

## **Scale-Up of Advanced Hot-Gas Desulfurization Sorbents**

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## **ABSTRACT**

The overall objective of this project is to develop regenerable sorbents for hot gas desulfurization in IGCC systems. The specific objective of the project is to develop durable advanced sorbents that demonstrate a strong resistance to attrition and chemical deactivation, and high activity at temperatures as low as 343°C(650°F). A number of formulations will be prepared and screened in a ½-inch fixed bed reactor at high pressure (1 to 20 atm) and high temperatures using simulated coal-derived fuel-gases. Screening criteria will include, chemical reactivity, stability, and regenerability over the temperature range of 343°C to 650°C. After initial screening, at least 3 promising formulations will be tested for 25-30 cycles of absorption and regeneration. One of the superior formulations with the best cyclic performance will be selected for investigating scale up parameters. The scaled-up formulation will be tested for long term durability and chemical reactivity.

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## **EXECUTIVE SUMMARY**

Additional sorbents were prepared and then tested for its hydrogen sulfide removal efficiency. Based on the results of the extensive testing conducted on this project so far, the zinc oxide-based sorbent is the best sorbent for hot gas application in the temperature range of 343°C to 538°C.

## **INTRODUCTION**

Advanced high-efficiency integrated gasification combined cycle (IGCC) power systems are being developed to produce power from coal under the U.S. Department of Energy's (DOE's) multibillion dollar Clean Coal Technology (CCT) Program. In these advanced systems, coal is gasified to produce a gas at high temperature and high pressure (HTHP) conditions. The hot gas is cleaned of contaminants, primarily particulates and sulfur gases such as hydrogen sulfide (H<sub>2</sub>S) and burned in a combustion turbine. IGCC systems are capable of higher thermal efficiency and lower gaseous, liquid, and solid discharges than conventional pulverized-coal-fired power plants. Hot gas cleanup offers the potentially key advantages of higher plant thermal efficiencies and lower costs due to the elimination of fuel gas cooling and associated heat exchangers

Sorbents based on zinc oxide are currently the leading candidates and are being developed for moving-, and fluidized-bed reactor applications. Zinc oxide based sorbents can effectively reduce the H<sub>2</sub>S in coal gas to 10 ppm levels and can be regenerated for multicycle operation. However, all of the current first-generation leading sorbents undergo significant loss of reactivity with cycling, as much as 50% or greater loss in only 25-30 cycles. Stability of the hot-gas desulfurization step over 100s of cycles is essential for improved IGCC economics over conventional power plants. Thus a pressing need exists for developing durable second generation sorbents with much improved and stable reactivity during cyclic operation.

The overall objective of this project is to develop regenerable sorbents for hot gas desulfurization in IGCC systems. The specific objective of the project is to develop durable advanced sorbents that demonstrate a strong resistance to attrition and chemical deactivation, and high activity at temperatures as low as 343°C(650°F).

## **RESULTS AND DISCUSSIONS**

The project consists of three major experimental tasks (Tasks 1-3) addressing the contract objectives described above.

Task 1: Optimization of Preparation

Task 2: Investigation of Scale-Up

Task 3: Preparation of 100 lb Batch

### **Task 1: Optimization of Preparation**

A highly promising method was recently developed to prepare suitable sorbents. Various sorbents were prepared by our proprietary method. The main parameters we have varied was various concentrations of starting materials and ageing conditions. The starting compounds was chosen based on water solubility, commercial availability and low costs and that avoid introducing elements that may be deleterious in the final sorbent or that cause difficulties in subsequent processing. These prepared sorbents were tested in the fixed bed reactor.

The following analytical techniques was used to characterize the fresh, sulfided and regenerated sorbents

1. X-ray Diffraction (XRD) for crystalline phase.
2. Surface area measurement will be based on the standard BET method.
3. Hg-porosimetry for pore volume, bulk density, average pore diameter and pore size distribution determination.
4. Atomic Absorption (AA) Spectrometry for elemental composition analysis.

### **Task 2. Investigation of Scale-Up**

A series of MCRH sorbents have been prepared in attrition resistant form (Table 1) with up to 75 % binder to provide a hard material. This results in a loss of capacity but for Sierra, a capacity of only 5 g/100 g is sufficient. The reactivity and regenerability are the more important parameters. Table 1 shows that the attrition resistance of the MCRH sorbents prepared with our proprietary binder is extremely high compared to first generation sorbents and it satisfies the target of Table 2, set by Kellogg.

**Table 1. Attrition Test of MCRH Sorbents**

| <b>Sorbent</b> | <b><u>3-hole attrition loss (wt %)</u></b> |                |
|----------------|--|----------------|
|                | <i>5 hour</i>                              | <i>20 hour</i> |
| MCRH-51        | 0.00                                       | 0.62           |
| MCRH-52        | 0.25                                       | 0.25           |
| 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-SorbIII      | 16.00                                      | 32.40          |

The sorbent selection criteria for the Sierra plant provided by Kellogg are shown in Table 2.

**Table 2: Sorbent Selection Criteria for Sierra-Pacific**

| <b><u>Sulfidation</u></b>         | <b><u>Properties</u></b>                        |
|-----------------------------------|---|
| 1 to 2 s contact time             | 80 $\mu\text{m}$ aps                            |
| <10 ppmv H <sub>2</sub> S leakage | >50 lb/ft <sup>3</sup> bulk density             |
| 482 to 538°C operation            |   |
| <b><u>Regeneration</u></b>        | <b><u>Attrition</u></b>                         |
| <538°C light-off                  | <2.5 x 10 <sup>-5</sup> lb/lb circulated (TRTU) |
| no O <sub>2</sub> breakthrough    | 3-hole air-jet attrition <5 %                   |
| neat air oxidation                | in 5 hours                                      |

An attrition resistant MCRH-61 (with attrition resistance equivalent to MCRH-56) was tested in the 2.0 inch HTHP fluidized-bed reactor simulating the Sierra-Pacific conditions for 10 cycles at sulfidation conditions of simulated Kellogg gasifier gas with 0.4 % H<sub>2</sub>S at 18.8 atm pressure, 480-510°C, and 15 slpm through a 145 g sorbent bed. The regeneration was conducted with pure air with an initial temperature of 480-510°C. The H<sub>2</sub>S breakthrough results shown in Figure 1 indicate essentially complete removal of H<sub>2</sub>S until a sharp breakthrough in all 10 cycles. The sorbent lost some capacity after the first cycle presumably due to pure air regeneration that increased the bed temperature to around 700°C. After the first cycle, the capacity stabilized even with temperature excursions to 675-700°C and no attrition of the sorbent occurred in the 10 cycle test. Due to pure air regeneration, some sulfate formation did occur as seen from the SO<sub>2</sub>





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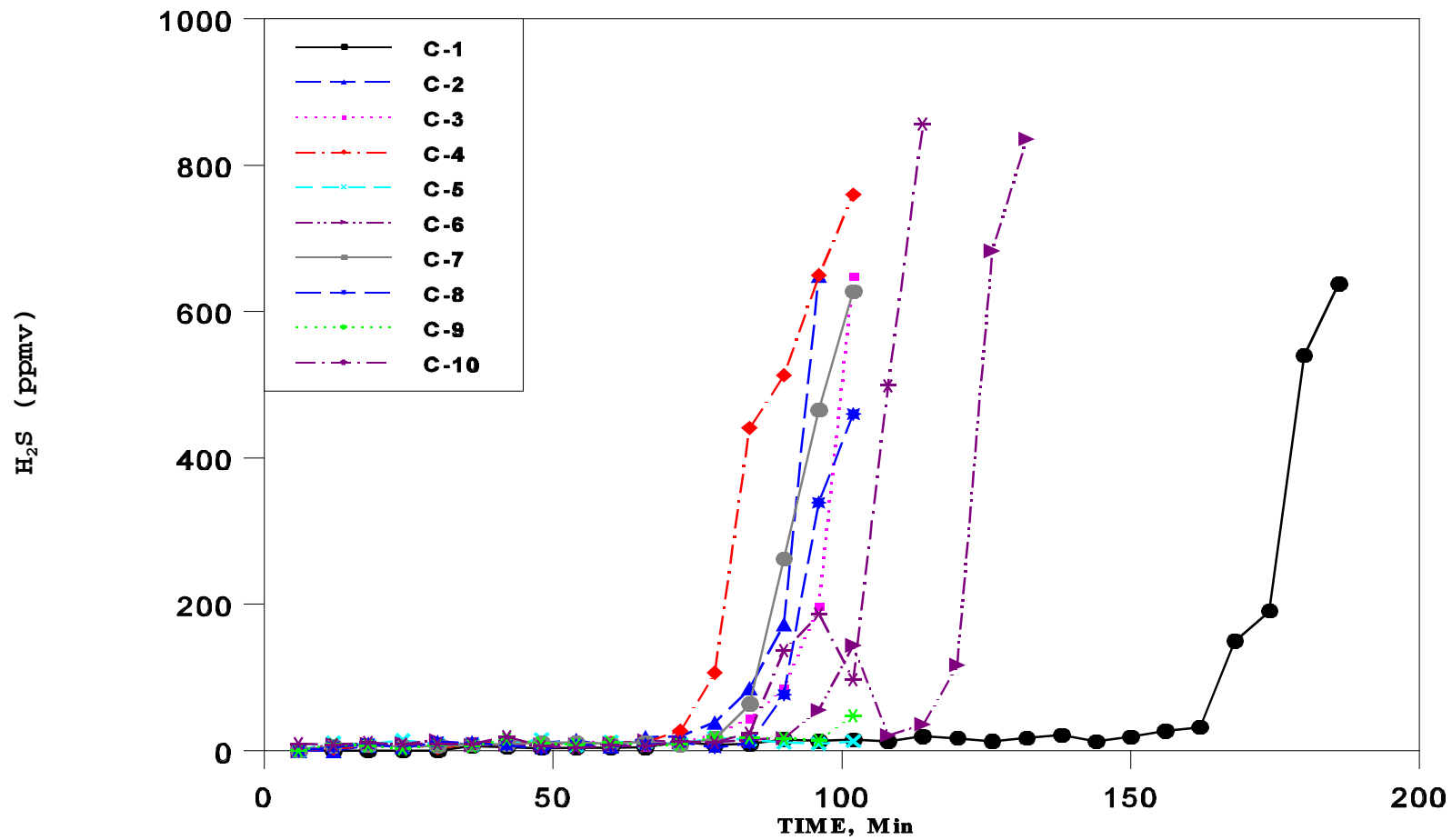


Figure 1. Breakthrough Behavior of MCRH-61

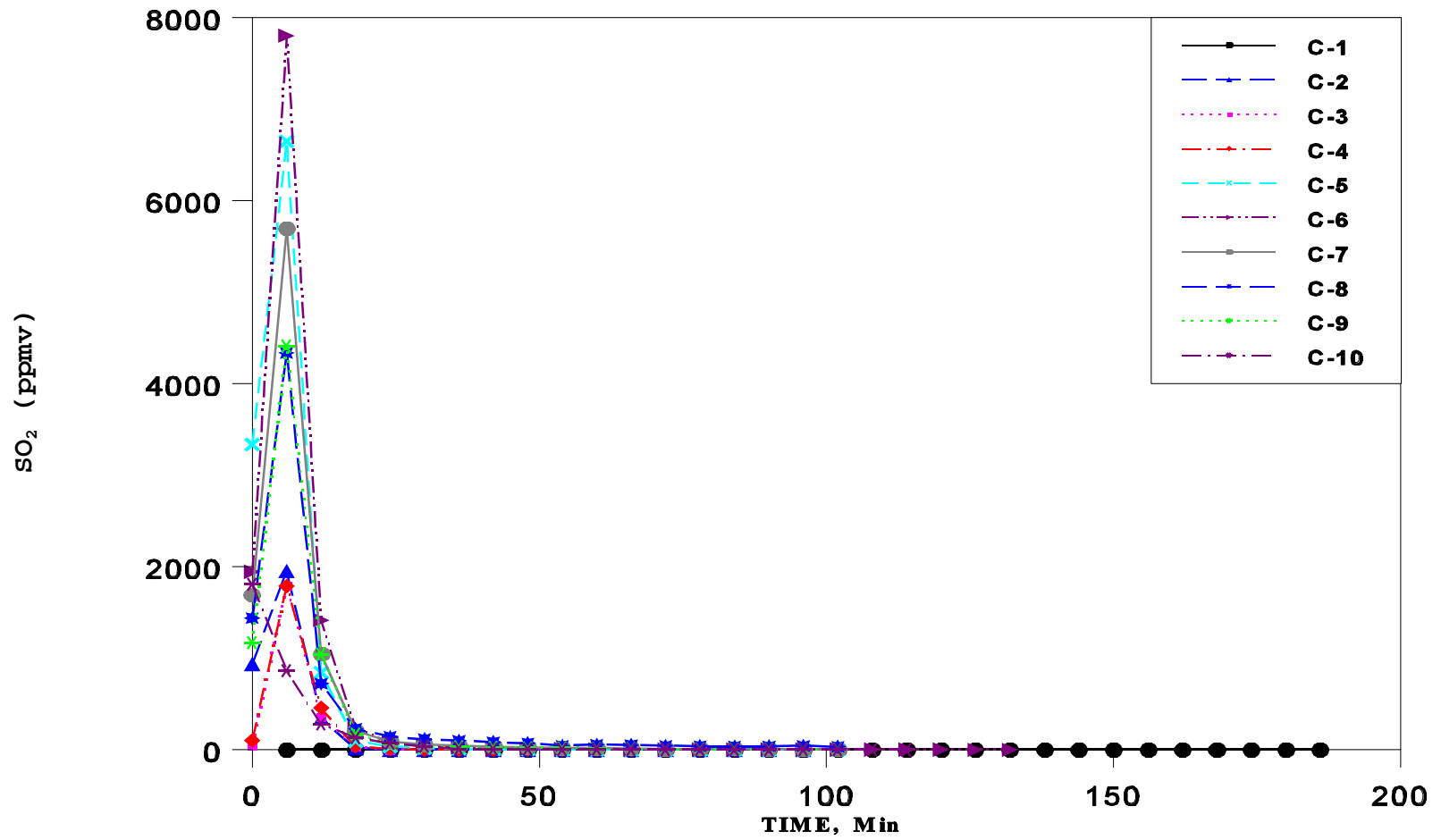


Figure 2. SO<sub>2</sub> Evolution During Sulfidation Due to sulfation

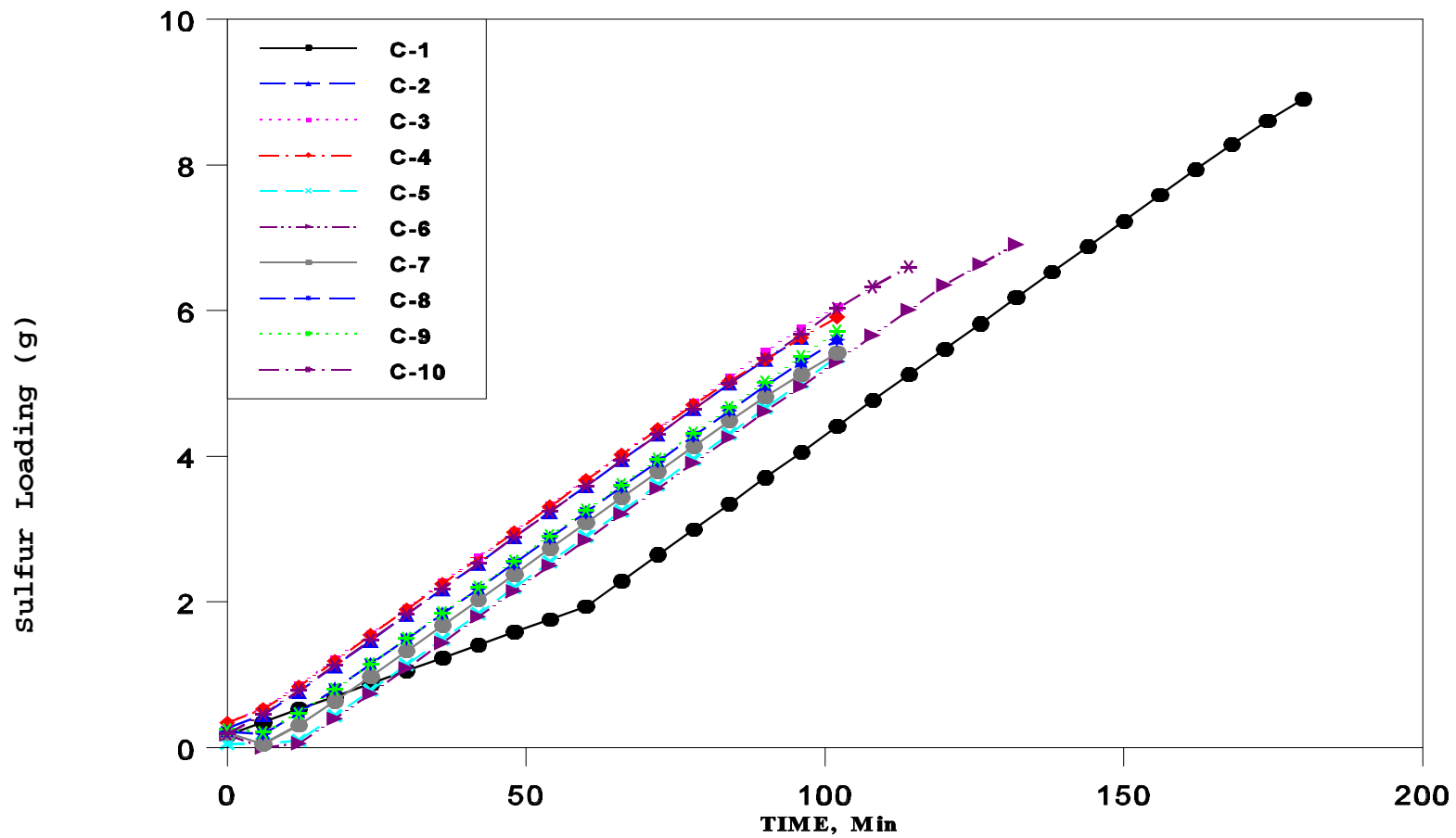


Figure 3. Cumulative Sulfur Loading for MCRH-61

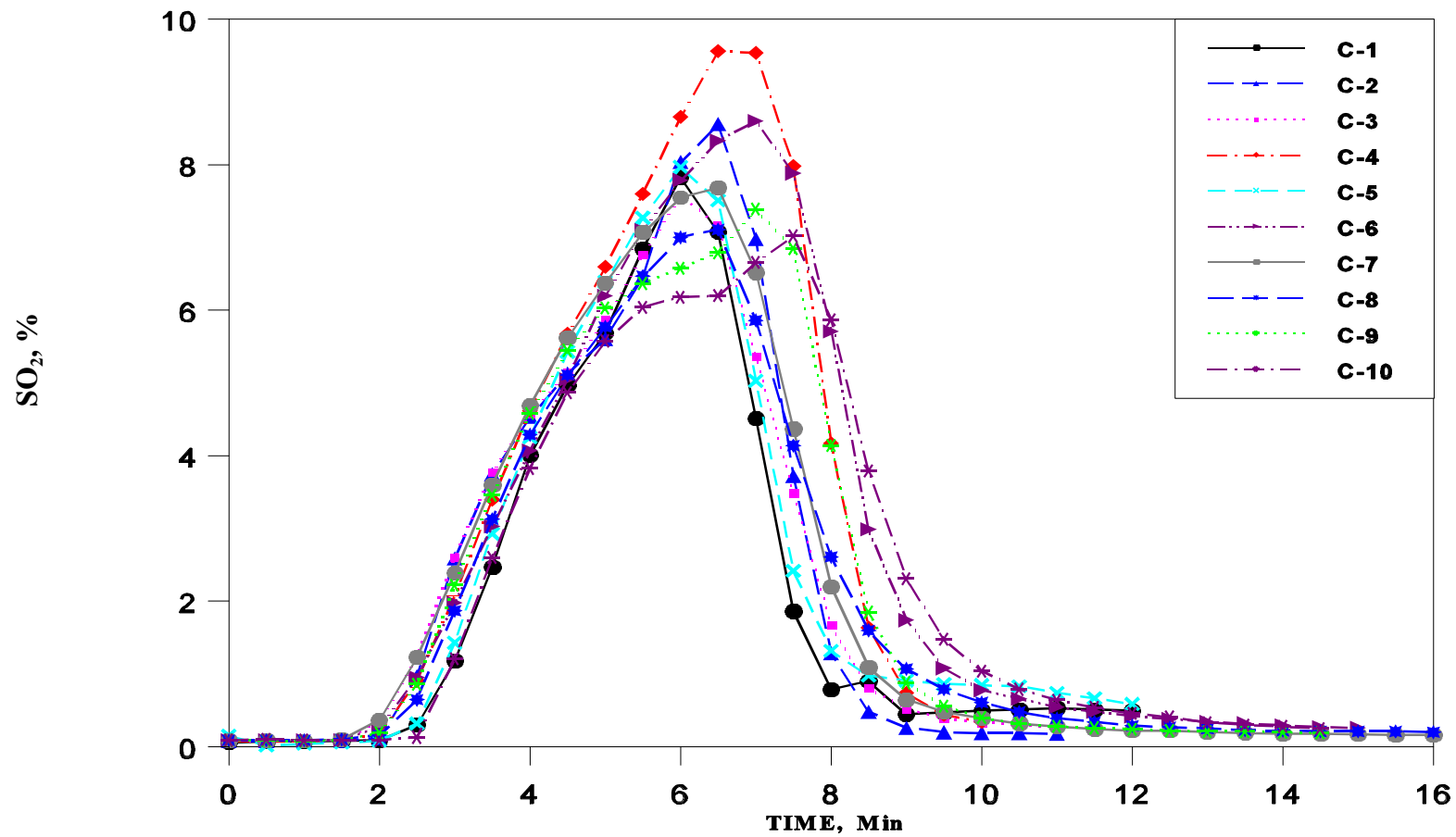


Figure 4. Regeneration of MCRH-61