Investigation on Durability and Reactivity of Promising Metal Oxide Sorbents During Sulfidation and Regeneration

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CONTENTS

	Page
DISCLAIMER	iii
LIST OF TABLES	v
LIST OF FIGURES	v
MILESTONES	1
EXECUTIVE SUMMARY	1
INTRODUCTION	1
EXPERIMENTAL SETUP	2
STATUS OF THIS RESEARCH PROJECT	4
PRESENTATION	7
PLANS ON FUTURE EXPERIMENTS	7

LIST OF TABLES

Table		Page
1	The following major equipment have been placed on order	5
2	The following parts and supplies have been placed on order.	6

LIST OF FIGURES

Figure		Page
1	A differential reactor.	2
2	A differential reactor assembly	3

SCHEDULE AND MILESTONES

	FY 1994-1995												FY 1995-1996											
	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
Procurements of Materials and Equipment																								
Fabrication of a Micro Batch Reactor																								
Development of Analytical Procedures for Concentrations of Sulfur compounds																								
Development of Experimental Procedures for Sulfidation Reaction of Fresh Metal Oxide Sorbents																								
Formulation of Durable Metal Oxide Sorbents with High-Sulfur Removal Capacity																								
Reaction Kinetics on Sulfidation of Metal Oxide Sorbents																								
Reaction Kinetics on Regeneration of Sulfur-loaded Metal Oxide Sorbents																								
Development of an Intraparticle Diffusivity Model for Sulfidation of Metal Oxide Sorbents																								
Delineation of Effects of Hydrogen Partial Pressures and Moisture Amounts on Sulfidation of Metal Oxide Sorbents																								
Equilibrium Absorption of Hydrogen Sulfide into Metal Oxide Sorbents																								
Development of a Micro Differential Reactor																								

EXECUTIVE SUMMARY

The main objectives of this research project during this quarter are to design a micro differential reactor, design a differential reactor assembly, and select and order necessary parts as well as accessories for the reactor and its assembly.

INTRODUCTION

Reactivity of formulated metal oxide sorbents was tested in the past, using a micro batch reactor. The temperature of the reactor is maintained at a desired constant temperature by submerging the reactor into a heated fluidized sand bath. For a short reaction duration, it is difficult to control a reaction temperature at a desired one. Since the temperature of the micro batch reactor is increased from room temperature to a desired reaction temperature for a short reaction duration, experimental reproducibility is poor.

Reaction of formulated metal oxide sorbents with hot wet hydrogen sulfide is rapid, and most of 100- 200 mesh formulated metal oxide sorbent particles are reacted with hot wet hydrogen sulfide for a short reaction duration. Reactivity of formulated metal oxide sorbents in the micro batch reactor was tested for the reaction duration range of 30 - 120 seconds to find initial reaction rates of formulated sorbents with wet hydrogen

sulfide. Reactivity of formulated metal oxide sorbents in the micro batch reactor can not be tested below 30 second reaction duration due to the difficulty in controlling a reaction temperature at a desired one. A newly-fabricated differential reactor will generate reaction data, which can not be obtained with a batch reactor.

EXPERIMENTAL SETUP

A differential reactor mainly consists of a 1" Swagelok cap and a 1" Swagelok plug. A 1" Hastelloy C frit welded to the 1" Swagelok plug, which becomes as a bottom part of the reactor, whereas a 3/4" Hastelloy C frit welded to the 1" Swagelok cap, which becomes as a top part of the reactor (see Figure 1).

Figure 1. A Differential Reactor

A differential reactor assembly mainly consists of four mass flow meters for gases, one differential reactor, one preheater, one high pressure liquid pump for water, one four-way switch valve, one muffle furnace, three filters for gases, four check valves, and one water collection bottle (see Figure 2).

Figure 2. A Differential Reactor Assembly

A length of a preheater for a feed stream to the reactor is calculated from the following equations.

$$\frac{hd}{k} = 3.66 + \frac{0.0668 \frac{d}{L} \text{RePr}}{1 + 0.04 \left[\left(\frac{d}{L} \right) \text{RePr} \right]^{\frac{2}{3}}} \quad (1)$$

$$\text{Re} = \frac{4m}{\pi d \mu} \quad (2)$$

$$\text{Pr} = \frac{C_p}{\mu} \quad (3)$$

where h : heat transfer coefficient
 k : thermal conductivity of a gas mixture
 d : diameter of a preheater
 L : length of a preheater
 Re : Reynolds number of the flow of a gas mixture in a preheater.
 Pr : Prandtl number
 m : mass flow rate of a gas mixture
 μ : viscosity of a gas mixture
 C_p : heat capacity of a gas mixture

Initial reactivity of formulated metal oxide sorbents with hot wet hydrogen sulfide in the batch reactor was tested by analyzing concentrations of hydrogen sulfide with a gas chromatograph, whereas initial reactivity of formulated metal oxide sorbents with hot wet hydrogen sulfide in a differential reactor was tested by measuring weights of sulfided metal oxide sorbents

A differential reactor was designed to test accurately initial reactivity of formulated metal oxide sorbents. Initial reactivity of formulated metal oxide sorbents with hot wet hydrogen sulfide in the differential reactor can be tested for any desired reaction duration. Reactive interaction of the reactor wall itself with hot wet hydrogen sulfide does not affect significantly experimental data generated from the differential reactor in comparison with those generated from the batch reactor.

The reactor containing a sorbernt for a test is preheated at a desired temperature with hot wet nitrogen from a preheater placed in a muffle furnace. A reaction mixture containing hydrogen sulfide, hydrogen, moisture and nitrogen also is preheated at a desired temperature by flowing the mixture in the preheater placed in the isothermal muffle furnace. The reaction starts by switching the wet nitrogen feed stream with the wet reaction mixture feed stream to the reactor. A reaction duration is controlled by switching the reaction mixture feed stream with the nitrogen feed stream at a desired reaction duration.

A moisture content in a reaction mixture is controlled by using a high pressure water pump. Concentrations of hydrogen sulfide, hydrogen and nitrogen in a simulated hot wet coal gas mixture are controlled with its individual mass flow meter. The temperature of the micro batch reactor is maintained up to 550°C, whereas the temperature of the differential reactor is maintained up to 1000°C to test initial reactivity of formulated metal oxide sorbents.

STATUS OF THIS RESEARCH PROJECT

Research activities and efforts of this research project were concentrated on designing a micro differential reactor as well as a differential reactor assembly, and selecting and ordering necessary parts as well as accessories for the reactor and its assembly (see Tables 1 and 2) for this research project during the period of October-December 1996.

Experiments on initial reactivity of sorbents were not performed due to failures of heating elements as well as the old existing temperature controller for the fluidized sandbath. The replacement parts are not available for the temperature controller. A new temperature controller for the fluidized sandbath has been ordered (see Table 1).

Table 1. The following major equipment have been placed on order.

Item No.	Equipment/Description	Supplier
1	OMNIFIT Glass Solvent Bottle, 100 ml plastic coated clear, 3 valves, 15 psi, 1/8" OD tubing	BODMAN Industries
2	Temperature Controller for a fluidized sand bath Celsius Readings, 1/2" high LCD panel, Max Temp: 600°C, K thermocouple probe (6"Lx0.2" D with 48" lead, 9-3/8"W x 6"H x 8-3/8" D, 14 lbm20 A circuit breaker, 6-ft three-wire cord and plug, Model Number: 3012000, TC-8D	Techne Incorporated
3	FLOW CONTROL SYSTEM, 500 ml/min (scc/min), Wetted Materials: anozed aluminum, 316 stainless steel, silicone elastomer, and NORYL, DC power adapter, Max pressure: 100 psi, Max temperature: 50°C Built-in miniature proportional valve and controller	Cole-Parmer Instrument Company
4	FLOW CONTROL SYSTEM, 500 ml/min (scc/min), Wetted Materials: anozed aluminum, 302 stainless steel, silicone elastomer, and NORYL, DC power adapter, Max pressure: 100 psi, Max temperature: 50°C, Built-in miniature proportional valve and controller	Cole-Parmer Instrument Company
5	FLOW CONTROL SYSTEM, 100 ml/min (scc/min), Wetted Materials: anozed aluminum, 302 stainless steel, silicone elastomer, and NORYL, DC power adapter, Max pressure: 100 psi, Max temperature: 50°C Built-in miniature proportional valve and controller	Cole-Parmer Instrument Company
6	FLOW CONTROL SYSTEM, 200 ml/min (scc/min), Wetted Materials: anozed aluminum, 302 stainless steel, silicone elastomer, and NORYL, DC power adapter Max pressure: 100 psi, Max temperature: 50°C Built-in miniature proportional valve and controller	Cole-Parmer Instrument Company
7	Kahl Pellet Hardness Tester, Pellet Diameter: 2- 22 mm, Hardness Range: 0.25 kg - 1 kg, chromed steel, 2 pounds	LCI Corporation

Table 2. The following parts and supplies have been placed on order.

Item No.	Parts & Supplies/Description	Supplier
1	1" hastelloy C Frit, 2 μ m	Valco Instrument Co. Inc.
2	1/16" OD 0.03" ID hastelloy C Tubing , 8 ft	Valco Instrument Co. Inc.
3	Unidirectional Nupro check valve, 316 SS, cracking pressure of 20 psig, 6000 psig, 400°F, neoprene seal, 1/4" Swagelok connection	Birmingham Valves & Fitting Co
4	1/16" Valco nut, 300 series SS, 0.75" long,	Alltech Associates, Inc
5	1/16" 4-port Switch Valve, 316 SS, 400 psig, 175°C, Carbon-filled Teflon seal	Alltech Associates, Inc
6	1"-diameter 0.063"-thick 2- μ m-pore 316-SS Frit	Alltech Associates, Inc
7	1/16" PEEK Tee, 0.8 mm bore, 1/4-28 UNF thread, 100°C, 500 psig	Alltech Associates, Inc
8	1/16" PEEK cross, 0.8 mm bore, 1/4-28 UNF thread, 500 psig, 100°C	Alltech Associates, Inc
9	1/16" Valco Ferrules, 316 SS, 10/pk	Alltech Associates, Inc
10	Fingertight nuts for 1/16" OD tubing, polypropylene, natural color, 1/4-28 UNF thread 500 psig, 100°C, 10/pk	Alltech Associates, Inc
11	Tetzel 1/16" bore frange-free ferrules 10/pk, 1/4-28 UNF thread	Alltech Associates, Inc
12	1/16" OD 0.05" ID 316 SS Tubing	Alltech Associates, Inc
13	PTFE Cones for 1/8" OD Tubing, Omnifit, 4/pk	Alltech Associates, Inc
14	Female 1/4-28 UNF to Female 10-32 UNF, PEEK internal union, 2/pk,	Alltech Associates, Inc
15	Finger-tight nuts for 1/8" OD tubing, 1/4-28 UNF thread, natural color, finger-tight nut, polypropylene, 10/pk	Alltech Associates, Inc
16	Flange-free ferrules for 1/8" bore, Tefzel, 10/pkg	Alltech Associates, Inc
17	One-piece fingertight nuts, 1/16" OD tubing, 10-32 UNF thread, 10/pk, natural color	Alltech Associates, Inc
18	1/4" brass gas-line filter , 7 μ m filter	Spelco, Inc.
19	1/4" stainless steel T-type line filter, 7 μ m filter	Spelco, Inc

PRESENTATION

A research paper, entitled "Reactivity of Promising Metal Oxide Sorbents for Removal of Hydrogen Sulfide from Hot Coal Gases", was presented for the Session 110-Reactive Separation Processes I at 3:35 PM, November 13, 1996, the 1996 Annual AIChE Meeting, Chicago, November 10 -15, 1996. Our paper was replaced with the paper 110d, entitled " Development of New Packings for Catalytic Distillation" by Ishida.

A research paper, entitled "Formulation of Metal Oxide Sorbents for Removal of Wet Hydrogen Sulfide", was accepted for presentation at the 1997 Spring National AIChE Meeting, Houston, March 9 - 13, 1997.

A research paper, entitled "Reactivity of Metal Oxide Sorbents for Removal of Wet Hydrogen Sulfide at High Temperatures", was submitted for publication in the proceedings for the Fifth Annual HBCU/Private Sector-Energy Research and Development Technology Transfer Symposium, Baton Rouge, Louisiana, March 4-5, 1997

PLANS ON FUTURE EXPERIMENTS

Various metal oxide sorbents will be formulated with various additives under various formulation conditions in order to search for a formula of a durable sorbent with high-sulfur-absorbing capacity. Initial reactivity of formulated metal oxide sorbents will be tested with the batch reactor as well as the newly-fabricated differential reactor. Hardness of formulated metal oxide sorbents will be tested with a Kahl pellet hardness tester, which has been placed on order (see Table 1).