Air Products and Chemicals

HOUDRY TECHNICAL CENTER

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HOT LOW BTU PRODUCER GAS DESULFURIZATION
IN FIXED BED OF IRON OXIDE FLY-ASH

QUARTERLY REPORT NO. 1
1 JULY TO 30 SEPTEMBER 1975

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ERDA CONTRACT E(49-18)2033

AIR PRODUCTS AND CHEMICALS, INC.
MARCUS HOOK, PENNSYLVANIA 19061

QUARTERLY REPORT NO. 1, 1 JULY TO 30 SEPTEMBER 1975

ABSTRACT

This is the first quarterly progress report of the APCI support program to assist ERDA in the development of their hot producer gas desulfurization process. An iron oxide-fly ash absorbent will be used in a cyclic fixed-bed operation. Specific objectives of APCI are absorbent development, definition of process scale-up criteria, and commercial process design.

Major emphasis this period has been in planning details for Task I, Absorbent Development, and Task II, Model Confirmation, and modifying and repairing the existing ERDA pressure reactor assembly. Absorbent preparation will begin in October 1975. Dynamic absorption tests of these materials are expected to begin in November 1975 in the repaired reactor assembly.

I. INTRODUCTION

The Air Products and Chemicals, Inc. Research, Development, and Engineering program is aimed at assisting ERDA in developing their hot producer gas desulfurization process. A cyclic fixed-bed technique using an iron oxide-fly ash absorbent at producer gas temperature and pressure is the ultimate objective. The process is being developed by ERDA at the Morgantown Energy Research Center.

Specific objectives of the APCI support program are absorbent development, definition of scale-up criteria, and process design of a commercial size system. The APCI project is divided into eight separate tasks with an estimated duration of 16 months. This is the first quarterly progress report.

II. CHEMICAL REACTIONS

Table I lists the absorption, regeneration and coke burning reactions, the accompanying heat generations, and gas and solid phase maximum adiabatic temperature increases. Heat removal from the bed will be one of the key problems since both the absorption and regeneration cycles generate heat. The magnitudes of the solid phase adiabatic temperature rise for regeneration and coke burning indicate another potential problem. Poor heat transfer in the solid phase and between the solid and gas phases can produce local solid phase temperatures high enough to destroy both the physical integrity of the absorbent as well as its chemical activity.

TABLE I

ERDA PRODUCER GAS DESULFURIZATION
WITH IRON OXIDE

REACTIONS

ABSORPTION

$$\Delta H = -21.85 \text{ KCAL/G-MOLE, Fe}_2\text{O}_3$$

$$\text{GAS ADIABATIC TEMPERATURE RISE} = 20^\circ\text{F/1\% H}_2\text{S}$$

$$\text{SOLID ADIABATIC TEMPERATURE RISE} = 100^\circ\text{F/10\% Fe}_2\text{O}_3$$

REGENERATION

$$\Delta H = -350.1 \text{ KCAL/G-MOLE, Fe}_2\text{O}_3$$

$$\text{GAS ADIABATIC TEMPERATURE RISE} = 195^\circ\text{F/1\% O}_2$$

$$\text{SOLID ADIABATIC TEMPERATURE RISE} = 1575^\circ\text{F/10\% Fe}_2\text{O}_3$$

COKE BURNING

$$\Delta H = -94.1 \text{ KCAL/G-MOLE, C OR O}_2$$

$$\text{GAS ADIABATIC TEMPERATURE RISE} = 235^\circ\text{F/1\% O}_2$$

$$\text{SOLID ADIABATIC TEMPERATURE RISE} = 565^\circ\text{F/1\% COKE}$$

A process model was developed for either absorption or regeneration operation under isothermal conditions by APCI during another ERDA contract, "Hot Stage Desulfurization of Gasified Coal by Limestone", E(49-18)1510. That isothermal model will be modified to include heat effects in both the gas and solid phases to define and understand the role of critical process parameters.

III. PROGRESS THIS QUARTER

Major emphasis during this period has been in two areas:

1. Planning the details for Task I, Absorbent Development, and Task II, Model Confirmation.
2. Modifying and repairing the existing ERDA pressure reactor assembly which had been previously used for the limestone ERDA contract.

Pertinent items are discussed below.

A. Tasks I and II Planning

Specific objectives of Absorbent Development (Task I) are to:

1. Identify practical sources of Fe_2O_3 .
2. Prepare absorbents using different sources and levels of Fe_2O_3 and evaluate H_2S absorption dynamics.
3. Evaluate other sources of fly ash by physical properties and absorption capacities and dynamics.
4. Evaluate bentonite and kaolin as binders by physical properties and absorption capacities and dynamics.

Full identification of a practical and optimum performance absorbent and knowledge of its absorption dynamics will be the product of this phase.

Specific objectives of Model Confirmation (Task II) are to:

1. Show that absorption dynamics uniquely correlates with the dimensionless absorption number (a function of gas H_2S concentration, absorbent H_2S saturation capacity, bed geometry and properties, and absorbent properties).

2. Develop predicted absorption curves for the 12-inch diameter ERDA MERC reactor.

The expected result from this phase is a model that describes absorption dynamics with consideration of all the process variable interactions. This model can be extended to regeneration dynamics and can be useful for scale-up to commercial size.

A list of absorbents to be prepared by APCI for Tasks I and II are presented in Table II. Prior to dynamic testing, the following physical properties will be determined:

1. Crushing strength.
2. Porosity (fresh and after 1200°F heat treat - 5 hours).
3. Pore size distribution and surface area.
4. H₂S saturation capacity, fresh.
5. H₂S saturation capacity after one regeneration.

A standard dynamic absorption test will be carried out for absorbent screening and development. Nominal conditions are:

Feed Gas Composition, Volume %

H ₂ S	0.6
CO	20.6
H ₂	14.7
CH ₄	2.0
CO ₂	6.8
N ₂	49.8
H ₂ O	5.5

(Typical low BTU producer gas but containing no tar and particulates.)

Operating Conditions

Temperature	1200°F
Pressure	2 Atmospheres
GHSV (Dry, STP)	6000
Duration	Until Effluent H ₂ S Content is at Least 95% of Effluent Content

TABLE II

ABSORBENTS TO BE PREPARED FOR
TASK I: ABSORBENT DEVELOPMENT
TASK II: MODEL CONFIRMATION

A. TEST OF DIFFERENT IRON OXIDE SOURCES

FIXED PARAMETERS

1. FORT MARTIN FLY ASH SUPPLIED BY ERDA MERC
2. BENTONITE BINDER
3. 25% Fe_2O_3
4. 1/4" PELLET DIAMETER

SOURCES

1. FISHER SCIENTIFIC TECHNICAL GRADE
2. U.S. STEEL PRECIPITATOR FINES
3. J & L STEEL PRECIPITATOR FINES
4. ARMCO STEEL OPEN HEARTH SLUDGE
5. }
6. } REPUBLIC STEEL, YOUNGSTOWN SHEET & TUBE,
7. } ERDA MERC SUGGESTIONS

TABLE II (CONTINUED)

B. TEST OF PROPER IRON OXIDE CONTENT

FIXED PARAMETERS

1. FORT MARTIN FLY ASH SUPPLIED BY ERDA MERC
2. BENTONITE BINDER
3. U.S. STEEL PRECIPITATOR FINES OR FISHER TECH GRADE
4. 1/4" PELLET DIAMETER

IRON OXIDE LEVELS

10, 15, 20, 25 AND 30% Fe_2O_3

C. TEST OF PELLET SIZE AND IRON OXIDE CONTENT INTERACTION

FIXED PARAMETERS

1. FORT MARTIN FLY ASH SUPPLIED BY ERDA MERC
2. BENTONITE BINDER
3. U.S. STEEL PRECIPITATOR FINES

<u>ABSORBENTS</u>	<u>% Fe_2O_3</u>	<u>PELLET DIAMETER, INCHES</u>
1	15	1/8
2	15	1/4
3	25	1/8
4	25	1/4

TABLE II (CONTINUED)

D. TEST OF DIFFERENT FLY ASHES & BINDERS

FIXED PARAMETERS

1. SOURCE OF IRON OXIDE CHOSEN FROM DYNAMIC TESTS
2. 1/4" PELLET DIAMETER

<u>ABSORBENTS</u>	<u>FLY ASH</u>	<u>BINDER</u>	<u>% Fe₂O₃</u>
1	FORT MARTIN	BENTONITE	OPTIMUM
2	FORT MARTIN	KAOLIN	OPTIMUM
3	"A"	BENTONITE	OPTIMUM
4	"A"	KAOLIN	OPTIMUM
5	"B"	BENTONITE	OPTIMUM
6	"B"	KAOLIN	OPTIMUM
7	FORT MARTIN	BENTONITE	0.75 OPTIMUM
8	FORT MARTIN	KAOLIN	0.75 OPTIMUM
9	"A"	BENTONITE	0.75 OPTIMUM
10	"B"	BENTONITE	0.75 OPTIMUM
11	"A"	KAOLIN	0.75 OPTIMUM
12	"B"	KAOLIN	0.75 OPTIMUM

FOUR OF ABOVE TWELVE TO BE CHOSEN FOR DYNAMIC TEST

The dynamic absorption characteristics will be determined from the effluent gas H_2S content-time on-stream relationship. Absorbents with low capacity to 10% H_2S breakthrough will be rejected.

Planned dynamic absorption experiments for model confirmation are listed in Table III. The interrelationships between operating conditions (temperature, pressure, GHSV), fixed-bed geometry (length only), absorbent characteristics (iron oxide content and pellet size) and feed gas H_2S content will be evaluated. It is expected that the dynamics will correlate with a single dimensionless number that is dependent on these variables.

B. Repair of Pressure Reactor

The pressure reactor assembly, originally constructed for another ERDA program carried out by APCI, requires modifications and repairs. Details of this unit are presented in "Final Report - Hot Stage Desulfurization of Gasified Coal by Limestone", E(49-18)1510. A simplified flow diagram is shown in Figure 1. The reactor loading is approximately one liter. Temperature and pressure limitations are 1600°F at 150 psig. All systems are functional except the adiabatic reactor and the on-line automatic gas chromatograph.

Extensive corrosion was observed at the hot end of the reactor at the completion of the ERDA limestone project. Absorbent baskets and reactor inlet lines also experienced some metal attack. The following steps are required to repair the reactor and reduce or eliminate corrosion problems:

1. Removal of the adiabatic reactor from the experimental assembly.
2. Removal of insulation, electrical heating coils, thermowells and thermoblocks from the reactor.
3. Cut sections of the hot end of the reactor to determine the extent of internal corrosion.
4. Procurement and machining of replacement materials of construction for the corroded sections of the reactor.
5. Procurement of materials of construction and fabrication of absorbent loading baskets and reactor inlet lines.
6. Alonizing of reactor internals, absorbent baskets and inlet lines.

TABLE III

PLANNED EXPERIMENTS FOR MODEL CONFIRMATION

<u>RUN NO.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
<u>VARIABLES</u>												
IRON OXIDE CONTENT, WT. %	15	15	25	25	25	25	25	25	15	25	25	25
PELLET DIAMETER, INCHES	1/8	1/4	1/8	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4
GHSV	6000	6000	6000	6000	3000	3000	6000	6000	6000	6000	6000	6000
TEMPERATURE, °F	1200	1200	1200	1200	1200	1200	1200	1200	1200	1400	1200	1400
PRESSURE, ATM.	2	2	2	2	2	2	2	2	2	2	10	10
LINEAR VELOCITY, FPS	4.4	4.4	4.4	4.4	2.2	1.1	2.2	4.4	4.4	4.9	0.9	1.0
FEED GAS VOL. % H ₂ S	0.6	0.6	0.6	0.6	0.6	0.6	0.6	1.8	1.8	0.6	0.6	0.6
BED LENGTH, INCHES	20	20	20	20	20	10	10	20	20	20	20	20
<u>VARIABLE STUDIED</u>												
IRON OXIDE CONTENT	X	X	X	X								
PELLET SIZE	X	X	X	X								
TEMPERATURE				X						X	X	X
PRESSURE				X						X	X	X
FEED GAS H ₂ S		X		X				X	X			
GHSV, VELOCITY & BED LENGTH				X	X	X						

FIGURE 1: SIMPLIFIED FLOW DIAGRAM FOR LINWOOD PRESSURE UNIT

7. Installation of reactor on experimental unit and addition of insulation and electrical heating circuits and control for adiabatic operation.

Items 1 through 5 have been completed in October 1975. Item 6 is in process. It is expected that Item 7 will be completed and that the pressure reactor will be available for absorbent tests in November 1975.

C. On-Line G.C. Analytical System

The on-line G.C. system had been plagued with considerable problems during the ERDA limestone project. The system failed to hold its calibration requiring frequent calibration adjustments. Some difficulties existed with the systems electronics. Efforts have been underway to define the sources of these problems and their solutions. The source of the difficulty was identified and eliminated after considerable time. Stray solder was apparently the problem. The vendor played a very active role in solving this problem.

D. Timetable

An estimated timetable for the various events for Tasks I and II is presented in Figure 2. These two tasks are carried out simultaneously. The estimated duration and date of completion for these tasks is 29 weeks and 2 February 1976.

IV. PLANS FOR 1 OCTOBER TO 30 DECEMBER 1975 QUARTER

Emphasis during the next quarter will be placed in the following areas:

1. Preparation of experimental absorbents.
2. Installation of the pressure reactor.
3. Evaluation of experimental absorbents.
4. Development of the mathematical model describing the absorption dynamics.

V. PREVIOUSLY-PREPARED APCI IRON OXIDE-FLY ASH ABSORBENTS

Prior to this present ERDA contract, APCI prepared four different experimental iron oxide on fly ash absorbents in accordance with an ERDA MERC-APCI purchase order agreement, ERDA No. P3051277. This purchase order required that APCI identify three low-cost commercial sources of iron oxide and prepare absorbents from these three sources plus one from technical grade iron oxide. Fort Martin fly ash was supplied by MERC.

FIGURE 2. ESTIMATED TIMETABLE FOR TASKS I AND II: ERDA CONTRACT E(49-18)-2033

Twenty pounds of each absorbent were shipped to MERC prior to 1 July 1975. These experimental absorbents are currently being evaluated at MERC. Physical and chemical properties determined by APCI are listed in Table IV. It is clear that a wide variation exists in the chemical composition of iron oxide powder obtained as by-products from steel manufacture. Absorbent physical properties are essentially the same for all sources of iron oxide. Most noteworthy is the high crushing strength of 5.2 to 7.4 pounds/MM which is characteristic of an unusually strong pellet.

VI. JOINT ERDA-APCI MEETING

Representatives of ERDA/Washington, ERDA/Morgantown, and APCI met in Washington on 4 August 1975. The purpose of this meeting was to:

1. Discuss APCI's support program, method of approach, and timetable.
2. Determine that ERDA MERC's and APCI's target dates are in phase with each other.
3. Establish inputs ERDA MERC requires from APCI and APCI requires from MERC.
4. Define a system of communication for rapid and easy transmittal of information between MERC and APCI.

ERDA agreed with the APCI methods of approach and timetable for Tasks I and II (as described in this report) and that they are consistent with MERC's requirements.

TABLE IV
PHYSICAL AND CHEMICAL PROPERTIES OF
APCI PREPARED 25% IRON OXIDE ON FLY ASH ABSORBENTS

CALCINED PELLET APCI CODE NO.	705X8- 5X4	705X9- 1X9	705X10- 1X4	705X11- 1X4
FLY ASH SOURCE	← BUREAU OF MINES, MORGANTOWN →			
IRON OXIDE SOURCE	FISHER SCIENTIFIC	U.S. STEEL HOMESTEAD, PA.	J & L STEEL PITTSBURGH, PA.	ARMCO STEEL MIDDLETOWN, OHIO
	LABORATORY GRADE	← ELECTROSTATIC PRECIPITATE →		OPEN HEARTH SLUDGE

COMPOSITION OF IRON OXIDE POWDER, WT. % (TYPICAL, AS REPORTED BY SUPPLIERS)

TOTAL IRON				
AS Fe	69.9	63.5	61.1	51.2
AS Fe ₂ O ₃	100.0	90.8	87.4	73.2
SULFUR		1.0	1.6	0.7
ZINC OXIDE		0.2	5.7	21.0
LEAD OXIDE		NR	1.4	0.6
SODIUM OXIDE		NR	NR	1.2
FLUORINE		NR	NR	1.2
CA, MN, CU, MG OXIDES		2.4	NR	2.8
AL, SI OXIDES		1.2	NR	0.8

PHYSICAL PROPERTIES OF CALCINED PELLETS

BULK DENSITY, Kg/L	1.152	1.151	1.075	1.115
PELLET DENSITY, Kg/L	1.996	1.942	1.905	1.979
TRUE DENSITY, Kg/L	2.912	2.935	2.882	3.025
PORE VOLUME, cc/g	0.157	0.174	0.177	0.174
SURFACE AREA, M ² /g	<5	<5	<5	<5
CRUSHING STRENGTH, Lb/mm.	7.4	5.6	5.2	6.5