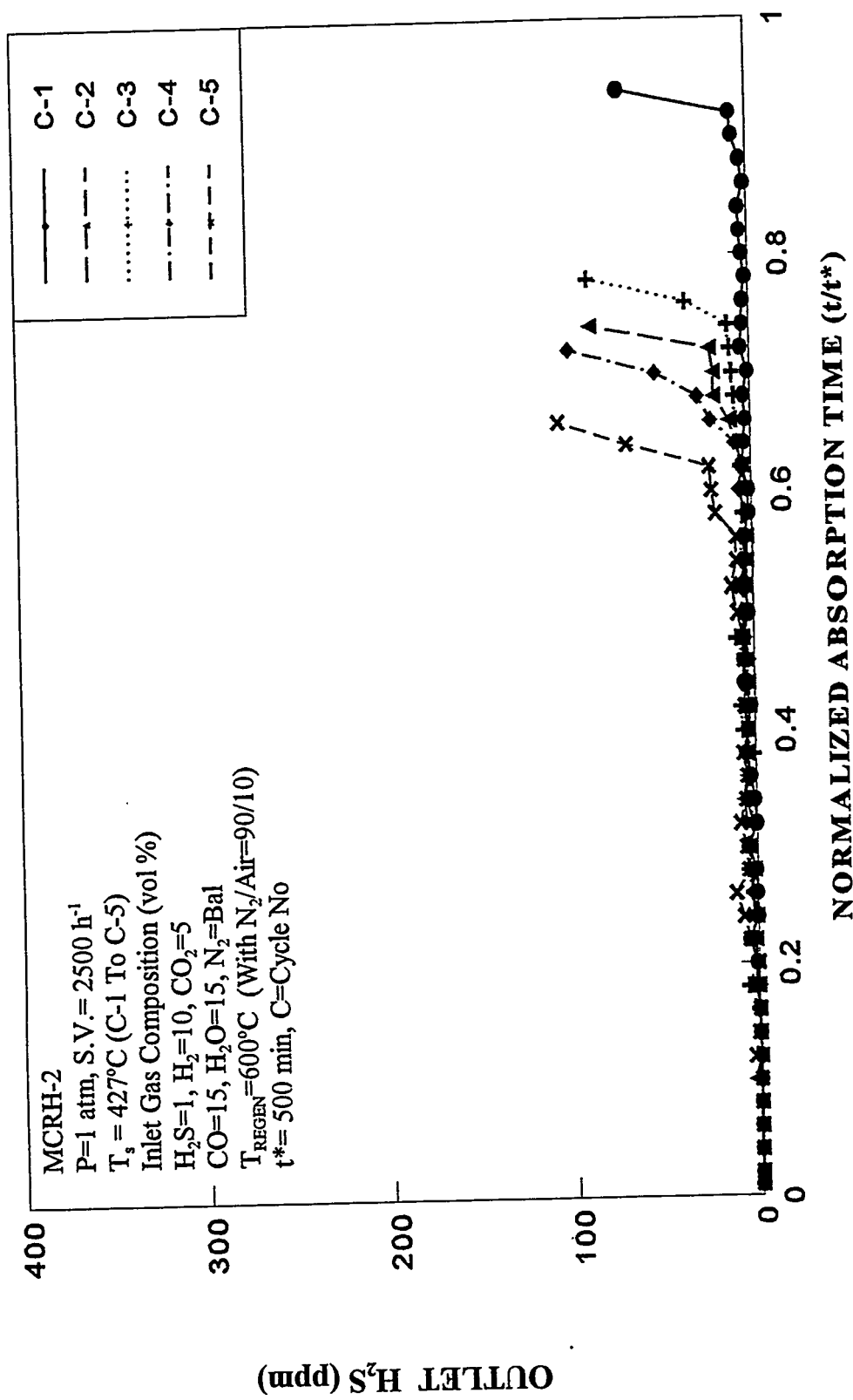Figure 5.   TGA Reactivities of MCRH-1 Sorbents

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Figure 6. H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-2 Sorbent

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MCRH-4 :   A mixed oxide sorbent (designated MCRH-4) was prepared by the same procedure as MCRH-1 in page 13. In tests with MCRH-4 sorbent conducted at 427°C, with a sulfidation gas containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at breakthrough was less than 10 percent. As shown in Figure 7, the H_2S level remained at 0 ppm until the breakthrough.

MCRH-7 :   A mixed oxide sorbent (designated MCRH-7) was prepared by the same procedure as MCRH-1 in page 13. In tests with MCRH-7 sorbent conducted at 427°C, with a sulfidation gas containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at breakthrough was 100 percent. As shown in Figure 8, the pre-breakthrough H_2S level remained below 30 ppm.

MCRH-8 :   A mixed oxide sorbent (designated MCRH-8) was prepared by the same procedure as MCRH-1 in page 13. In tests with MCRH-8 sorbent conducted at 427°C, with a sulfidation gas containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at breakthrough was 70 percent. As shown in Figure 9, the prebreakthrough H_2S level remained below 30 ppm.

MCRH-10 :   A mixed oxide sorbent (designated MCRH-10) was prepared by the same procedure as MCRH-1 in page 13. The SEM morphology of the MCRH-10 fresh sorbent is depicted in Figure 10. In tests with MCRH-10 sorbent conducted at 427°C, with a sulfidation gas containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at

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Figure 7. H$_2$S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-4 Sorbent

MCRH-4
P=1 atm, S.V. = 2500 h^{-1}
T$_s$=427°C (C-1 To C-3)
Inlet Gas Composition (vol %)
H$_2$S=1, H$_2$=10, CO$_2$=5
CO=15, H$_2$O=15, N$_2$=Bal
T$_{REGEN}$=600°C (With N$_2$/Air=90/10)
t*=325 min, C=Cycle No

C-1
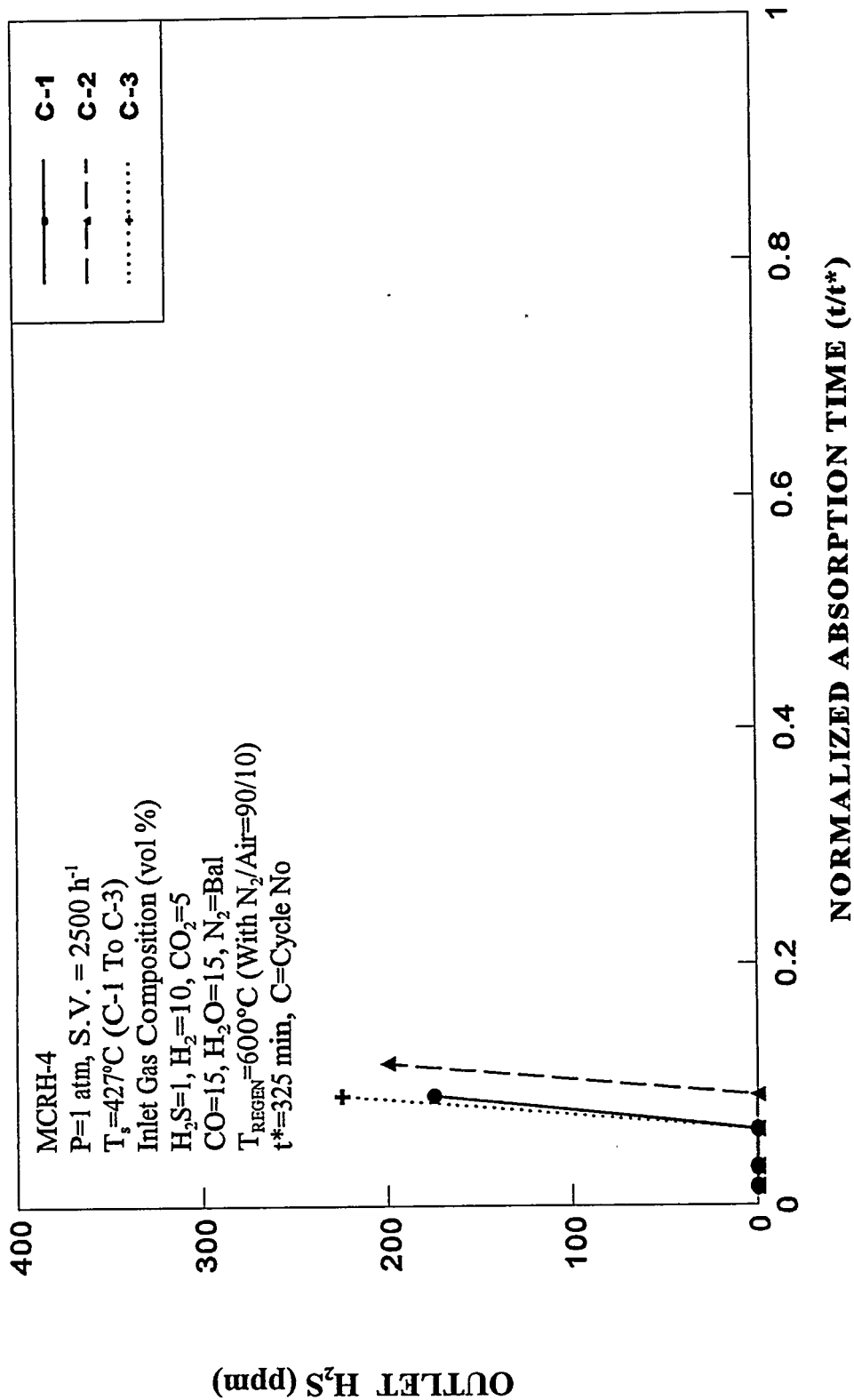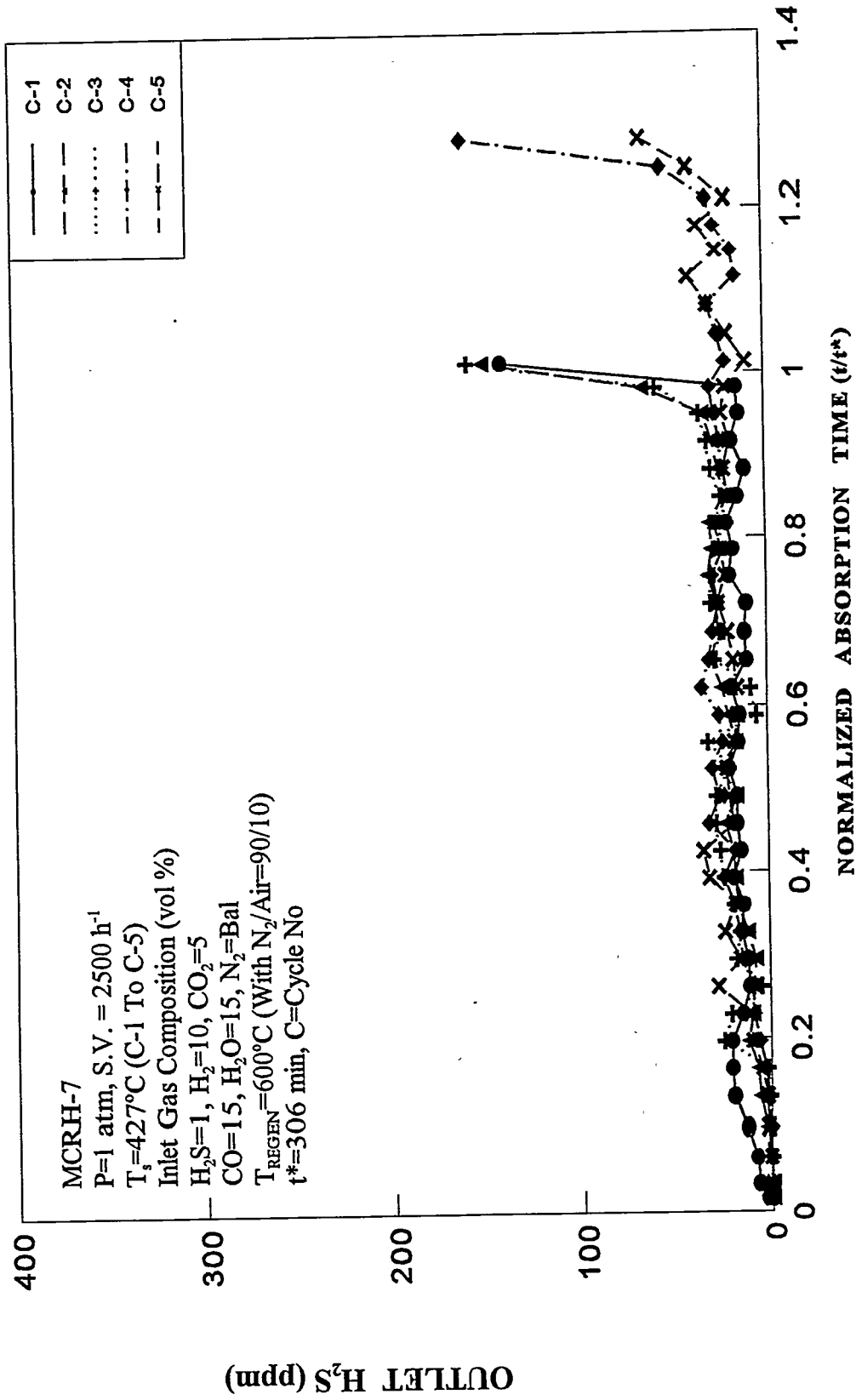C-2
C-3

NORMALIZED ABSORPTION TIME (t/t*)

OUTLET H$_2$S (ppm)

Figure 8. H_2S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-7 Sorbent
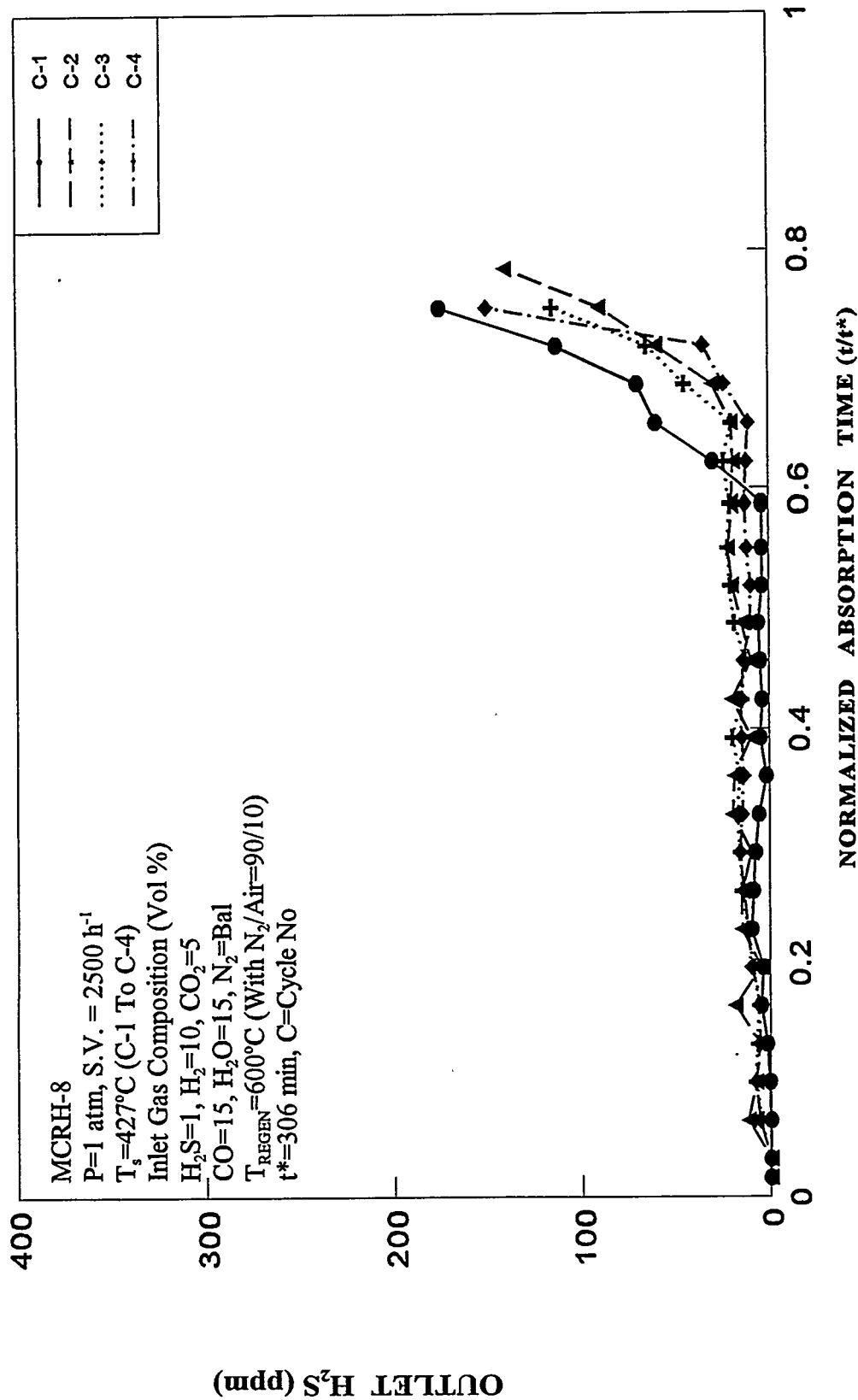
22

Figure 9. H_2S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-8 Sorbent

Figure 10. SEM Micrographs of MCRH-10 Fresh Sorbent

breakthrough was 90 percent. As shown in Figure 11, the prebreakthrough H_2S level remained below 60 ppm. The sulfur capacities of the MCRH-10 sorbent during cycles 4 was 21.06 gS/100 g of sorbent. Sulfur capacity is calculated using the concentration of H_2S in feed, breakthrough time and the amount of sorbent used.

MCRH-24 : A mixed oxide sorbent (designated MCRH-24) was prepared by the same procedure as MCRH-1 in page 13. This material was tested for sulfidation in a laboratory scale reactor. Regeneration between cycles was conducted with 10 vol% air-90 vol% with N_2 at 600°C. The gas hourly space velocity was about 2500 h^{-1} (STP) both in sulfidation and in regeneration. As shown in Figure 12, at 427°C, with a sulfidation gas containing (vol %)10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at breakthrough was greater than 95 percent and the pre-breakthrough was about 100 ppm. The sulfur capacities of the MCRH-24 sorbent during cycles 4 was 23.77 gS/100 g of sorbent. Sulfur capacity is calculated using the concentration of H_2S in feed, breakthrough time and the amount of sorbent used.

MCRH-14 : A mixed oxide sorbent (designated MCRH-14) was prepared by the same procedure as MCRH-1 in page 13. The SEM morphology of the MCRH-14 fresh sorbent is depicted in Figure 13 and for the sulfided sample in Figure 14. In tests with MCRH-14 sorbent conducted at 427°C, with a sulfidation gas containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at breakthrough was 70 percent. As shown in Figure 15, greater than 70 % sorbent conversion was observed at breakthrough at 427°C and the pre-breakthrough H_2S level was below 80 ppm. The sulfur capacities of the MCRH-14 sorbent

25
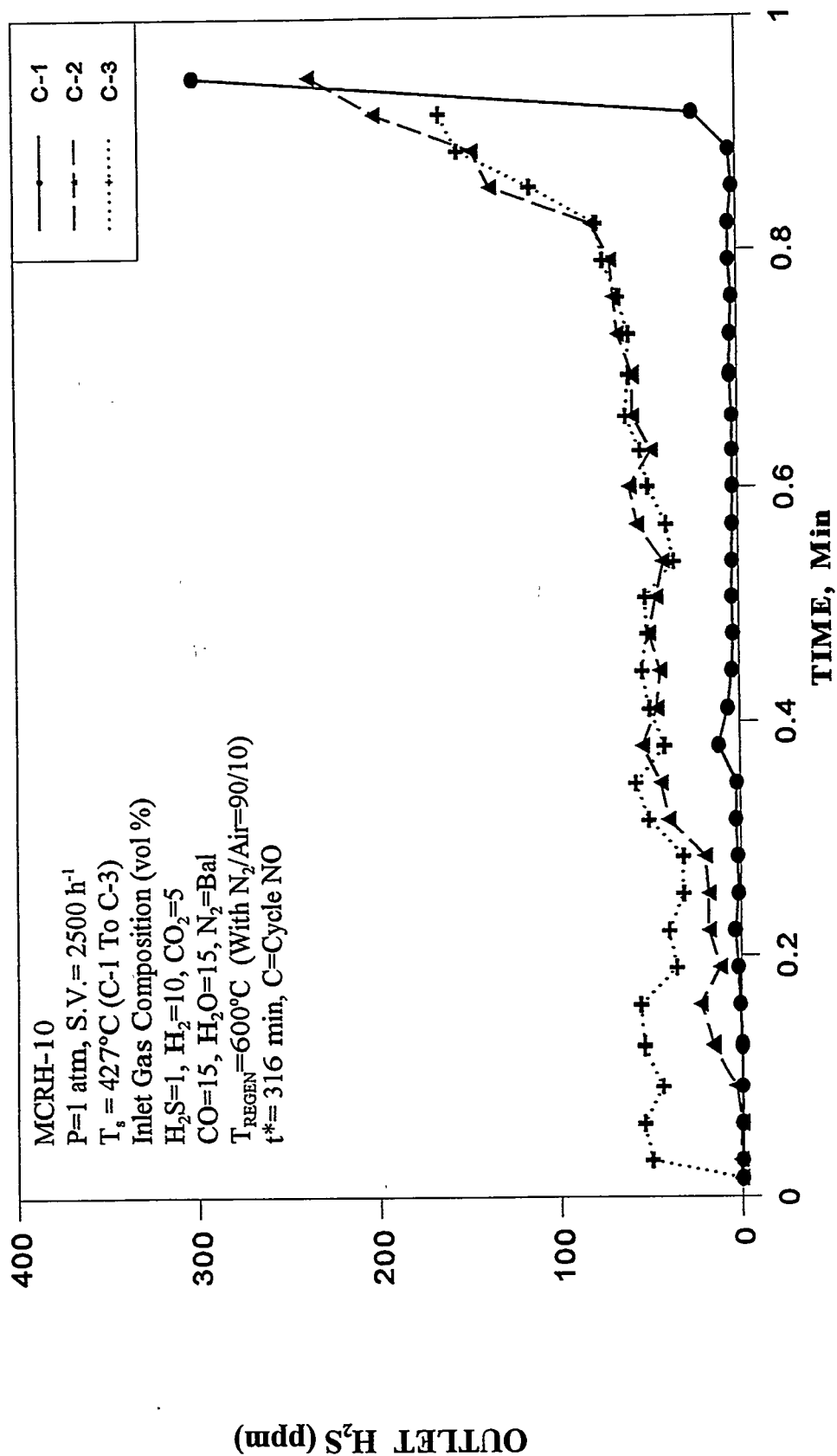
Figure 11. H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-10 Sorbent

The plot axes and legend:

- Y-axis: OUTLET H₂S (ppm), ranging 0 to 400
- X-axis: TIME, Min, ranging 0 to 1

Legend:
- C-1
- C-2
- C-3

Conditions:
MCRH-10
P=1 atm, S.V.= 2500 h⁻¹
Tₛ = 427°C (C-1 To C-3)
Inlet Gas Composition (vol %)
H₂S=1, H₂=10, CO₂=5
CO=15, H₂O=15, N₂=Bal
T_REGEN=600°C (With N₂/Air=90/10)
t*= 316 min, C=Cycle NO

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Figure 12.   H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-24 Sorbent

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Figure 13.   SEM Micrographs of MCRH-14 Fresh Sorbent

Figure 14.   SEM Micrographs of MCRH-14 Sulfided Sorbent
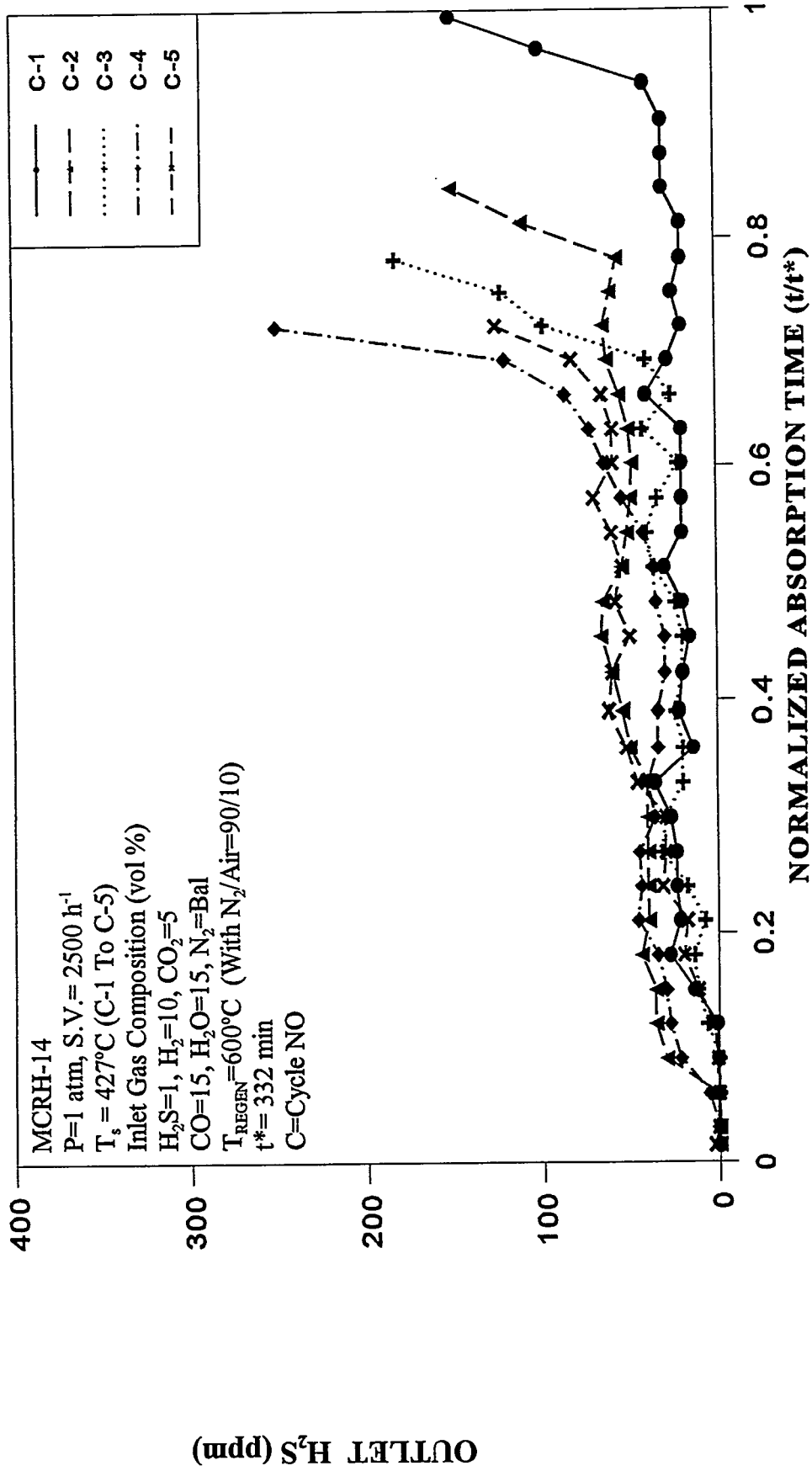
Figure 15. H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-14 Sorbent

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during cycles 4 was 17.31 gS/100 g of sorbent. Sulfur capacity is calculated using the concentration of H_2S in feed, breakthrough time and the amount of sorbent used.

MCRH-18 : A mixed oxide sorbent (designated MCRH-18) was prepared by the same procedure as MCRH-1 in page 13. The SEM morphology of the MCRH-18 fresh sorbent is depicted in Figure 16 and for the sulfided sample in Figure 17. In tests with MCRH-18 sorbent conducted at 427°C, with a sulfidation gas containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at breakthrough was less than 10 percent after cycle 1. As shown in Figure 18, 80 % sorbent conversion was observed at cycle 1 breakthrough at 427°C and the pre-breakthrough H_2S level was below 5 ppm. After the cycle 1, the sorbent deteriorated very fast and the sorbent conversion at cycle 4 was only about 4 %. Copper seems to be a very bad catalyst.

MCRH-23: A mixed oxide sorbent (designated MCRH-23) was prepared by the same procedure as MCRH-1 in page 13. The SEM morphology of the MCRH-23 fresh sorbent is depicted in Figure 19. As shown in Figure 20, 80 % sorbent conversion was observed at cycle 1 to 3 breakthrough at 427°C and the pre-breakthrough H_2S level was below 80 ppm. After the cycle 3, the sorbent deteriorated very fast and the sorbent conversion at cycle 4 and was only about 30. The sulfur capacities of the MCRH-23 sorbent during cycle 4 was 7.81 gS/100 g of sorbent. Sulfur capacity is calculated using the concentration of H_2S in feed, breakthrough time and the amount of sorbent used.

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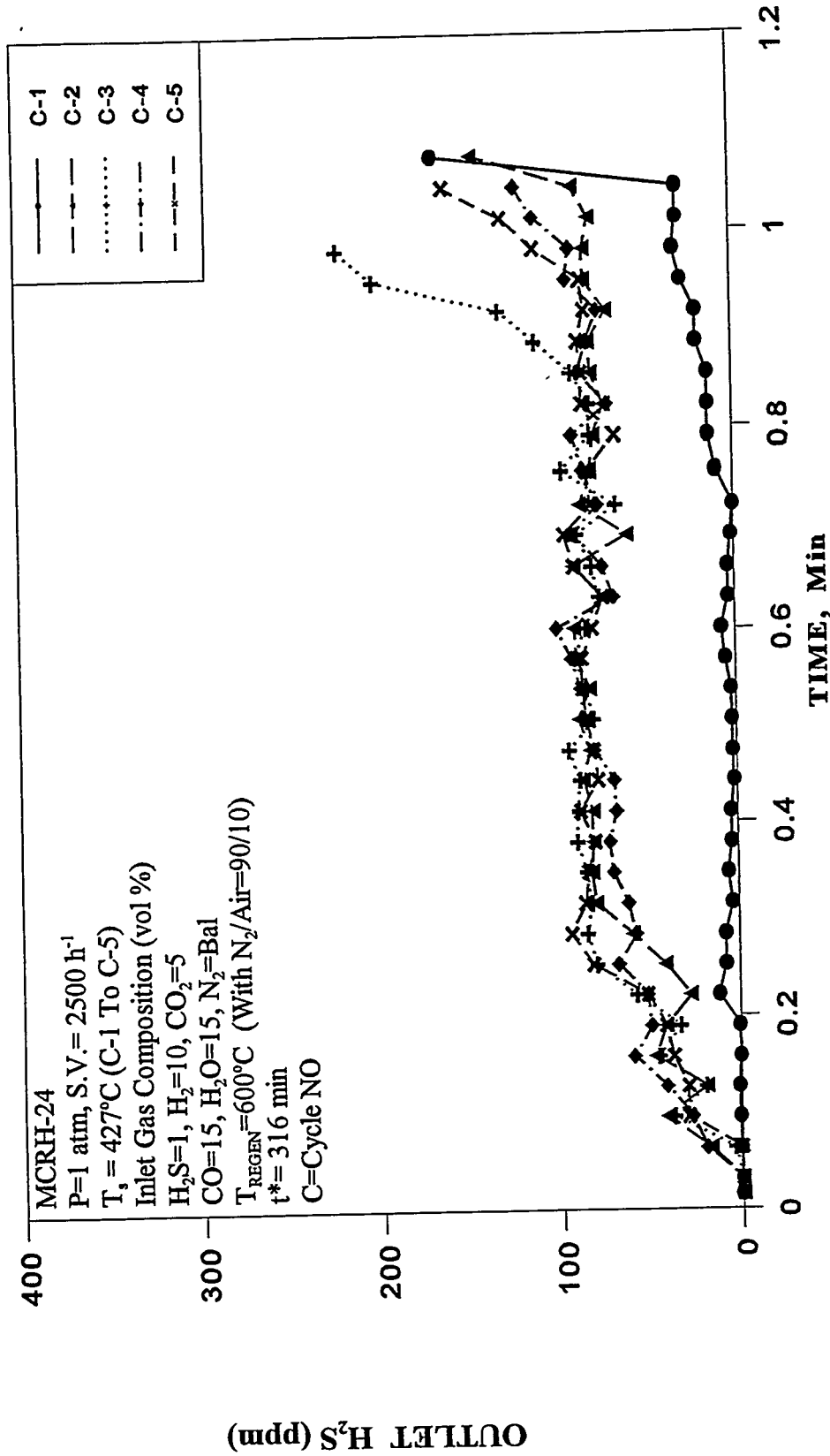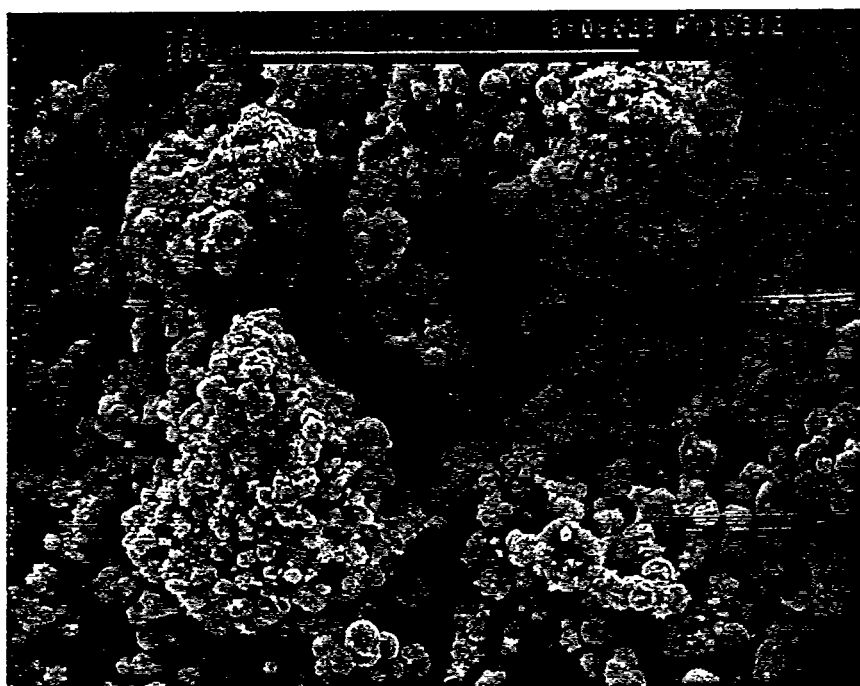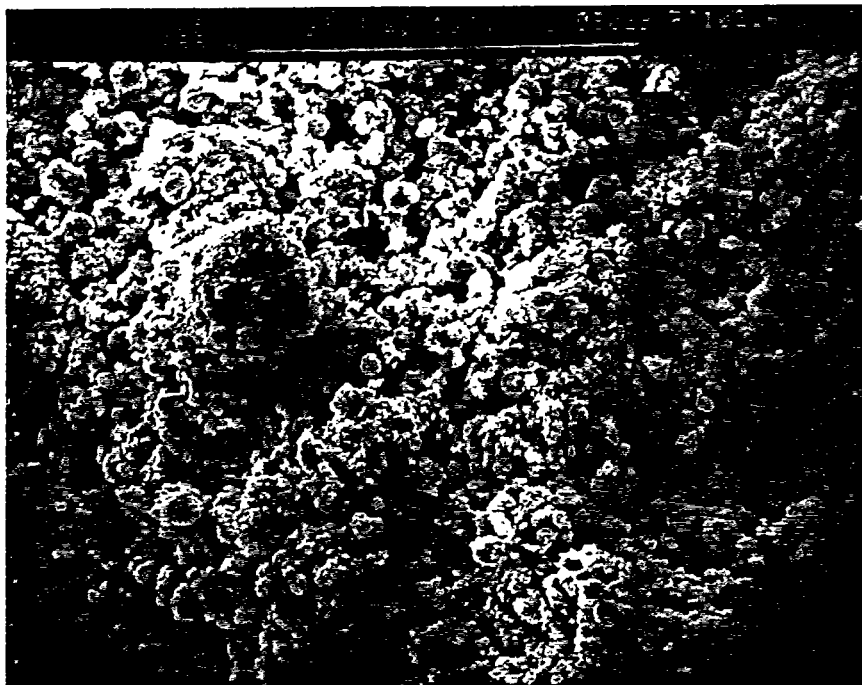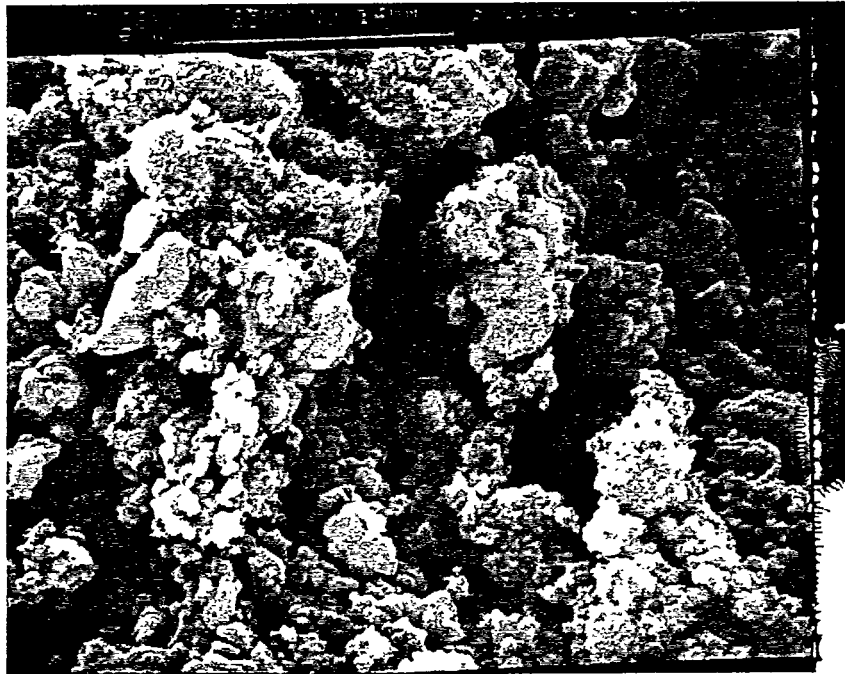Figure 16.　SEM Micrographs of MCRH-18　Fresh Sorbent

Figure 17.   SEM Micrographs of MCRH-18 Sulfided Sorbent
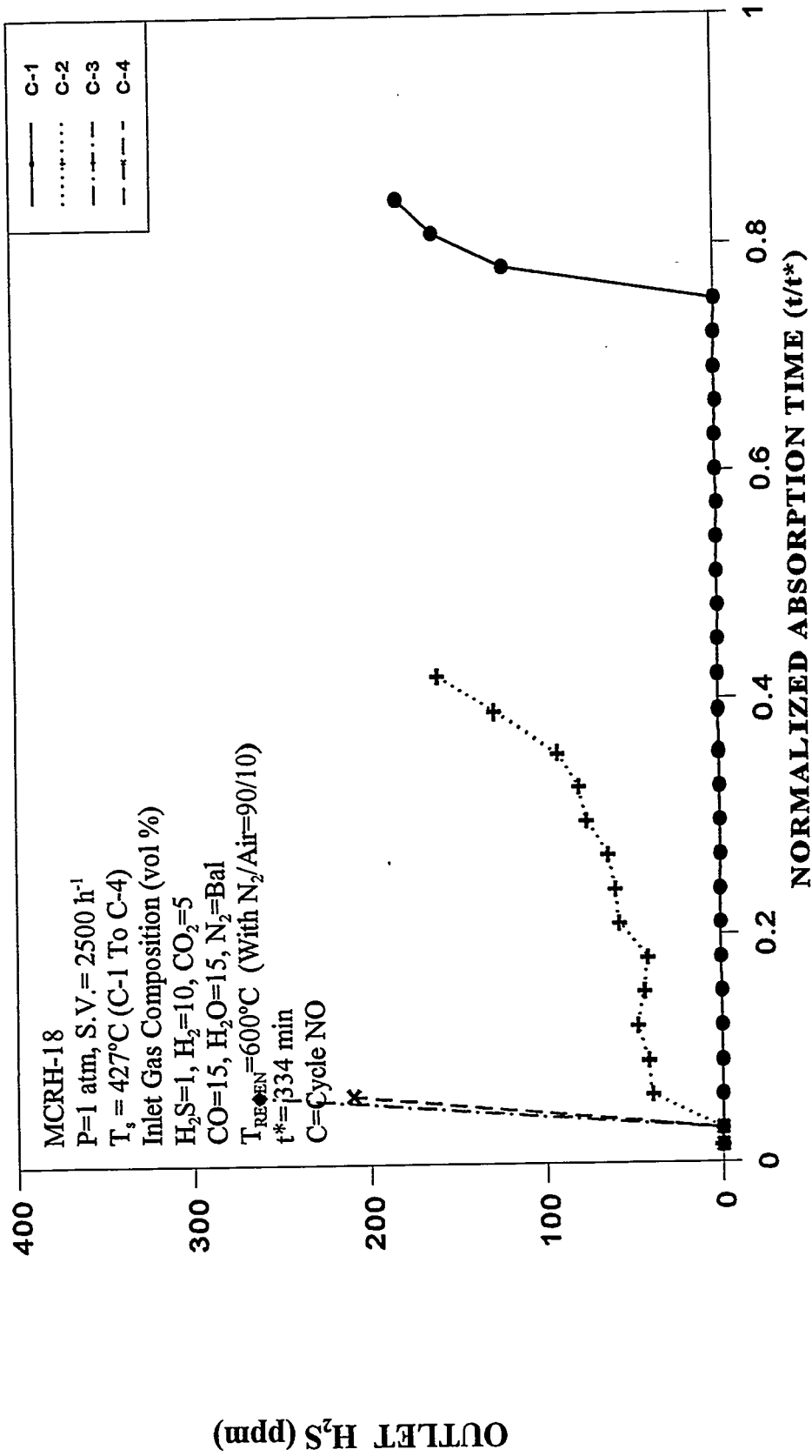
Figure 18.   H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-18 Sorbent

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Figure 19.   SEM Micrographs of MCRH-23 Fresh Sorbent
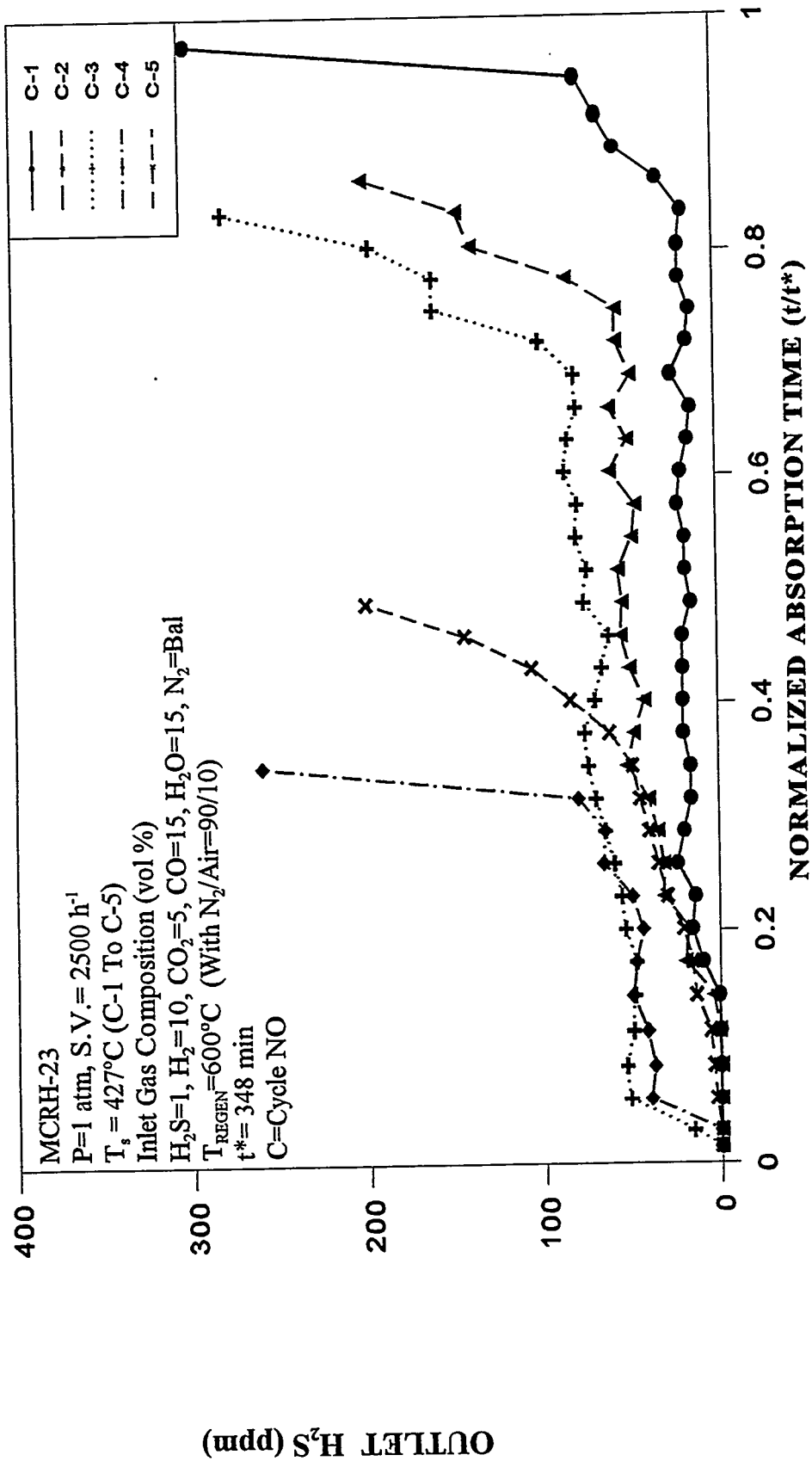
Figure 20. H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-23 Sorbent

MCRH-25 :   A mixed oxide sorbent, (designated MCRH-25) was prepared by the same procedure as MCRH-1 in page 13. The SEM morphology of the MCRH-25 fresh sorbent is depicted in Figure 21. The experimental results are discussed in multicycle section.

MCRH-26 :   A mixed oxide sorbent (designated by MCRH-26) was prepared by the same procedure as MCRH-1 in page 13. The SEM morphology of the MCRH-26 fresh sorbent was depicted in Figure 22. As shown in Figure 23, 40 % sorbent conversion was observed at breakthrough at 427°C and the pre-breakthrough H_2S level was below 30 ppm. The sulfur capacities of the MCRH-26 sorbent during cycles 4 was 11.89 gS/100 g of sorbent. Sulfur capacity is calculated using the concentration of H_2S in feed, breakthrough time and the amount of sorbent used.

MCRH-27 :   A mixed oxide sorbent (designated MCRH-27) was prepared by the same procedure as MCRH-1 in page 13. The SEM morphology of the MCRH-27 fresh sorbent is depicted in Figure 24. In tests with MCRH-27 sorbent conducted at 427°C, with a sulfidation gas containing (vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at breakthrough was 90 percent. As shown in Figure 25, the pre-breakthrough H_2S level was below 80 ppm. The sulfur capacities of the MCRH-27 sorbent during cycles 4 was 23.73 gS/100 g of sorbent. Sulfur capacity is calculated using the concentration of H_2S in feed, breakthrough time and the amount of sorbent used.

MCRH-31:   A mixed oxide sorbent (designated MCRH-31) was prepared by the same

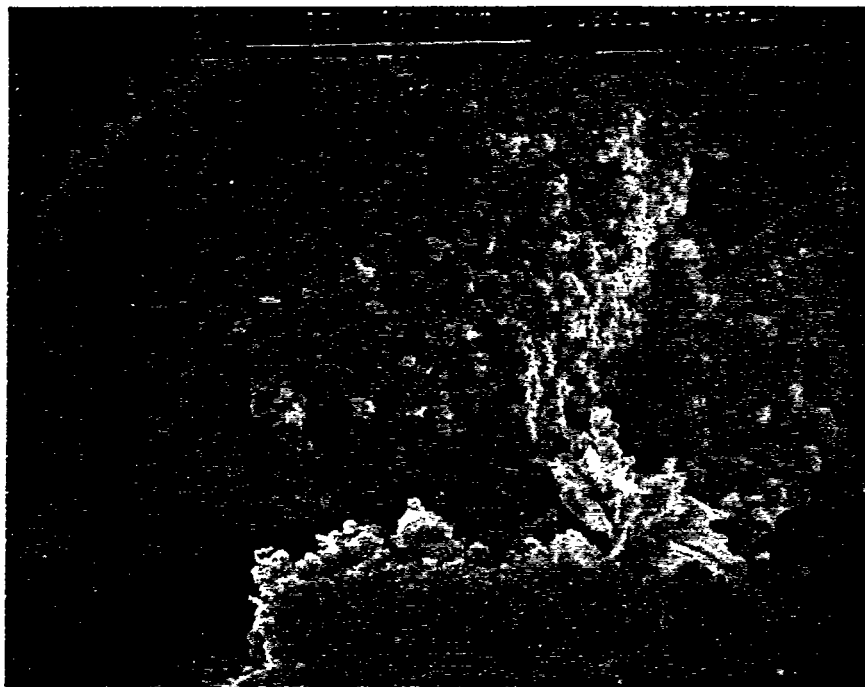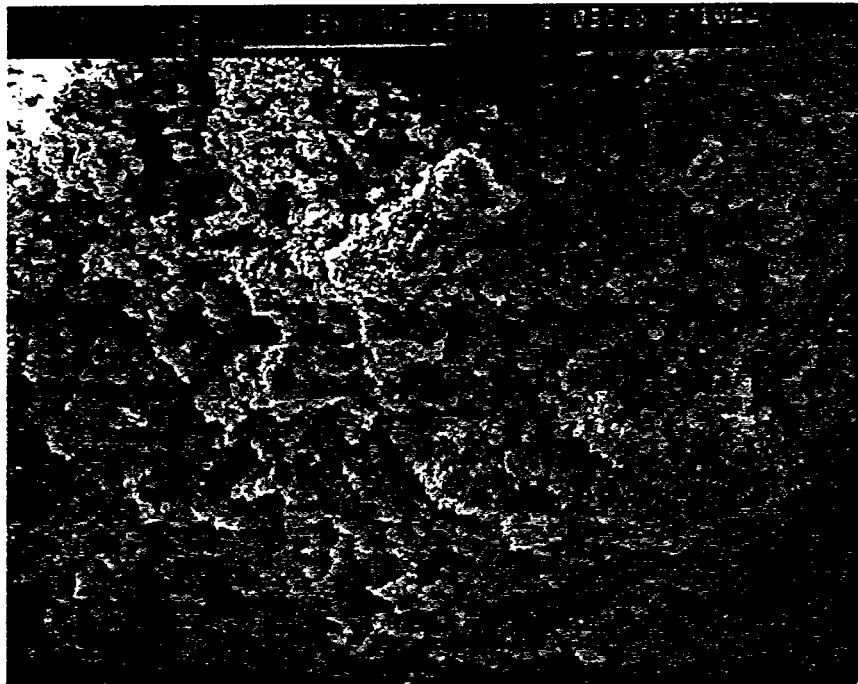Figure 21. SEM Micrographs of MCRH-25 Fresh Sorbent

Figure 22.   SEM Micrographs of MCRH-26 Fresh Sorbent
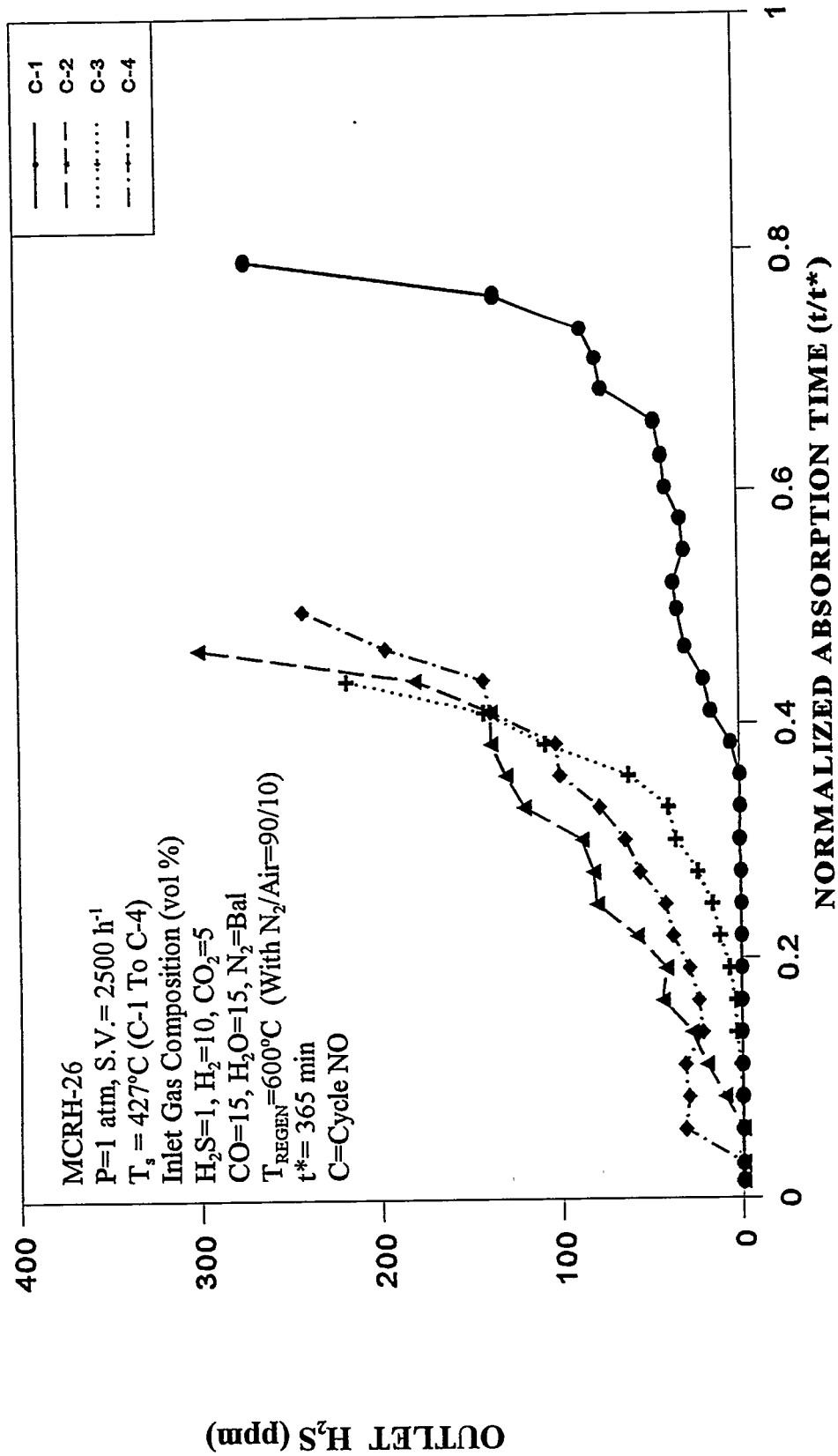
Figure 23. H$_2$S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-26 Sorbent

MCRH-26
P=1 atm, S.V.= 2500 h^{-1}
T$_s$ = 427°C (C-1 To C-4)
Inlet Gas Composition (vol %)
H$_2$S=1, H$_2$=10, CO$_2$=5
CO=15, H$_2$O=15, N$_2$=Bal
T$_{REGEN}$=600°C (With N$_2$/Air=90/10)
t*= 365 min
C=Cycle NO

C-1
C-2
C-3
C-4
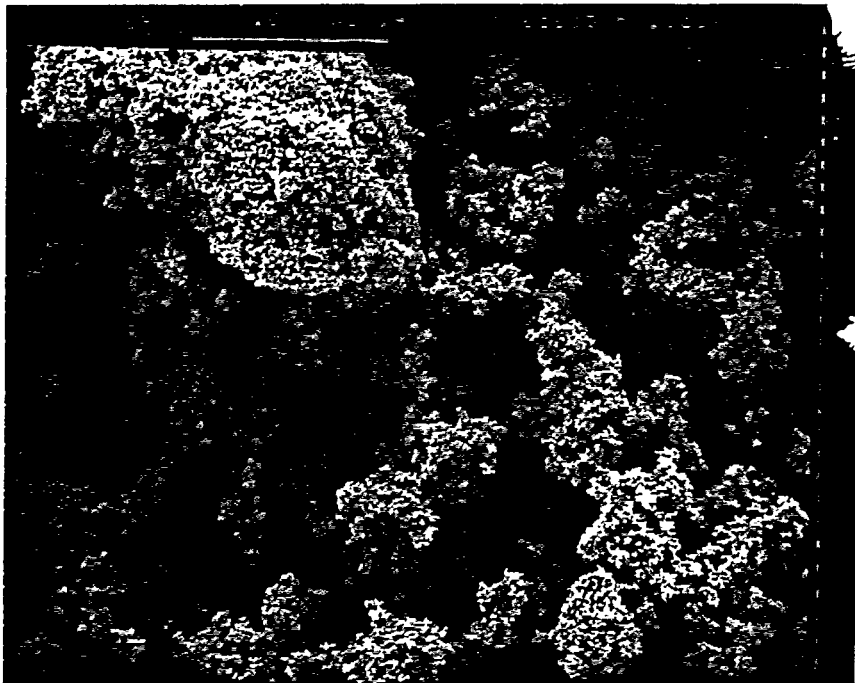
Figure 24. SEM Micrographs of MCRH-27 Fresh Sorbent
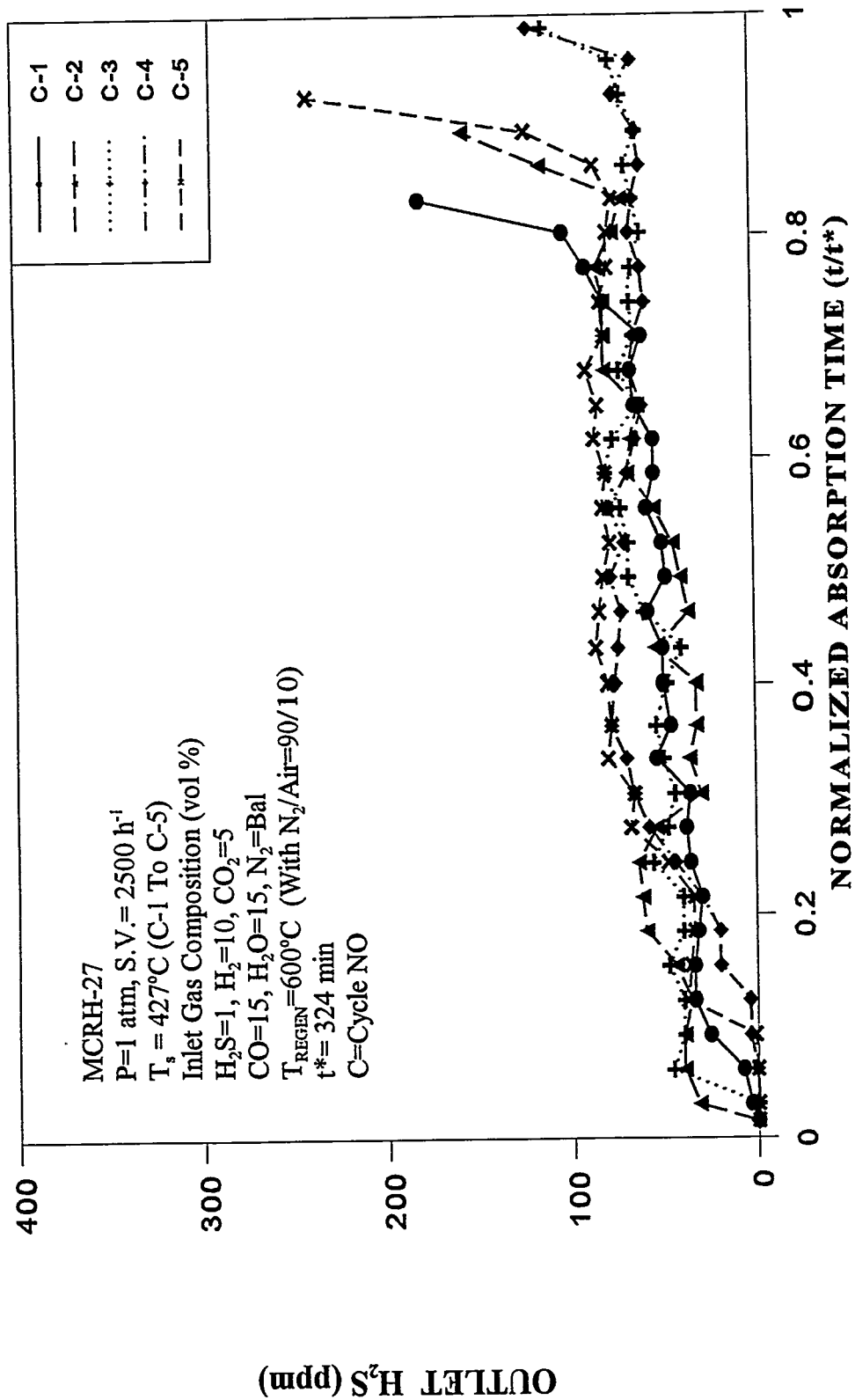
Figure 25. H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-27 Sorbent
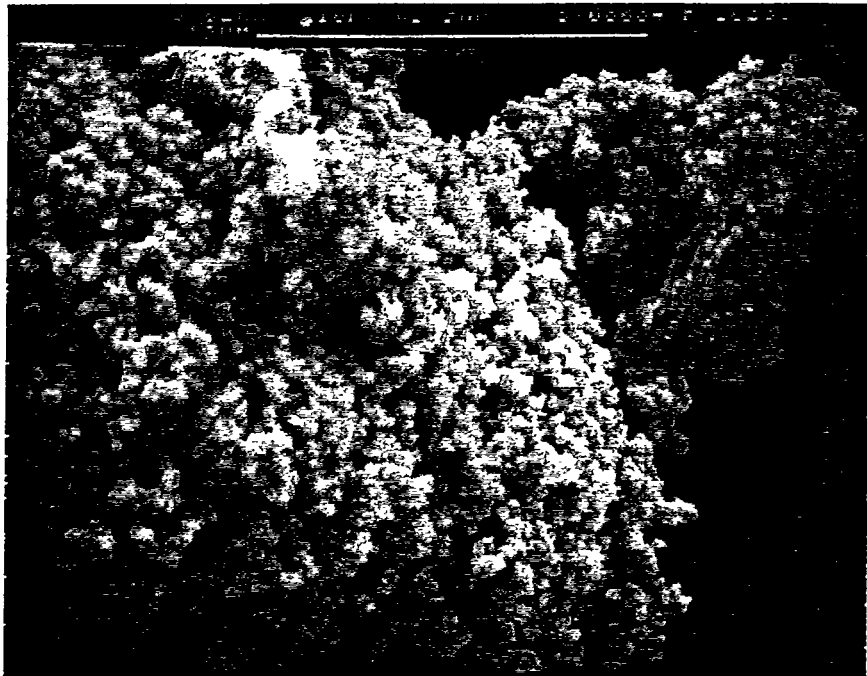
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procedure as MCRH-1 in page 13. In tests with MCRH-31 sorbent conducted at 427°C, with a sulfidation gas containing(vol %) 10 H_2, 15 CO, 5 CO_2, 1 H_2S, 15 H_2O, balance N_2, the sorbent conversion at breakthrough was 90 percent. As shown in Figure 26, the pre-breakthrough H_2S level was below 50 ppm.

LIGHT-OFF

Regeneration light-off temperatures of the sorbents are considered as one of the important parameters for sorbent performance evaluation because problems of decrepitation and spalling have occurred after sulfidation and regeneration of the sorbents. Measurements of surface area, structure, porosity, and acidity of the sorbents can be related to the sorbent performance. For sorbents, however, one direct measurement of its performance is to determine its light-off temperature, the temperature at which significant regeneration reactions occur. In general, it is true that the lower the light-off temperature, the more effective will be the sorbent performance. In this study research focused towards adding catalyst additives to zinc-based sorbents to reduce the regeneration light-off temperature to prevent sulfate formation. Experiments are carried out to find the regeneration light-off temperature of the zinc-based sorbents using both fixed and fluidized bed reactors.

A range of zinc based samples were prepared by doping with other metal ions during precipitation. These were required for investigation of the catalytic activity of the metal and to reduce the regeneration light-off temperature to prevent sulfate formation. The doped and undoped zinc based sorbents were evaluated by a two-step test procedure. In the first step, the sorbents were sulfided using a simulated gas at 427°C, until the breakthrough. In the second step,

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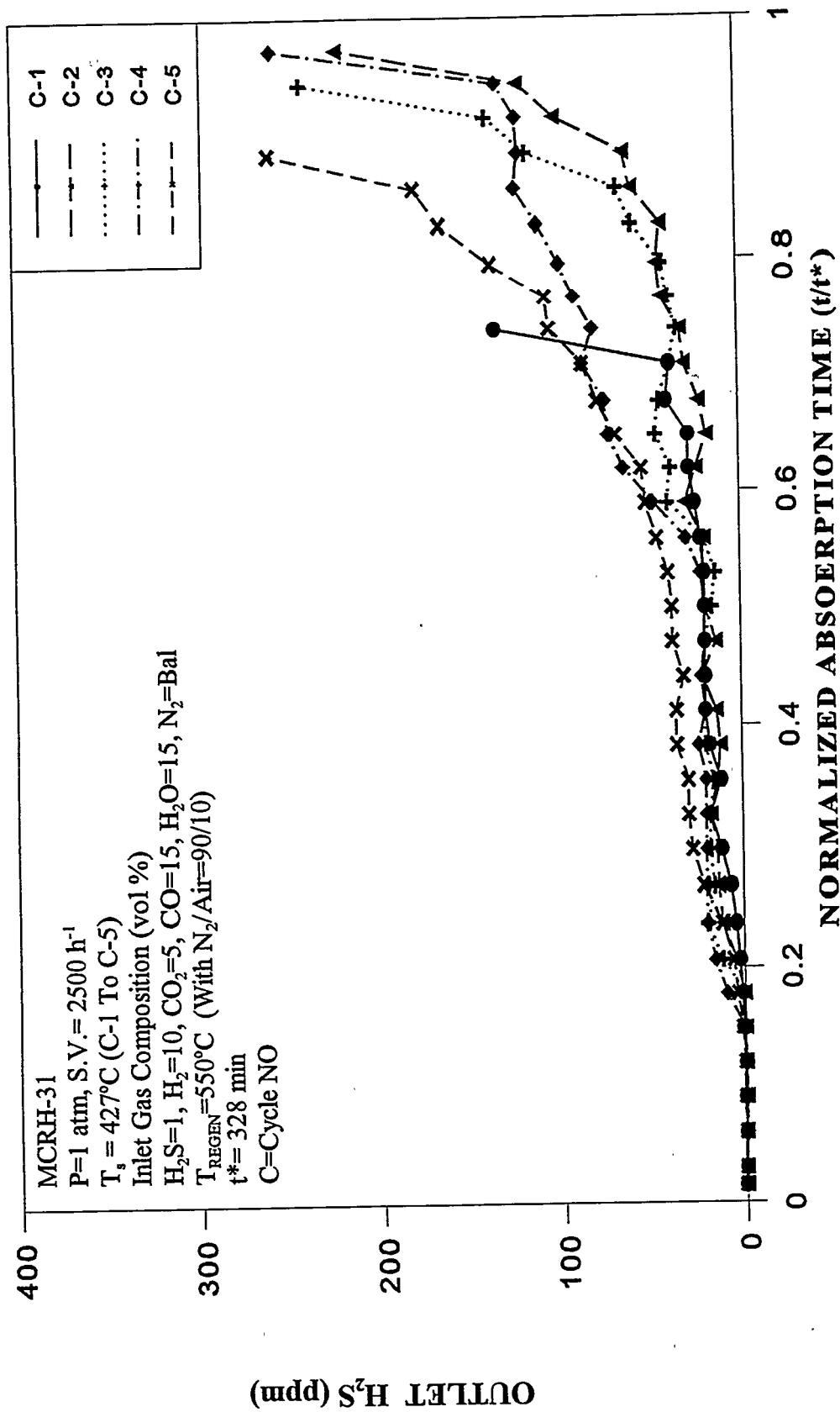
Figure 26. H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-31 Sorbent

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the sulfided sorbents were regenerated with 2% O_2 in nitrogen. The reactant gas mixture was introduced into the reactor at about 450°C and the reaction temperature was raised in 50°C increments after a steady-state condition was reached at each temperature. The regeneration light-off temperature was thus identified at which the reaction occurred with ZnS conversion to ZnO exceeding 90%. The light-off temperatures were found to be a strong function of the sorbents that were modified by doping with different metal as shown in Figure 27 and 28. A light-off temperature of 650°C was found for unmodified zinc based sorbents. Thus, addition of metal catalysts significantly lowered the light-off temperature of zinc based sorbents. These results were also confirmed using the TGA. The regeneration light-off temperature for various sorbents tested are shown in Table 2

Table 2. Regeneration Light-off Temperature for MCRH Sorbents

SORBENT	LIGHT-OFF T°(C)
MCRH-10	650 °C
MCRH-14	600 °C
MCRH-18	600 °C
MCRH-23	600 °C
MCRH-24	650 °C
MCRH-25	500 °C
MCRH-26	600 °C
MCRH-27	550 °C
MCRH-29	600 °C
MCRH-30	550 °C
MCRH-31	600 °C

Since the MCRH-25 sorbent showed excellent sulfidation and regeneration behavior in the 100 cycle test (as will be discussed in the multicycle section), it was decided to investigate the feasibility of low temperature regeneration, at about 500°C. The low temperature regeneration capability of the sorbent is required for Kellogg's transport reactor application. The MCRH-25 sorbent was evaluated in a bubbling fluidized-bed mode. The following paragraphs provide the

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Figure 27. Regeneration Light-Off Temperature for MCRH Sorbents

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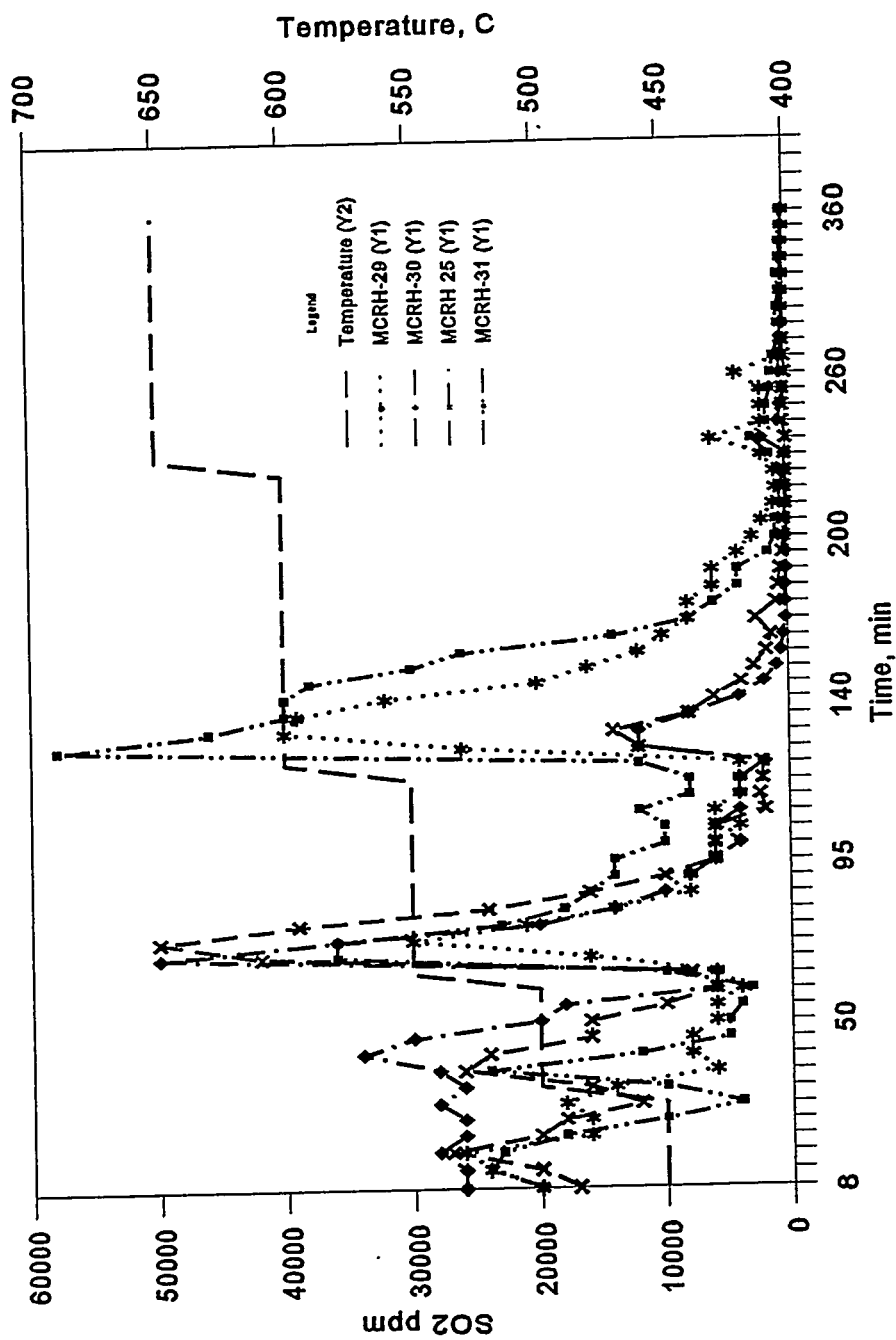
Figure 28. Regeneration Light-Off Temperature for MCRH Sorbents

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detailed description of the experimental system and procedure.

The MCRH-25 sorbent was evaluated in an atmospheric quartz fludized-bed bench-scale unit at RTI (Figure 29). The fludized-bed reactor is a quartz tube (26 mm I.D. and 100 cm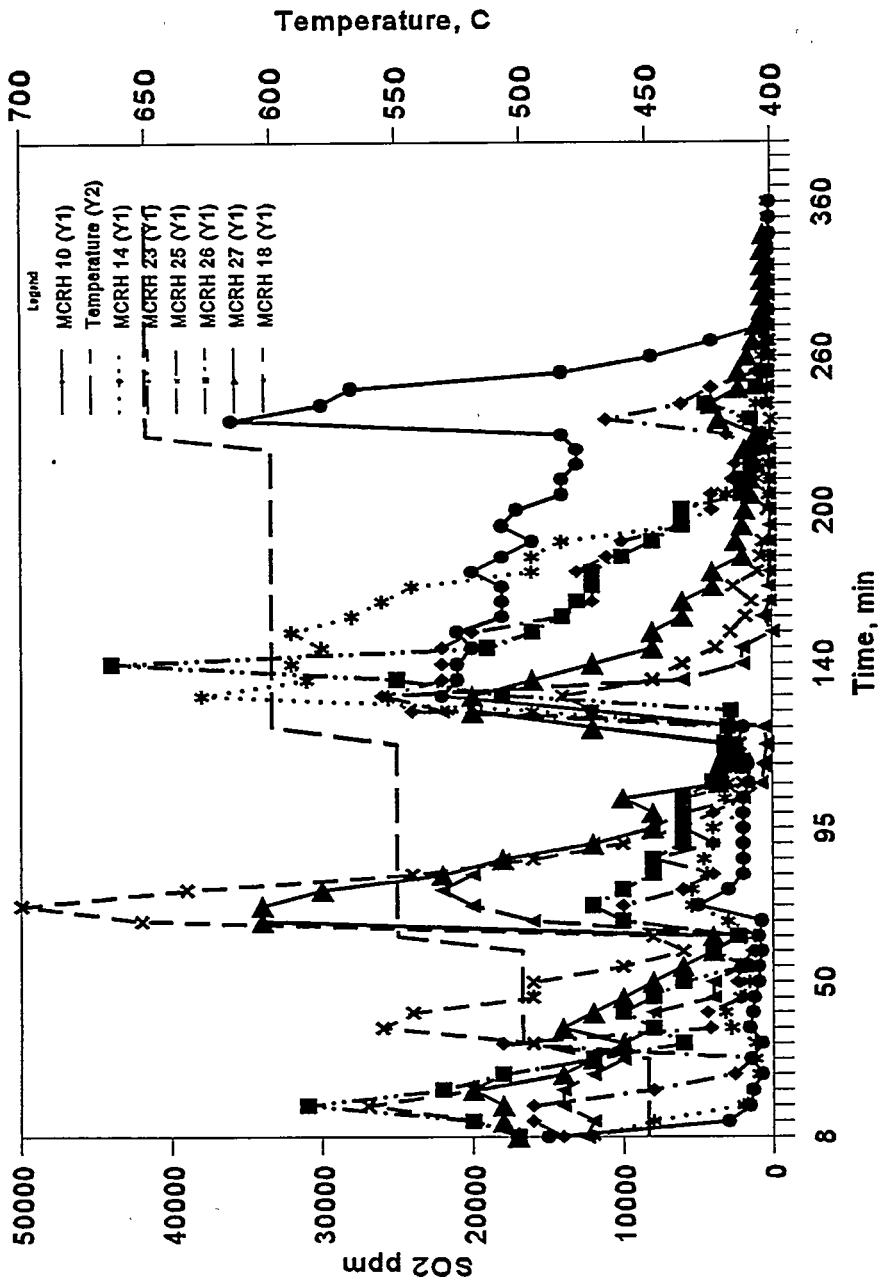 long) separated by a coarse quartz frit located midway in the tube. The sorbent powder is supported on the quartz frit. The section below the frit (lower section of the reactor which is 50 cm long) is packed with quartz rings (approximately 0.5 cm diameter and 0.7 cm long). The reactor is heated by an electric furnace.

During sulfidation, the coal gas source is a tank consisting of premixed gases, namely, 49.8% H_2, 23.4% CO_2, 13.4% CO, 12% N_2 and 1.4% H_2S. Steam is generated by feeding water through a syringe pump. Desired composition of coal gas (44.3% H_2, 20.8% CO_2, 11.9% CO, 11.05% H_2O, 10.7% N_2, and 1.25% H_2S) is obtained by feeding metered quantity of dry coal gas and water at the reactor bottom. During regeneration, desired concentration of O_2 is obtained by feeding metered quantities of N_2 and air.

The effluent gas from the sorbent bed is passed through a condenser, where the steam is condensed and collected in a catch pot. The coolant in the condenser is maintained at 5°C using a chiller. During sulfidation, the effluent gas after the condenser catch pot is directly vented to the hood without measuring the reactor outlet H_2S concentration. However, during regeneration, the effluent gas after the catch pot is analyzed using a Western Research SO_2 Analyzer (Model 721-AT) and the O_2 concentration by using a Teledyne Trace O_2 Analyzer. The dead volume of the catch pot creates a lag time in detecting the SO_2 and O_2 concentration in the reactor exit gas.

Typical experiment consisted of loading the reactor with 17.5 g of MCRH-25 sorbent and heating the sorbent bed in N_2. After the bed reached 427°C , 900 sccm of coal gas (of
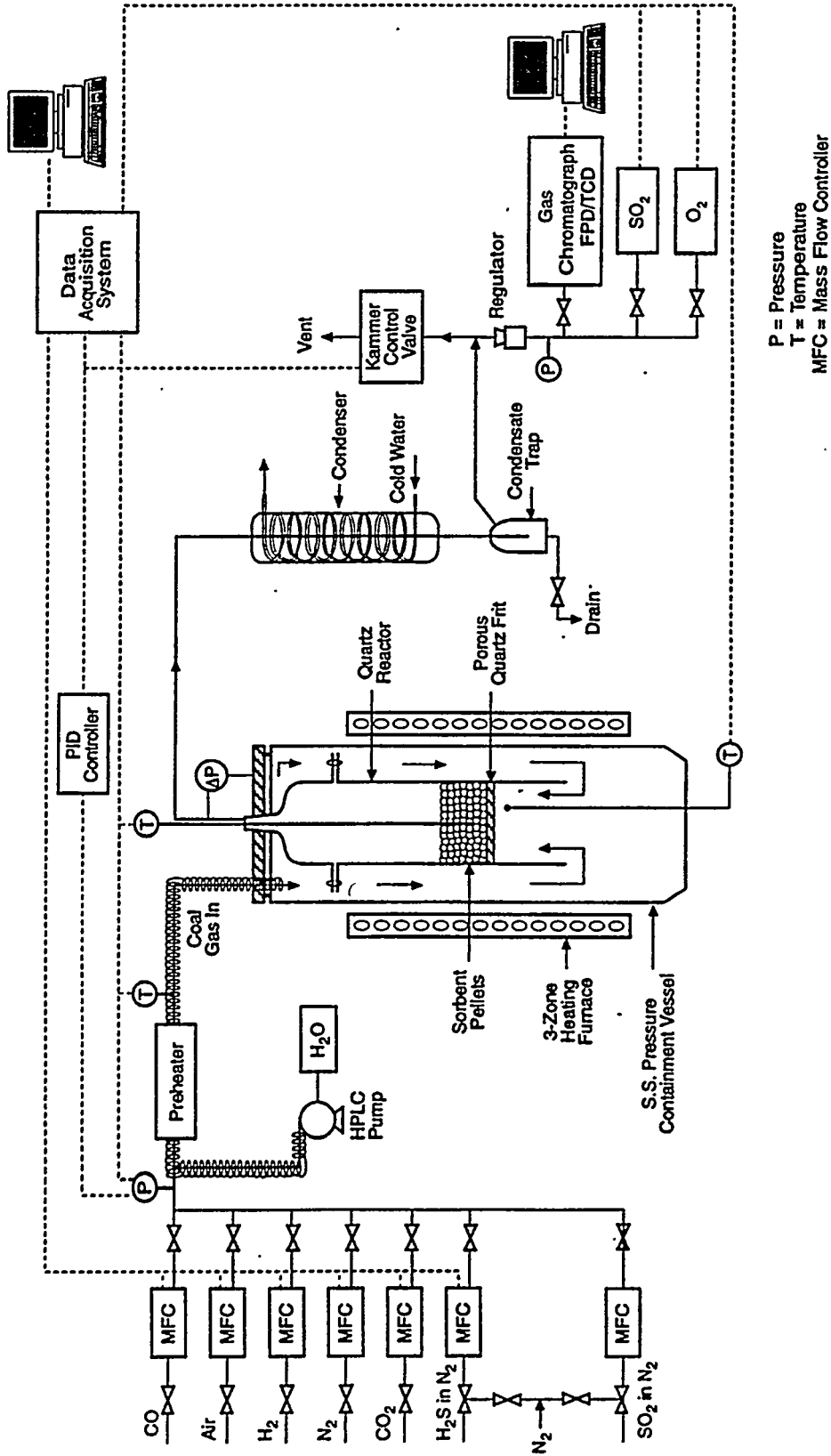
Figure 29. RTI Bench-Scale Test Facility

P = Pressure
T = Temperature
MFC = Mass Flow Controller

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composition as given above) was passed for 4 h. After sulfidation, the reactor was purged with N_2 for about 10 minutes before initiating sorbent regeneration.

During regeneration, 500 sccm of approximately 3 vol.% O_2 gas was fed to the reactor, but the bed temperature was varied based on the SO_2/O_2 concentration in the exit gas. The regeneration was started at an initial low temperature of 475-525 °C. However, at the onset of decrease in SO_2 concentration in the exit gas (or at the onset of O_2 breakthrough), the bed temperature was increased by about 25°C. The bed temperature was increased to sustain the regeneration and/or to decompose the sulfates formed. This increase in bed temperature by 25°C at the onset of decrease in SO_2 concentration was continued till the bed temperature reached 625°C. At 625°C, the regeneration was continued until O_2 breakthrough occurred, following which the bed was cooled under N_2 flow.

The sorbent was subjected to sulfidation and regeneration cycle testing. The regeneration was started at 475°C (Figure 30). As seen in Figure 30, the results clearly show that the sulfided sorbent can be ignited at temperatures as low as 475°C. Also, any sulfate that forms at these low temperatures is the basic, easy to decompose sulfate. These results confirms our TGA results.

Attrition-Resistant Sorbents

This section describes the efforts directed towards the development of sorbents for fluidized-bed reactors. The Sierra-Pacific plant employs the M.W.Kellogg (Kellogg) circulating fluidized-bed (transport) HGD process whereas the TECO plant employs the General Electric (GE) moving-bed HGD process. The key barrier issues facing the successful development of a fluidized-bed HGD process are chemical degradation, physical attrition, high regeneration light-

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Figure 30.   Regeneration Using MCRH-25 Sorbent

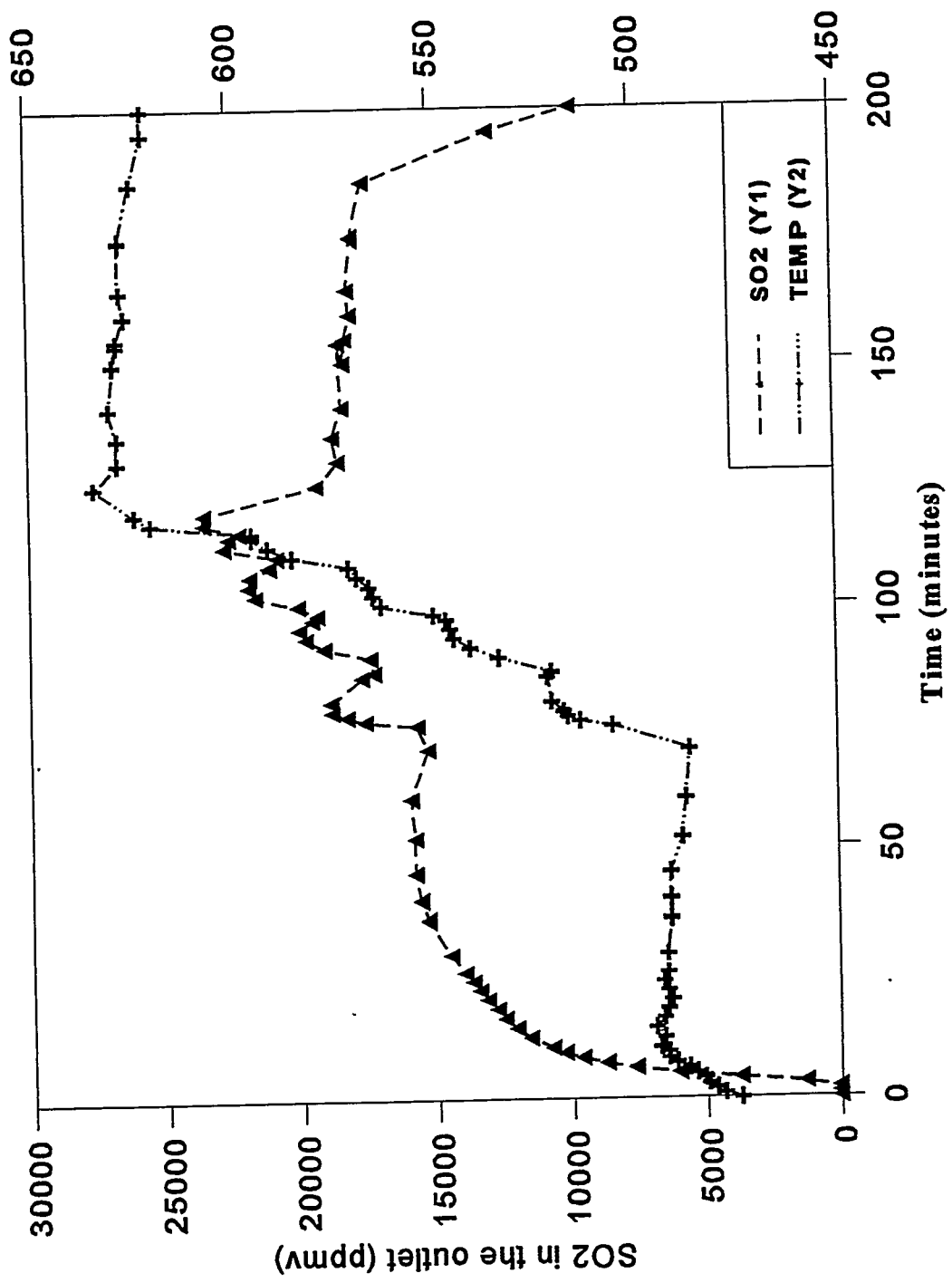off (initiation) temperature compared to sulfidation temperature, and high cost of the sorbent. Current leading first generation sorbents such as zinc titanate (ZT-4) typically prepared with an average particle size (aps) of 170 μm using a granulator and Phillips Petroleum's Z-Sorb III (175 μm aps) undergo significant chemical degradation, losing their reactivity and capacity by as much as 50 % in just 50 cycles and they cost as much as $8-10 per lb. These sorbents also have very low attrition resistance compared to bench-mark fluid catalytic cracking (FCC) catalysts (70-80 μm aps) prepared by spray drying and employed in a petroleum refinery. The larger aps of 170 μm results in reduced entrainment and allows greater throughput and flexibility in the choice of reactor type, but has not to date been successfully made using a spray drier. Also, the regeneration light-off temperature of first generation zinc titanate sorbents is around 630-650°C, which is unacceptably higher than the 480-550°C sulfidation temperature being employed at Sierra. To allow efficient heat integration, the sulfidation and regeneration light-off temperatures need to be the same or quite close to each other.

Fluidized-bed HGD systems are also receiving a lot of emphasis due to several potential advantages over fixed- and moving-bed reactors, including excellent gas solid contact, fast kinetics, pneumatic transport, ability to handle particles in the gas, and ability to control the highly exothermic regeneration process. However, an attrition-resistant sorbent that can withstand stresses induced by fluidization, transport, chemical transformation, and rapid temperature swings must be developed.

MCRH-39 : A zinc oxide-based fluidizable sorbent was prepared, using a proprietary technique with proprietary binders. The sorbent was dried at 120°C and then calcined in an oxygen-

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containing atmosphere at 600°C for 2 hours.

As shown in Figure 31, two cycles of sulfidation and regeneration were carried out in a bench-scale reactor over the resultant sorbent. The sulfidation was carried out with 85% of coal gas (containing 0.6% H_2S, 12% H_2, 18% CO, 6% CO_2, and balance N_2) and 15% steam with 180 sccm total flow at 450°C. Regeneration of the sorbent to convert ZnS to ZnO was carried out with 3% O_2 and balance N_2 at 600 °C. 18 grams of sorbent was used for these tests. The surface area of the fresh and sulfided samples were 104.9 and 95.8 m^2/g, respectively as shown in Table 3.

The following results were found during the above tests. During the first cycle, the sulfidation was carried out for 3 ½ hours and no H_2S breakthrough was observed by gas chromatograph-flame photometric detector (GC-FPD). The sulfided sorbents were then purged with N_2 for 30 minutes followed by regeneration at 600°C. The regeneration was stopped after 75 minutes when the flue gas contained ~2600 ppm of SO_2. The sorbents were then kept in N_2 and cooled to 450°C overnight. The second cycle was started the following morning. The H_2S breakthrough was undetectable for the first 2 hours and 45 minutes. Then, the H_2S concentration increased fast and reached 350 ppm after 3 hours and 30 minutes on stream.

These results demonstrate that very high sulfur removal efficiency can be achieved with this ZnO based sorbent prepared in this project. It is particularly noteworthy that H_2S remained undetectable prior to initial breakthrough, which indicates that the sorbent has a high reactivity and retains a high reactivity following regeneration.

Table 3. BET Surface Area of the Attrition-Resistant MCRH Sorbents

Sorbent	BET Surface Area, m^2/g
MCRH-39 (F)	104.9
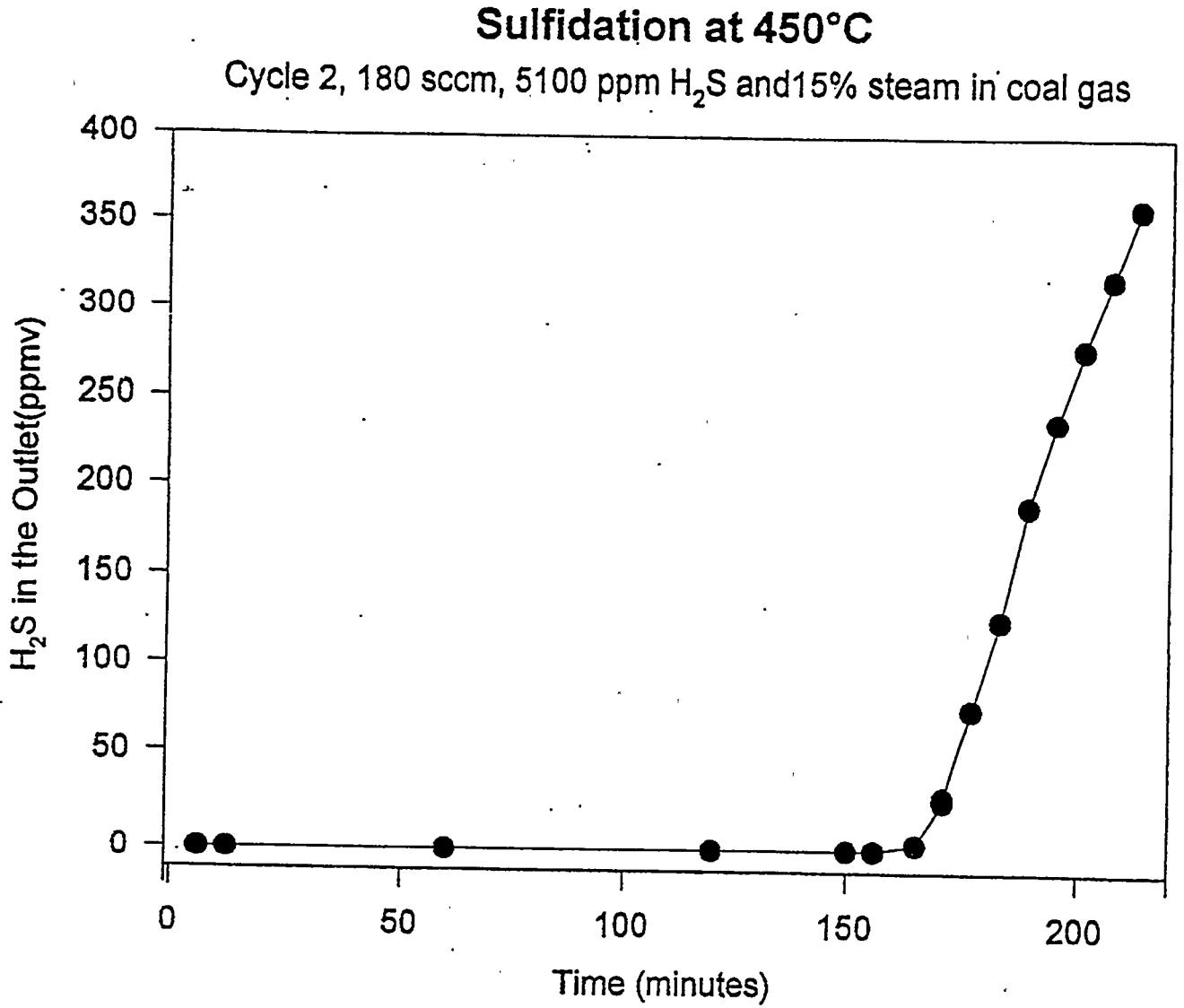
Figure 31. H_2S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-39 Sorbent

MCRH-39 (S)	95.8
MCRH-51 (F)	79.4
MCRH-51 (S)	63.1
MCRH-53 (F)	78.6
MCRH-53 (S)	71.9
MCRH-54 (F)	82.1
MCRH-54 (S)	71.5
MCRH-55 (F)	99.8
MCRH-55 (R)	90.8
MCRH-56 (F)	100.9
MCRH-60 (F)	101.2
MCRH-61 (F)	102.9

MCRH-51 : A fluidizable zinc oxide-based sorbent was prepared, using the proprietary technique. The sorbent was dried at 120°C and then calcined in an oxygen-containing atmosphere at 600°C for 2 hours.

A sulfidation test was then carried out on this sorbent with a sulfidation gas containing 10% H_2, 15% CO, 5% CO_2, 0.4% H_2S, 15% H_2O, balance N_2 (volume %). As shown in Figure 32, at 482°C sulfidation temperature, the stable conversion achieved by this sorbent was found to be 100%, and the pre-breakthrough H_2S level in the desulfurized gas was found to be less than 100 ppm. Regeneration of this sorbent was conducted with 2 volume percent O_2 in N_2 at 550 °C. Sulfidation and regeneration of the sorbent was repeated for a total of five cycles. The sorbent capacity and activity was stable for the 5 cycles it was tested for. The sulfur capacity of the sorbent was measured during cycle 4 and found to be 9.12 g(sulfur)/100 g of sorbent. The surface area of the fresh and sulfided samples were measured and found to be 79.4 and 63.1 m^2/g.
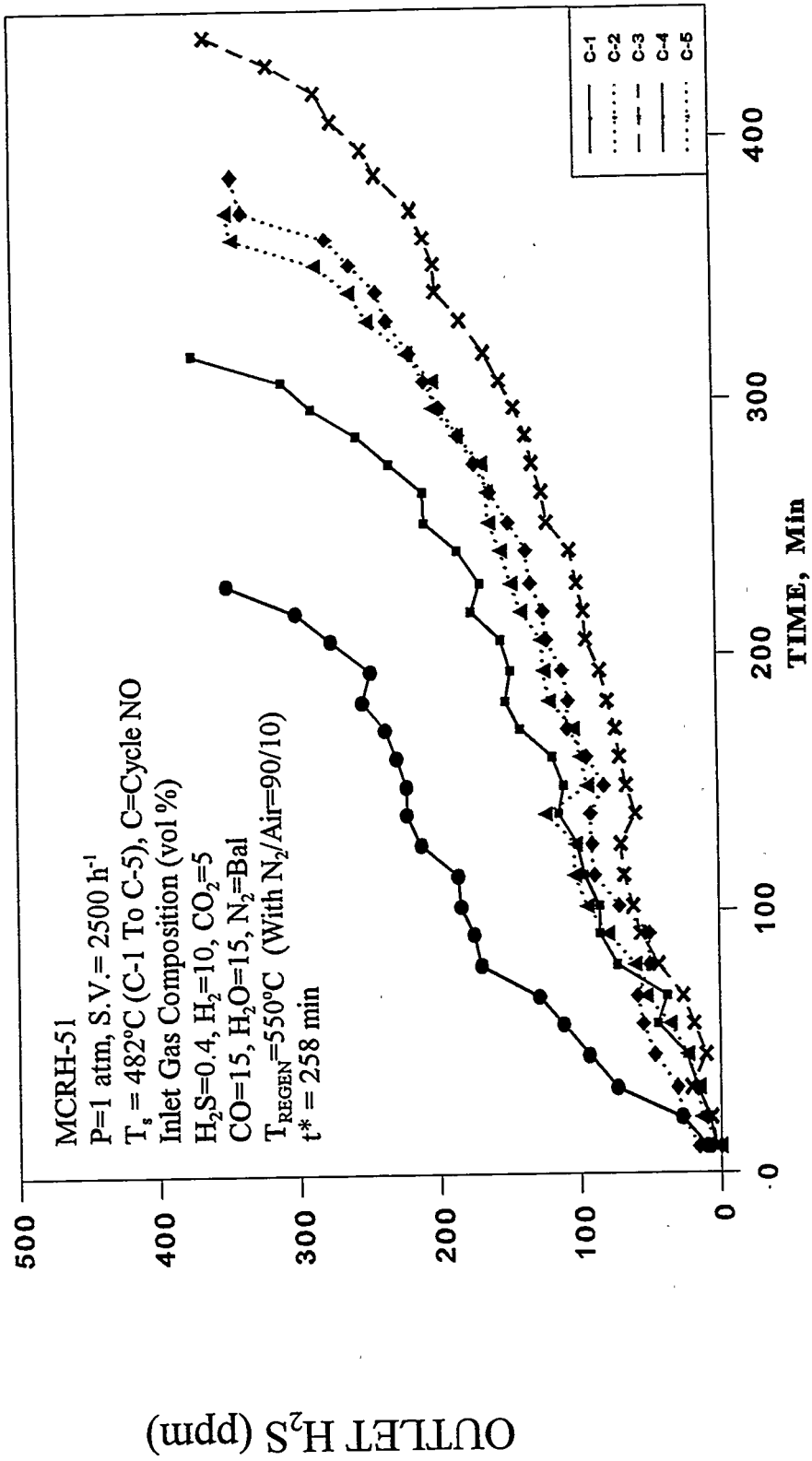
Figure 32. H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-51 Sorbent

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The 5 hour and 20 hour attrition loss of the fresh sorbent were tested and found to be 0.0 and

0.62 wt.%, respectively in a standard 3-hole tester as shown in Table 4. The high stable

conversion achieved by the sorbent of this example indicates rapid kinetics and little or no loss of

surface area in successive cycles.

Table 4. Attrition Test of MCRH Sorbents

Sorbent	3-hole attrition loss (wt %)	
	5 hour	20 hour
MCRH-51	0.00	0.62
MCRH-53	0.28	0.56
MCRH-54	0.36	0.36
MCRH-55	0.56	1.41
MCRH-56	**0.00**	**1.06**
ZT-4	40.00	89.00
Z-sorb III	16.00	32.40

MCRH-53 :   A fluidizable zinc oxide-based sorbent was prepared, using the proprietary

technique. The sorbent was dried at 120°C and then calcined in an oxygen-containing

atmosphere at 600°C for 2 hours.

A sulfidation test was carried out on the resultant sorbent with a sulfidation gas containing

10% H_2, 15% CO, 5% CO_2, 0.4% H_2S, 15% H_2O, balance N_2 (volume %). Regeneration of this

sorbent was conducted with 2 volume percent O_2 in N_2 at 550 °C. Sulfidation and regeneration

were repeated for a total of five cycles.

As shown in Figure 33, it was found that at 482°C sulfidation temperature, the stable

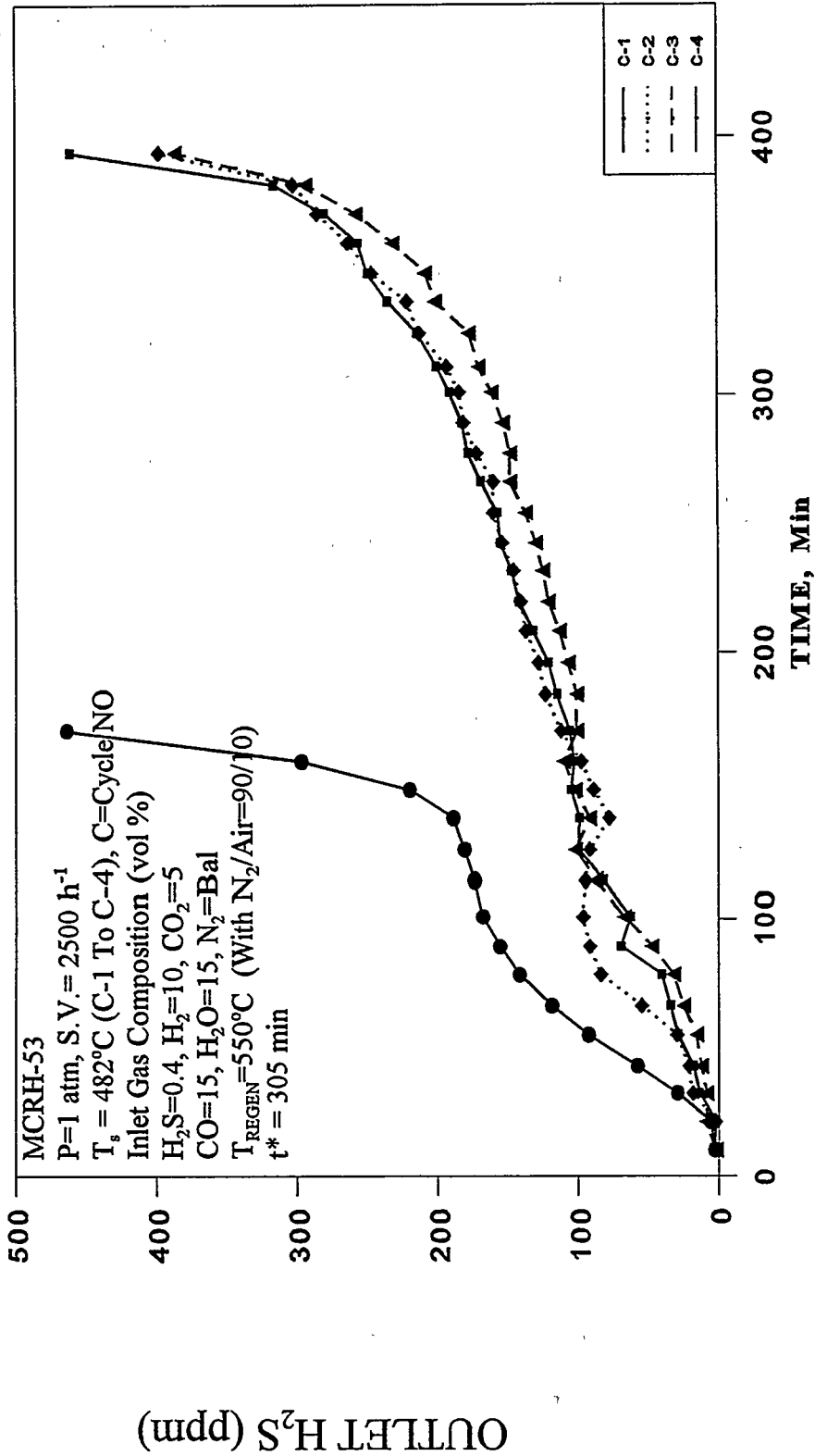conversion, i.e., sulfur removal, achieved by the sorbent was 100% and the pre-breakthrough H_2S

Figure 33.   H$_2$S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-53 Sorbent

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level was less than 100 ppmv. The high stable conversion indicates rapid kinetics and little or no loss of surface area in successive cycles. The sulfur capacities of the sorbent of this example was measured during cycle 4 and was found to be 10.43 g(S)/100 g of sorbent. The activity and capacity of the sorbent were stable for all 5 cycles of the test. The surface area of the fresh and sulfided samples were found to be 78.6 and 71.9 m^2/g. The 5 hour and 20 hour attrition loss of the fresh sorbent were found to be 0.28 and 0.56 wt.%, respectively, in a standard 3-hole tester as shown in Table 4.

MCRH-54: A zinc oxide-based fluidizable sorbent was prepared, using the proprietary technique. The sorbent was dried at 120°C and then calcined in an oxygen-containing atmosphere at 600°C for 2 hours.

A sulfidation test was carried out with a sulfidation gas containing 10% H_2, 15% CO, 5% CO_2, 0.4% H_2S, 15% H_2O, balance N_2 (volume %). Regeneration of this sorbent was conducted with 2 volume percent O_2 in N_2 at 550 °C. Sulfidation and regeneration were repeated to achieve a total of five cycles. As shown in Figure 34, at 482°C sulfidation temperature, the stable conversion achieved by this sorbent was found to be 100% and the pre-breakthrough H_2S level was less than 100 ppmv. The high stable conversion indicates rapid kinetics and little or no loss of surface area in successive cycles. The sulfur capacities of this sorbent was measured during cycle 4 and was found to be 11.98 g(S)/100 g of sorbent. The sorbent activity and capacity was stable for the 5 cycles of the test. The surface area of the fresh and sulfided samples were 82.1 and 71.5 m^2/g. The 5 hour and 20 hour attrition loss were 0.36 and 0.36 wt.%, respectively, in a standard 3-hole tester as shown in Table 4.
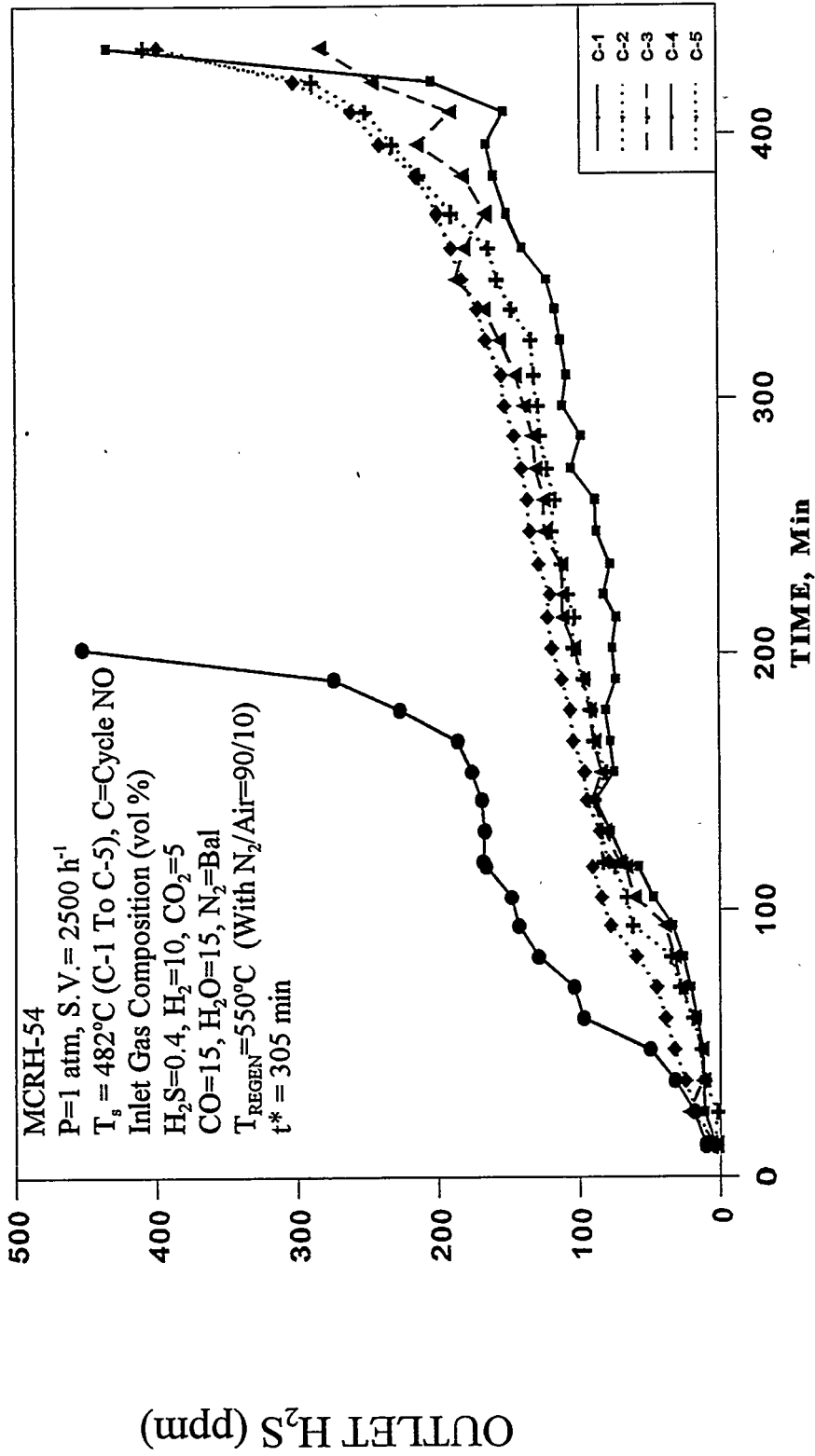
Figure 34. H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-54 Sorbent

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MCRH-55:   A fluidizable zinc oxide-based sorbent was prepared, using the proprietary

technique. The sorbent was dried at 120°C and then calcined in an oxygen-containing

atmosphere at 600°C for 2 hours.

A sulfidation test was carried out with a sulfidation gas containing 10% H_2, 15% CO, 5%

CO_2, 0.4% H_2S, 15% H_2O, balance N_2 (volume %). Regeneration of this sorbent was conducted

with 2 volume percent O_2 in N_2 at 550 °C. Sulfidation and regeneration were repeated to achieve

a total of five cycles.

As shown in Figure 35, it was found that at 482°C sulfidation temperature, the stable

conversion achieved by this sorbent was 100% and the pre-breakthrough H_2S level was less than

100 ppmv. The high stable conversion indicates rapid kinetics and little or no loss of surface area

in successive cycles. The sulfur capacities of this sorbent was measured during cycle 4 and was

11.98 gS/100 g of sorbent. The sorbent activity and capacity was stable for the 5 cycles of the

test. The surface area of the fresh and sulfided samples were 99.8 and 90.8 m^2/g. The 5 hour and

20 hour attrition loss were 0.56 and 1.41 wt.%, respectively, in a standard 3-hole tester as shown

in Table 4.

MCRH-56:   A fluidizable zinc oxide-based sorbent was prepared, using the proprietary

technique. The sorbent was dried at 120°C and then calcined in an oxygen-containing

atmosphere at 600°C for 2 hours.

A sulfidation test was carried out with a sulfidation gas containing 10% H_2, 15% CO, 5%

CO_2, 0.4% H_2S, 15% H_2O, balance N_2 (volume %). Regeneration of this sorbent was conducted

with 2 volume percent O_2 in N_2 at 550 °C. Sulfidation and regeneration were repeated to achieve

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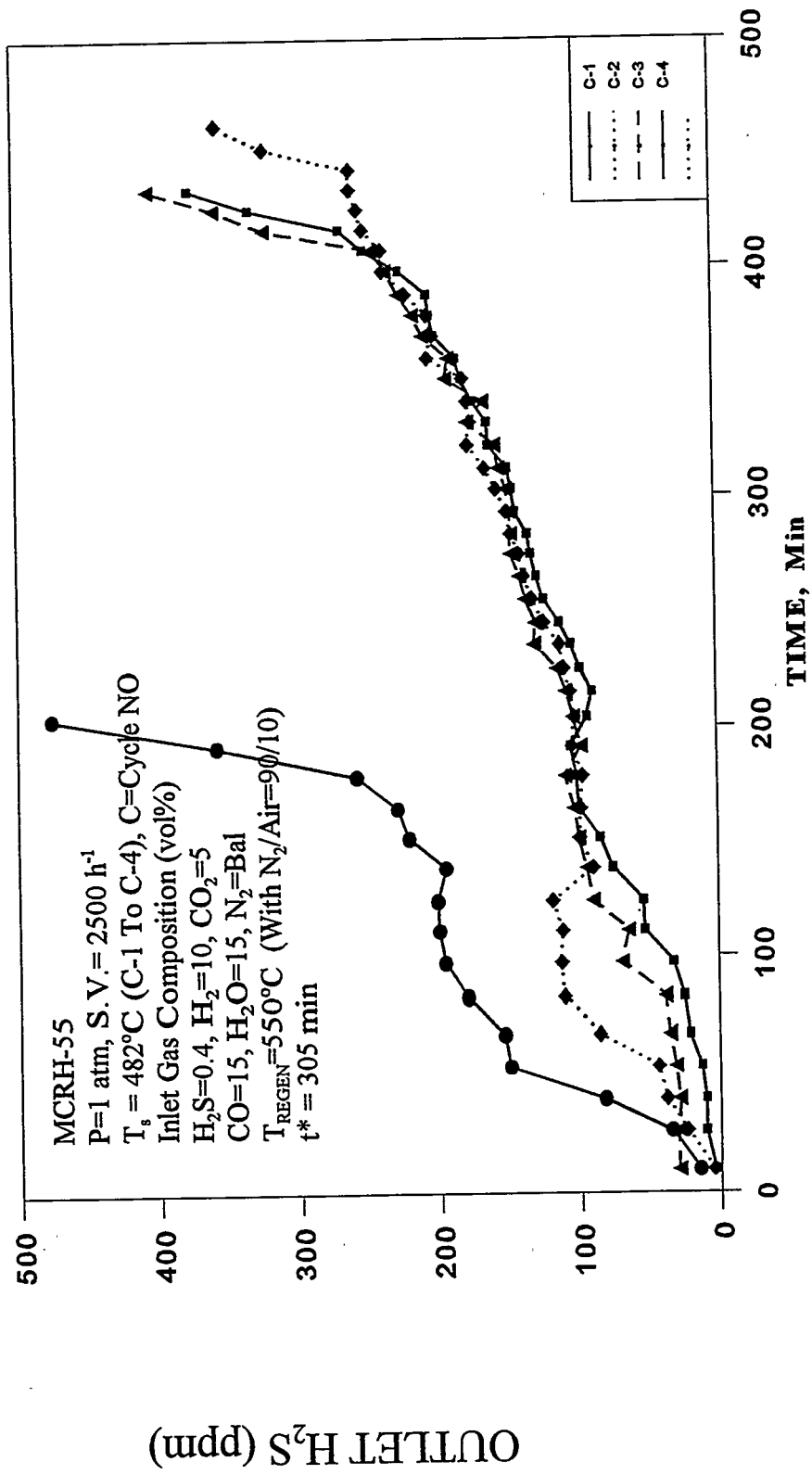
Figure 35. H_2S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-55 Sorbent

MCRH-55
P=1 atm, S.V.= 2500 h^{-1}
T_s = 482°C (C-1 To C-4), C=Cycle NO
Inlet Gas Composition (vol%)
H_2S=0.4, H_2=10, CO_2=5
CO=15, H_2O=15, N_2=Bal
T_{REGEN}=550°C (With N_2/Air=90/10)
t* = 305 min

a total of five cycles.

As shown in Figure 36, at 482°C sulfidation temperature, the stable conversion achieved by the sorbent was found to be 100% and the pre-breakthrough H_2S level was less than 100 ppm. The high stable conversion indicates rapid kinetics and little or no loss of surface area in successive cycles. The sulfur capacities of this sorbent was measured during cycle 4 and was found to be 10.52 g(S)/100 g of sorbent. The sorbent capacity and activity was stable for the 5 cycles of the test. The surface area of the fresh sample was 100.9 m^2/g. The 5 hour and 20 hour attrition loss of the fresh sorbent were 0.0 and 1.1 wt.%, respectively, in a standard 3-hole tester as shown in Table 4.

The extensive data base and analysis presented in sections 3.0 and 4.0 were used to guide the selection of the most promising H_2S sorbents for further studies under Task 3. The criteria used for selection of the sorbents were, namely high H_2S removal efficiency and sulfur loading as low as at 343°C with a simulated coal gas, good performance regenerability with a lower light-off temperature, high attrition resistant and stable reactivity in cyclic operation.

TASK 3. CYCLIC TESTING

The ability of a sorbent to maintain its reactivity through a number of sulfidation/ regeneration is of paramount importance. The objective of the cyclic test was to determine how well the sulfidation performance of the sorbent was retained in many cycles of sulfidation/ regeneration experiments.

MCRH-25 sorbent was tested for 100 cycles of sulfidation in a laboratory scale reactor. Regeneration between cycles was conducted with 10 vol% air-90 vol% with N_2 at 580°C. The gas
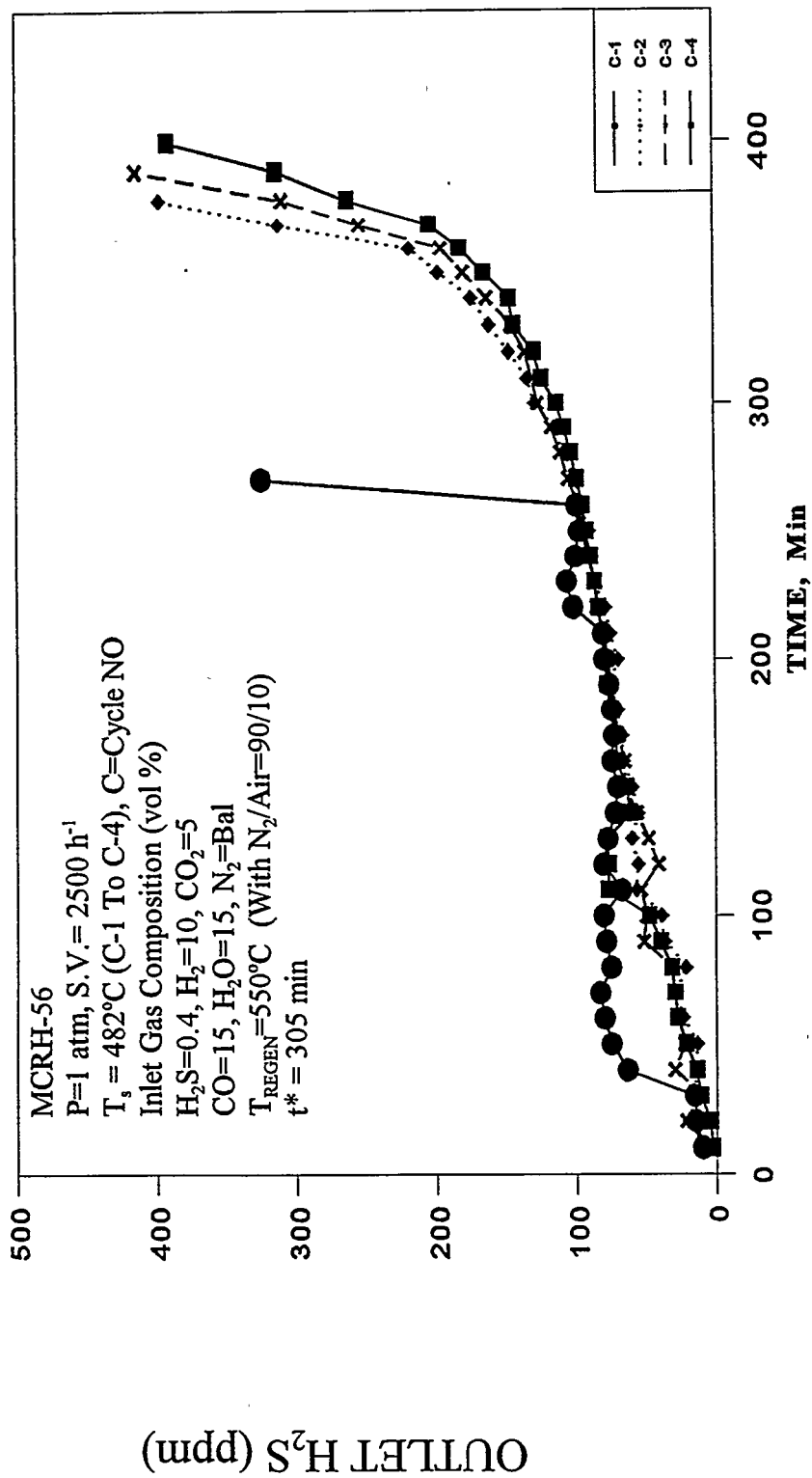
Figure 36. H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-56 Sorbent

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hourly space velocity was about 2500 h⁻¹ (STP) both in sulfidation and in regeneration. Sulfidation tests were carried out with a sulfidation gas containing 10 mol %H_2, 15 mol% CO, 5 mol% CO_2, 1 mol% H_2S, 15 mol% H_2O and balance N_2. As shown in Figure 37, at 427°C sulfidation, for cycles 1 to 20 the pre-breakthrough conversion was between 80-90% and for cycles 21-30 the conversion increased from 90 to 100% and remained constant at 100% conversion up to the 100 cycles. **There was no deactivation in 100 cycles in this fixed-bed study.** The sulfur capacities of the MCRH-25 sorbent during cycles 1, 25, 50, 75 and 100 were 22.5, 27.7, 27.7, 27.7 and 27.7 gS/100 g of sorbent, respectively, again indicating a 100 percent capacity utilization even after 100 cycles. Sulfur capacity was calculated using the concentration of hydrogen sulfide in the feed, breakthrough time and the amount of sorbent used. The chemical reactivity is measured by using TGA for fresh, and 100 cycle regenerated sorbent. As shown in Figure 38, the TGA results indicated that the rate of sulfur pickup for the fresh and the 100 cycle used sorbent remained relatively constant. The interesting thing is that the reactivity of the 100 cycle used sorbent is higher in TGA results. This clearly explains the increase in breakthrough in the 100 cycle fixed-bed study.

MCRH-60:   A fluidizable zinc oxide-based sorbent was prepared, using the proprietary technique. The sorbent was dried at 120°C and then calcined in an oxygen-containing atmosphere at 600°C for 2 hours.

Figure 39 shows the breakthrough profiles for MCRH-60. This sorbent was modified to regenerate at temperatures as low as 475 to 525°C. It was tested for 30 cycles of sulfidation in the laboratory-scale reactor. Regeneration between cycles was conducted with 2 volume percent
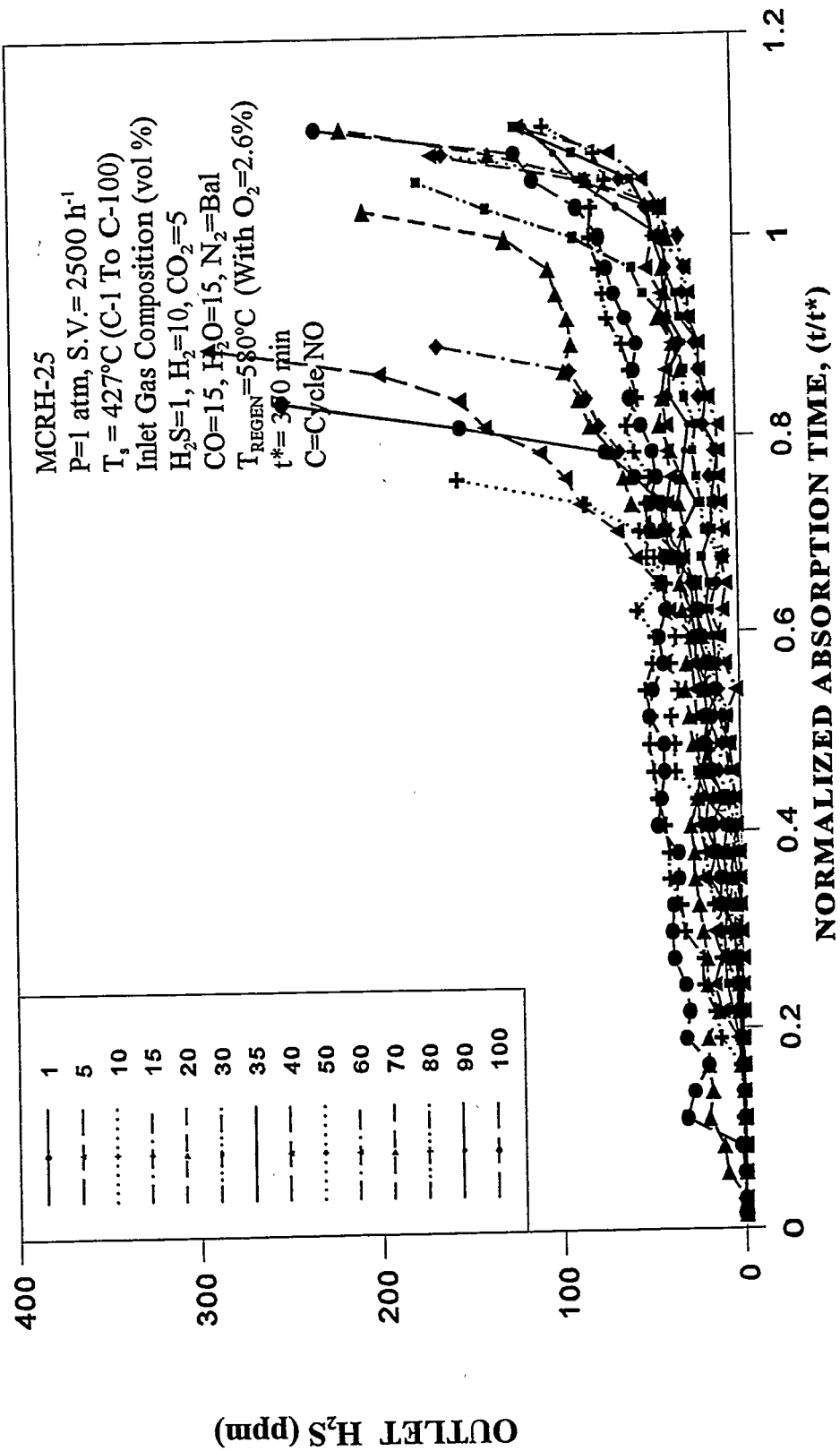
Figure 37.   H$_2$S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-25 Sorbent

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MCRH—25 FRESH AND REGENERATED SAMPLE
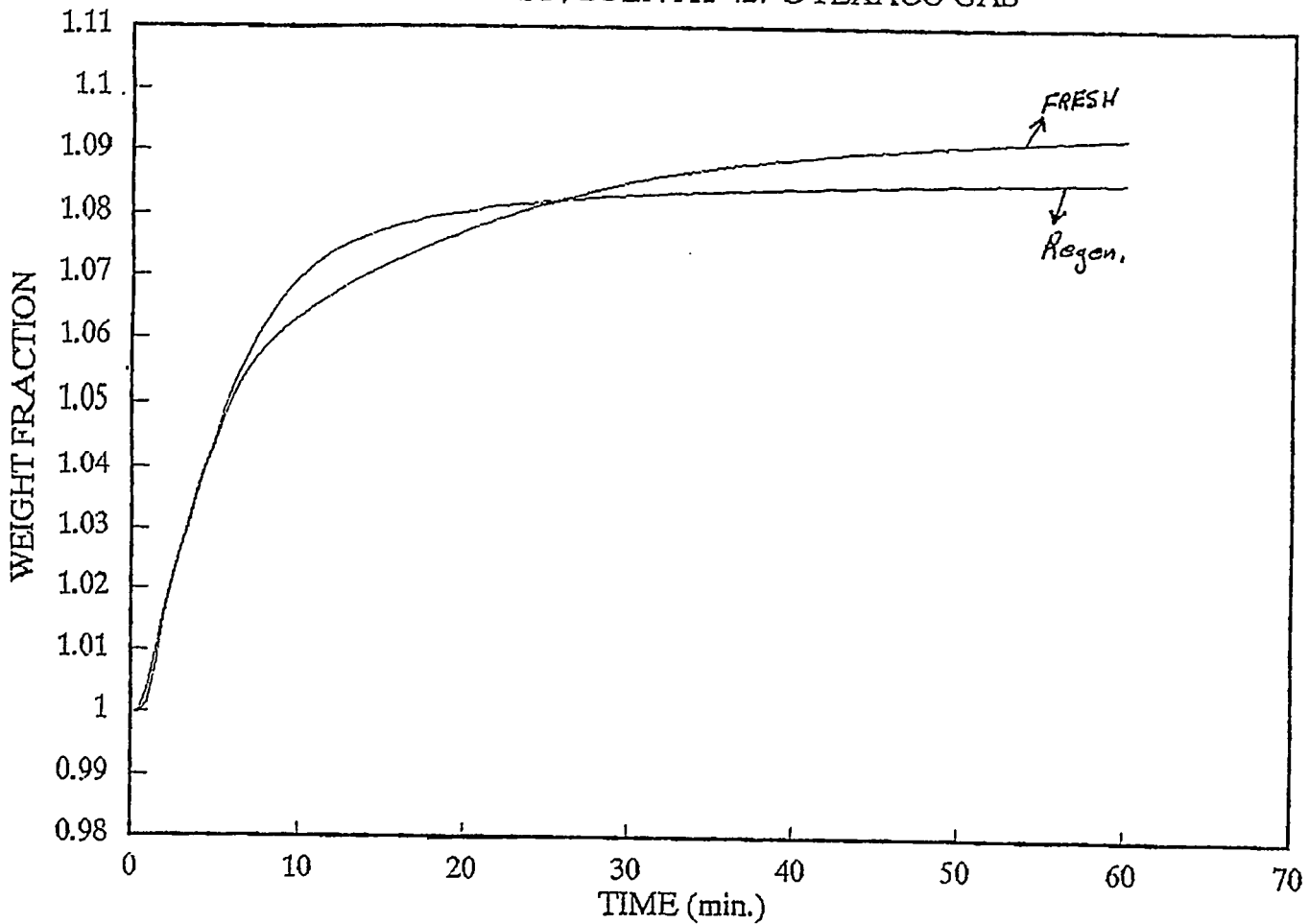TGA TEST / SULF. AT 427°C TEXACO GAS

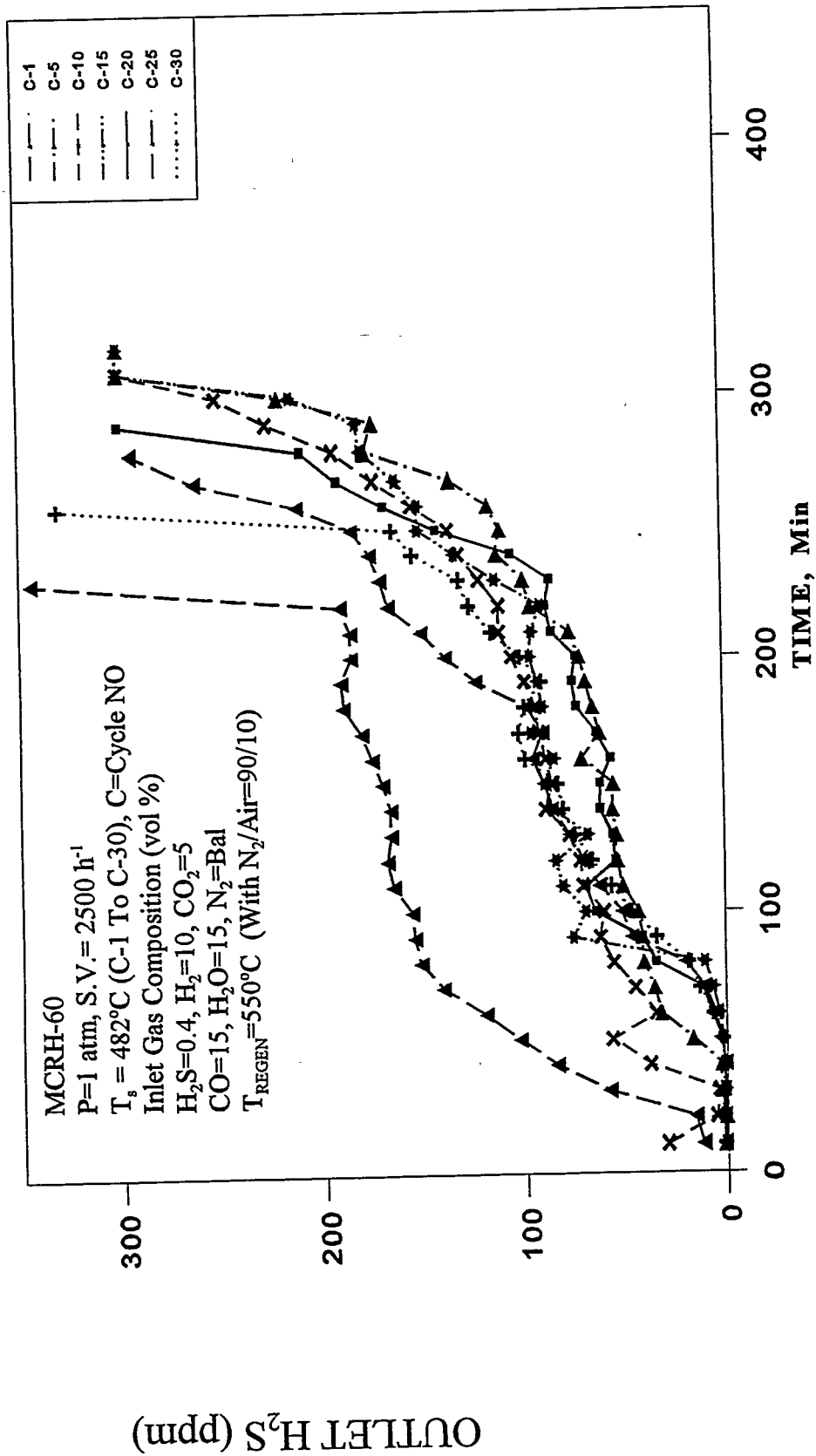Figure 38.   TGA Reactivities of MCRH-25 Sorbents

Figure 39. H₂S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-60 Sorbent

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O_2 in N_2 at 550°C. The gas hourly space velocity for the 30-cycle test was about 2500 h^{-1} both in sulfidation and in regeneration. Sulfidation tests were carried out with a sulfidation gas containing (vol%): H_2=10%, CO=15%, CO_2=5%, H_2S=0.4%, H_2O=15% and bal N_2. MCRH-60 sorbent showed excellent sulfidation behavior. The pre-breakthrough H_2S level was less than 100 ppm and the breakthrough conversion was 100%. **There was no deactivation in 30 cycles in this fixed bed study.**

MCRH-61:   A fluidizable zinc oxide-based sorbent was prepared, using the proprietary technique. The sorbent was dried at 120°C and then calcined in an oxygen-containing atmosphere at 600°C for 2 hours.

Figure 40 shows the breakthrough profiles for MCRH-61. This sorbent was modified to regenerate at temperatures as low as 475 to 525°C. It was tested for 50 cycles of sulfidation in the laboratory-scale reactor at 482°C. Regeneration between cycles was conducted with 2 volume percent O_2 in N_2 at 550°C. The gas hourly space velocity for the 50-cycle test was about 2500 h^{-1} both in sulfidation and in regeneration. Sulfidation tests were carried out with a sulfidation gas containing (vol%): H_2=10%, CO=15%, CO_2=5%, H_2S=0.4%, H_2O=15% and bal N_2. MCRH-61 sorbent showed excellent sulfidation behavior. The pre-breakthrough H_2S level was less than 100 ppm and the breakthrough conversion was 100%. **There was no deactivation in 50 cycles in this fixed bed study.**
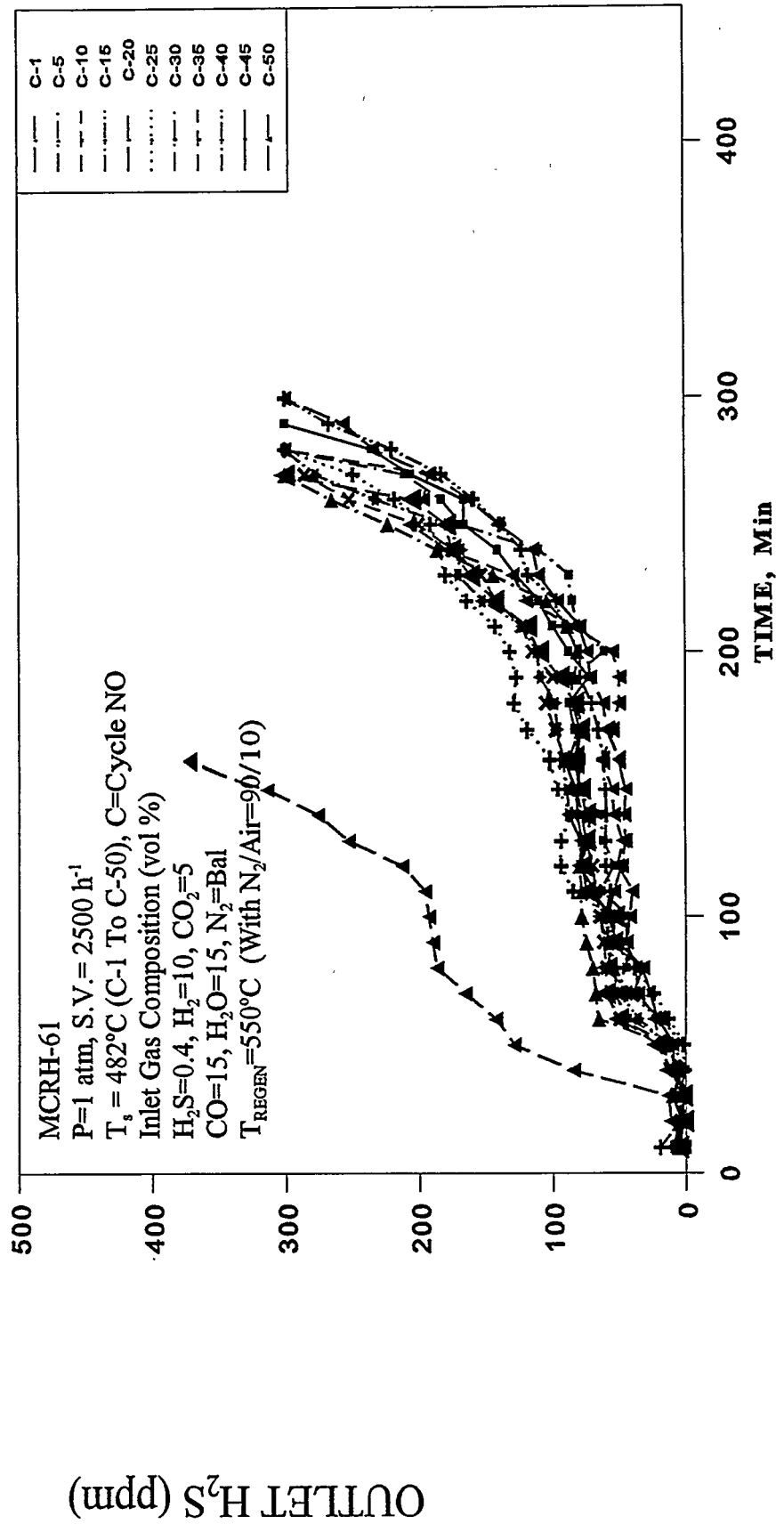
Figure 40. H_2S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-61 Sorbent

5.0 CONCLUSIONS

Preparation of mixed metal oxide sorbents with high surface area is crucial for good sorbent performance. The sorbent preparation techniques employed in this project have successfully demonstrated the feasibility of preparing stable sorbents that achieve greater than 99% H_2S removal at temperatures as low as 343°C and retain their activity over 50 to 100 cycles.

Doped and undoped zinc-based sorbents were compared in this work in terms of their regeneration light-off temperature. Over all, in this work we have shown that (i) a fixed bed reactor is an excellent tool to quickly evaluate reactivity (ii) effect of selected catalyst additives during regeneration is dramatic (iii) promising catalyst additives can be incorporated in the sorbent to reduce regeneration light-off temperature to 500°C or less from the current >650° C (iv) the sulfided sorbent can be lighted-off at a temperature as low as 475° C.

Fundamental understanding of phenomena leading to chemical deactivation and high regeneration light-off temperature has enabled us to successfully prepare a MCRH-25 sorbent. A 100-cycle test clearly demonstrated that the MCRH-25 sorbent does not chemically deactivate. In fact, the capacity at breakthrough increased between cycles 1 to 25 from 22.5 to 27.7 gS/100 g sorbent and remained stable thereafter. TGA and physical property data confirmed the breakthrough data. This is in contrast to existing leading sorbents that deactivated significantly, as much as 50 % in 50 to 100 cycles. Furthermore, the MCRH-25 sorbent regenerated at temperatures as low as 475°C, in contrast to current zinc-based sorbents that require 650°C or higher.

The problem of physical attrition is being addressed by incorporating binders into the MCRH-25 recipe. This effort to date has led to the preparation of MCRH-61 (70 μm aps)

sorbent with high attrition resistance suitable for a transport reactor. This sorbent removed H_2S to below 20 ppmv and lighted-off nicely at 480°C during regeneration. There was no deactivation in 50 cycles in this fixed bed study. This sorbent needs to be scaled up and tested in a bench-scale fluidized-bed reactor. The scale-up of this sorbent and further required modifications to improve its performance is being addressed in another grant (DE-FG22-95MT95011) to Hampton University by DOE.

6.0 RECOMMENDATIONS

Future work should address the following issues:

- Because the complex nature of coal gas cannot be duplicated completely in the laboratory, additional parametric and long term tests on the MCRH-61 sorbent and improved sorbents based there on should be performed at high pressure typical of IGCC and temperatures as low as 343°C.

- Further studies should be aimed toward determining the effect of trace contaminants such as chloride, alkali, and particulates on the sorbent kinetics and performance

- Testing of MCRH-61 or improved sorbents based there on should be carried out in bench-scale fluidized-bed reactors and M.W. Kellogg's transport reactor test unit. Arrangements for this testing is being made in a companion grant (Grant No.DE-FG22-95MT95011) to Hampton University by DOE.

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