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Zinc Titanate Tests in Transport Reactor

Authors:

Santosh K. Gangwal
William M. Campbell
Raghubir P. Gupta
Gunnar B. Henningsen

Contractor:

Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709-2194

Subcontractor:

The M.W. Kellogg Company
P.O. Box 4557
Houston, TX 77210-4557

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4.3 Zinc Titanate Tests in Transport Reactor

CONTRACT INFORMATION

Contract Number	DE-AC21-88MC25006
Contractor	Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709-2194 919-541-8023
Contractor Project Manager	Santosh K. Gangwal
Subcontractor	The M.W. Kellogg Company P.O. Box 4557 Houston, TX 77210-4557 713-537-8534
Subcontractor Project Manager	William M. Campbell
Principal Investigator	Raghubir P. Gupta (RTI) GunnarB. Henningsen (MWK)
METC Project Manager	Daniel C. Cicero
Period of Performance	June 1995 - September 1995

OBJECTIVES

The M.W. Kellogg Company is developing a Transport reactor process which promises to reduce the cost of the hot gas desulfurization system in IGCC power plants. Research Triangle Institute (RTI) has been developing proprietary fluidized-bed zinc titanate sorbents for hot gas desulfurization applications for the past five years with DOE/METC sponsorship. These sorbents are prepared using granulation and spray drying techniques. Recently, RTI and Contract Materials Processing (CMP), Inc. have teamed up to produce a spray-dried zinc titanate formulation, ZMP-5, in the 100-250 μm particle size range. This size range is preferred by Kellogg for the Transport reactor application.

Kellogg, in cooperation with RTI, will perform scoping and multi-cycle tests with ZMP-5 sorbent in its new bench-scale Transport Reactor Test Unit (TRTU-II). The objective of the test program is to establish an appropriate range of operating conditions for the use of this sorbent formulation in a Transport reactor system.

BACKGROUND INFORMATION

A fixed-bed hot gas desulfurization (HGD) system was tested at the KRW, Waltz Mill, Pennsylvania, Process Development Unit. In this unit zinc ferrite was tested in both bulk and polishing modes of operation. When the Piñon Pine Power project was selected by the USDOE in Clean Coal Round IV, three zinc-based sorbents were tested at the Morgantown Energy Technology Center (METC) for the fixed-bed HGD application. In this testing, zinc ferrite and zinc titanate tended to decrepitate over extended multi-cycle testing. It was thought that this decrepitation was caused by the inherent high loading of sulfur on the sorbent in the fixed bed configuration. A third material, Z-Sorb sorbent, developed by Phillips Petroleum Company, showed no signs of decrepitation, but tended to lose capacity over time when regenerated in the presence of steam.

One way to avoid the high sulfur loading on the sorbent and to avoid using steam for heat dissipation during regeneration is to use a Transport reaction system. Kellogg first checked this idea in proof-of-concept tests in 1993. In these first tests, the Z-Sorb sorbent was used and there was no detectable leakage of sulfur from the Transport Absorber over a wide range of operating conditions. By limiting the amount of oxidant used during regeneration, such that only partial regeneration is accomplished, the sorbent acted as the heat sink and the oxidative exotherm was controlled. After a series of additional tests in 1994 in Kellogg's Transport Reactor Test Unit (TRTU) and a detailed technical review and comparison of both fixed-bed and Transport concepts, it was decided to include a Transport HGD system on the Piñon Pine Power project.

This paper reports on the results of recent HGD tests in Kellogg's new TRTU using spray-dried zinc titanate developed by RTI and supplied by CMP, Inc.

PROJECT DESCRIPTION

Figure 1. is a sketch of Kellogg's new Transport Reactor Test Unit (TRTU-II). The TRTU-II was built for tests not related to this HGD test program but it was selected for this test program because the new design offers greater flexibility and is more like a commercial reactor configuration than the TRTU used in previous HGD testing.

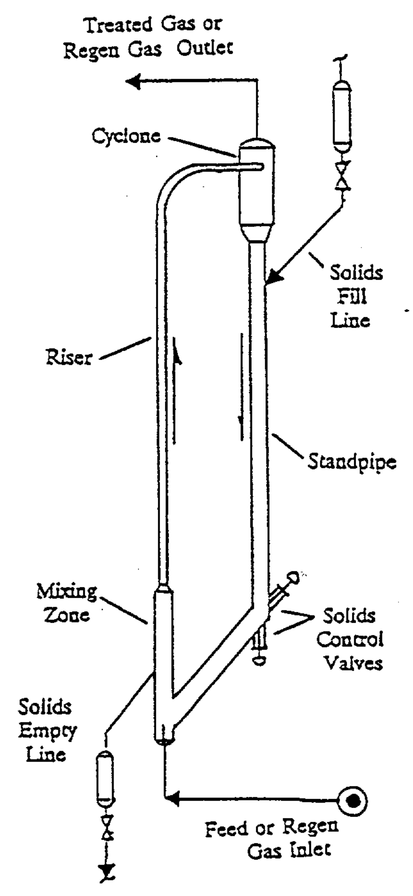

Figure 1.
Kellogg's Transport Reactor Test Unit

Transport reactors are devices that circulate fluidized solids at sufficiently high velocity to fully entrain the solid materials. The circulating solids are of substantially smaller diameter than those normally found in fixed-bed reactors, which results in improved reaction rates. The high circulation rates provide substantial gas-solid and solid-solid contact for excellent mass and heat transfer.

The TRTU-II consists of a 1-1/2 inch diameter Mixing Zone which is ten feet long, a Riser one inch in diameter and 32 feet long, a solids disengaging cyclone, and a 1-1/2 inch standpipe which returns the disengaged solids to the bottom of the Mixing Zone. The standpipe maintains an inventory of solids and includes a plug-like valve which permits controlling the rate of solids circulation in the reactor. The reactor is made of schedule 160 alloy piping materials which permits operation up to 1800°F and 100 psig. The reactor is heavily insulated and is heated by a number of electrical elements that permit accurate temperature control when determining yield data and kinetic reaction rates.

The TRTU is designed for proof-of-concept testing and data collection on gasification and combustion technologies as well as other gas-solid reaction systems where highly exothermic or endothermic reactions take place. The circulating solids provide a large heat sink to moderate temperature changes. The Mixing Zone of the reactor permits staging either gaseous reactants or solid, liquid and gas feeds. Staging is used on the oxidant during sorbent regeneration.

TEST PROGRAM

There are a number of sorbent characteristics that are essential to successful operation of a Transport HGD system. Most important are the reactivity of the sorbent at operating conditions and its attrition resistance. High sulfur capacity is not of primary concern since the sorbant is regenerated continuously.

In the absorption mode two independent variables are of interest; process gas temperature and sorbent density in the Riser. Typically, the absorption reaction rate is very high and the effect of temperature is not great, indicating a diffusion-controlled reaction. The temperature range of interest is 1000-1200°F. Solid circulation rate can be varied to determine the effect on sulfur leakage of sorbent concentration in the Riser. Low circulation rate is desirable since sorbent attrition losses should be directionally lower.

Surprisingly, even though the regeneration reaction is highly exothermic, the reaction rate is relatively slow. The proper combination of temperature and oxygen and sulfur concentrations is important. Since zinc titanate tends to form sulfate in the presence of excess oxygen, the initial mode of operation will be to operate in the substoichiometric oxygen range. Sulfur concentration can be increased by raising the level in the spent sorbent or by increasing the circulation of sorbent in the regenerator. The exotherm is controlled by limiting the amount of air fed.

The temperature at which regeneration initiates is a key variable to be studied for any given sorbent formulation. If the regeneration initiation temperature or the temperature required for effective regeneration is significantly higher than the temperature in the Absorber, then the sorbent has to be heated and cooled on each regeneration pass. One purpose of the mixing zone in the Regenerator and of the staged oxidant introduction is to bring the sorbent up to an effective regeneration temperature before the sorbent enters the Riser where the highest temperature is experienced.

The ideal sorbent would operate at the same temperature in both absorption and regeneration modes. The effectiveness of any given sorbent formulation in a Transport reaction system depends upon finding an effective balance between the operating conditions of the Absorber and Regenerator. Multi-cycle (repeated absorption and regeneration) tests indicate whether these conditions vary as the sorbent ages.

RESULTS

At the time of publication the test program had not been initiated. A failure of several heating elments in theTRTU-II during reactor shakedown forced the test program to be delayed. Testing is expected to be completed in the next few months.

Anyone interested in receiving a copy of this paper, updated to reflect the results of the test program should write or FAX (713-753-7836) the author and a copy will be forwarded as soon as available.

FUTURE WORK

In addition to the testing in Kellogg's TRTU, METC is currently building a HGD Process Development Unit to support continued sorbent development. Figure xx is a schematic of METC's HGD-PDU. The unit is designed to process 150,000 SCFH of simulated gasifier fuel in either the fluid-bed or Transport mode of operation.

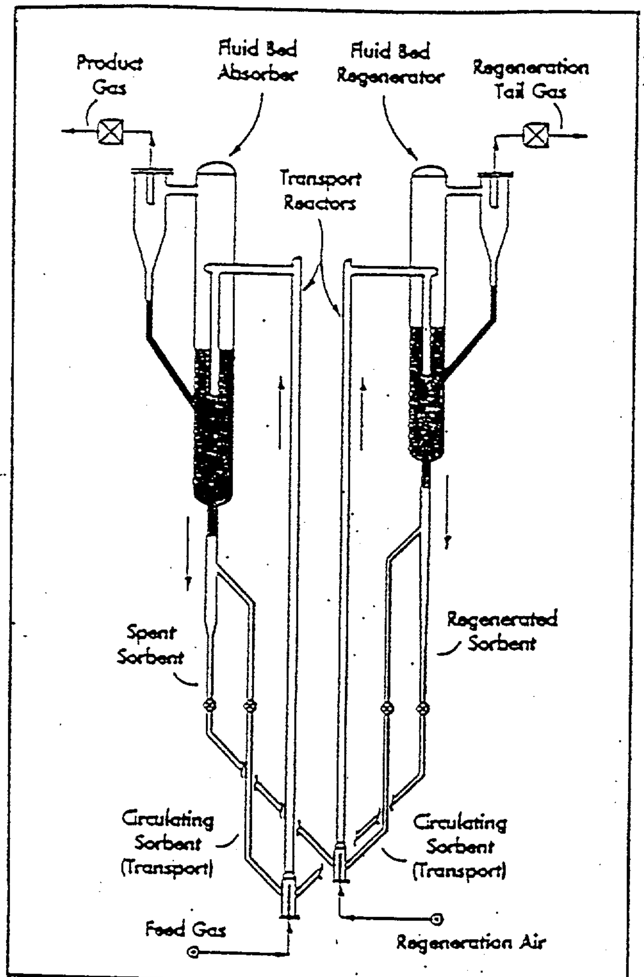

Figure xx
Schematic of METC's HGD-PDU

The diameters of the Transport Absorber and Regenerator are 6 inches and 2 inches respectively. This unit will be capable of testing a variety of sorbents over a range of operating conditions.

Figure yy is a sketch of the Transport HGD system for Sierra Pacific Power Company's 100 MWe Piñon Pine Power Poject. The Transport reactor for the Piñon Pine project has an Absorber diameter of 42 inches and a Regenerator diameter of 2-1/2 inches. The notable difference in reactor diameters is due to the large gas flow to the Absorber and the low level of sulfur in the gas.

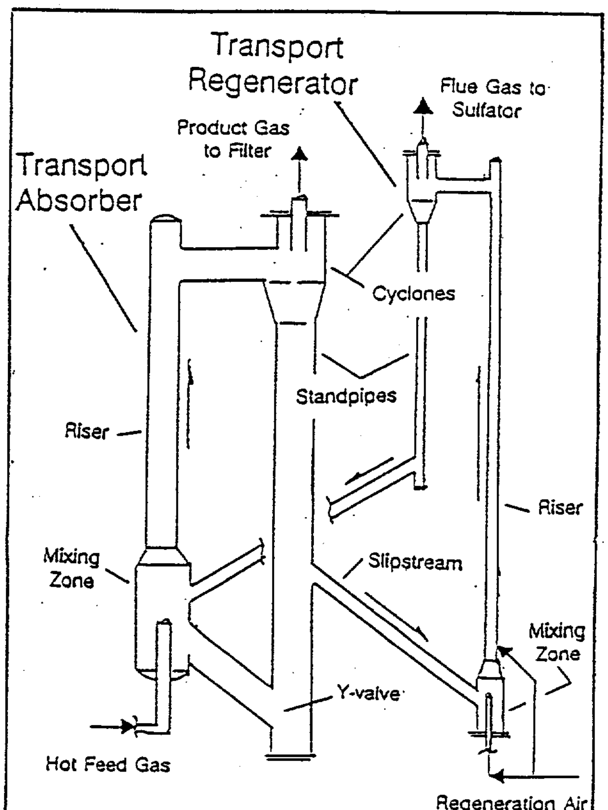

Figure yy
Piñon Pine Transport Desulfurizer