A THERMOGRAVIMETRIC SYSTEM FOR CORROSIVE ENVIRONMENTS AT HIGH PRESSURES AND TEMPERATURES[*]

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ABSTRACT

A high-pressure thermogravimetric analysis system based on the duPont 951 Thermogravimetric Analyzer and the duPont 990 Thermal Analyzer has been constructed. There are two components in the system, a reactor and a gas feed system. The reactor consists of a stainless steel high-pressure enclosure, which houses the balance mechanism from the duPont 951 TGA, and an externally heated vertical reactor tube. This design provides spatial separation between the housing and the reaction zone to protect the balance mechanism from thermal and chemical attack. The gas feed system provides for blending, feeding, and metering of up to seven different gases.

The system is designed to have an operating capability of 60 atm and 1100°C with corrosive gases such as hydrogen and hydrogen sulfide. It was proved to operate successfully with aluminide-coated stainless steel reactor tubes for studies of the calcination of dolomite in CO_2/N_2 atmospheres and sulfidation in H_2S/N_2 mixtures up to 30 atm and 850°C.

INTRODUCTION

In recent years, interest in high-pressure thermogravimetry has greatly increased, particularly in the area of kinetic studies of coal gasification related reactions. Dobner et al.[1] presented a summary of the chronology of development of high-pressure thermobalances over the past two decades, and described one of their own design. Their system is a modified duPont 950 TGA. Its pressure capability was increased to 30 atm by essentially enclosing the balance and furnace module inside a high-pressure chamber. The balance mechanism is thermally protected by a pancake cooling coil located on the face of the balance housing. A line carrying purge nitrogen directly to the rear of the balance permits positive flow of purge gases at all times. O'Neill et al.[2,3] reported a system patterned after the design of Ruth[3], which was the predecessor of the system described by Dobner et al., capable of pressures up to

10 atm. Both systems have been designed for studies of gas/solid reactions involving sulfur-containing gases.

In conjunction with a study of the mechanism of the H_2S–dolomite reaction at high temperatures and pressures, a TGA system of a different design, capable of operating at pressures up to 60 atm and temperatures up to 1100°C with corrosive gases has been built and tested. This report describes the operation of the system and some of the kinetic results obtained.

EXPERIMENTAL SYSTEM

Figure 1 is a schematic drawing of the experimental system. The balance mechanism from the duPont 951 Thermogravimetric Analysis module is enclosed in a high-pressure housing from which hangs a long vertical reactor tube. The sample is suspended from one arm of the microbalance into the lower end of the reactor tube by a fine wire. A furnace with three independently powered windings provides a nearly uniform temperature profile in the vicinity of the sample. The gas feed system provides a continuous nitrogen purge around the microbalance, and, through a separate line, a reactant gas of chosen composition to the reactor tube. The reactant
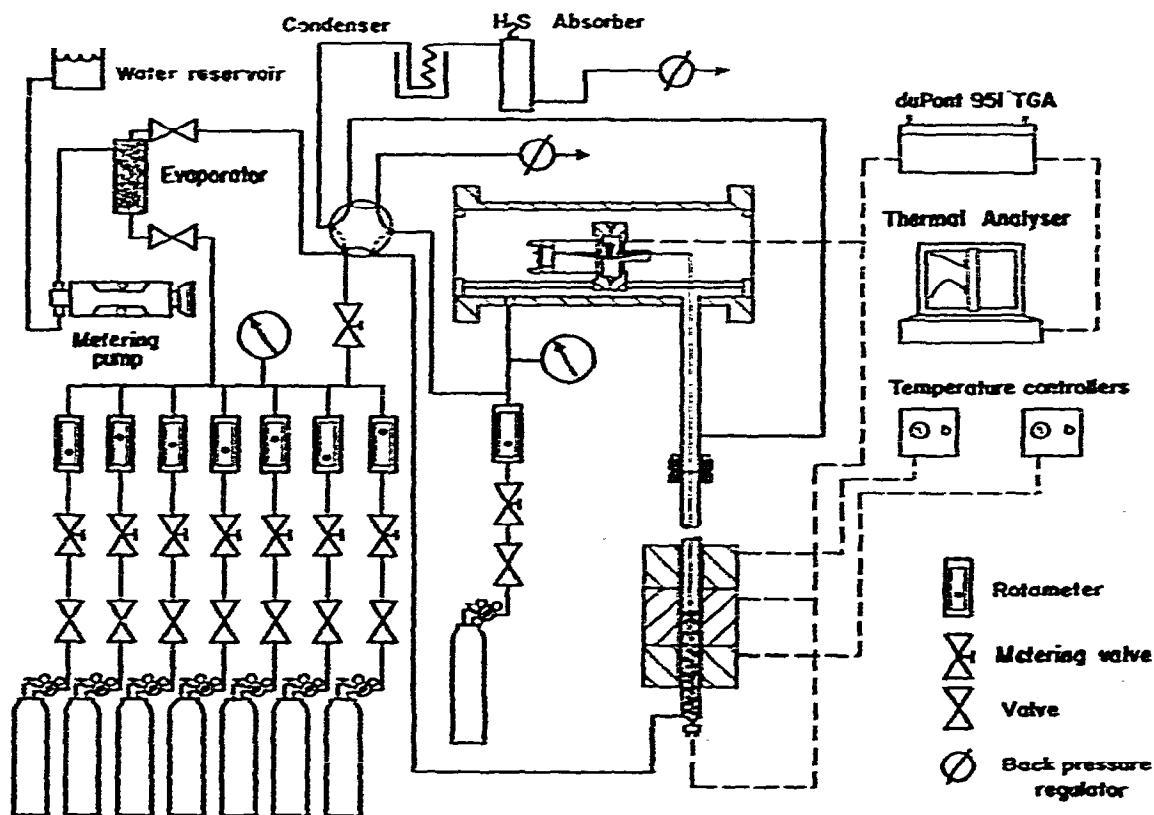

Fig. 1. Schematic of the experimental system.

gas is brought to the desired operating temperature in a preheating zone packed with ceramic beads in the bottom quarter of the reactor tube. Hot, corrosive gases from the reaction zone are prevented from reaching the balance mechanism by the combined action of a series of baffles near the top of the reactor tube and the continuous nitrogen purge.

Several interchangeable reactor tubes have been tested. Stainless steel reactor tubes, 1 in. in outside diameter with walls 1/8 in. thick, have been found adequate for temperatures up to 850°C and pressures up to 30 atm, but failed rapidly when exposed to temperatures in excess of 900°C even at moderate pressures. Reactor tubes intended for service above 850°C will therefore be constructed of Inconel 617 alloy. Both stainless steel and Inconel reactor tubes are protected from H_2S corrosion by an alumide coating. The aluminide-coated stainless steel reactor tube used in all sulfidation experiments thus far completed shows no sign of corrosion by H_2S.

The three-winding furnace consists of two vertical halves that can be separated for easy removal and replacement of reactor tubes. Power to the central winding is controlled by the duPont 990 Thermal Analyzer, while the two end windings are powered by auxilliary temperature controllers. Sample temperature is measured by a calibrated thermocouple located about 3 mm below the sample. It has been possible to obtain a zone about 8 cm long near the center of the furnace in which the temperature varies less than 5°C axially. The furnace can be brought up to operating temperature in less than 20 min, and after steady-state conditions have been reached, the temperature can be maintained within 5°C for several hours.

The gas feed system has provisions for metering and blending of up to seven gases. In addition, water can be fed at a controlled rate to an evaporator just upstream of the reactor tube by a high-pressure liquid metering pump. Reactant gas pressure is measured by a Bourdon tube gage to an accuracy of about 1%, and gas flow rates are measured by rotameters, calibrated at each pressure against a wet test meter or, at low flow rates, against a bubble meter. The two calibration methods overlap in a substantial range of flow rates, including most of the experimentally useful range at low pressures, and within this range agree to better than 0.25%. The gas mixture in the reaction zone can be sampled and fed to a Varian Model 202-C gas chromatograph. By this means, the reactant gas composition can be determined to within 1%. Before discharging into the atmosphere, the exit gas from the reactor passes through a condenser where water vapor is removed and a packed bed of ZnO extensions where H_2S is absorbed.

An experiment is performed as follows. A lump of dolomite is shaped into a rough sphere and weighed. The sample is then suspended from the quartz arm of the microbalance in a wire basket and the balance is tared. After steady-state flow conditions are established, the balance reading is electronically corrected for buoyancy and drag effects. After the furnace is brought to the desired operating temperature, sample weight and temperature are continuously recorded on the X–Y recorder of the duPont 990 Thermal Analyzer. The sample is again weighed after the conclusion of the experiment and saved for further reaction or for structural analysis. The

total weight change recorded by the TGA for each run is found to agree to better than 0.5% with the weighing on a Stanton Model CL5D analytical balance.

APPLICATIONS

The TGA system has been used in studies of the half-calcination and subsequent sulfidation of dolomite, $CaMg(CO_3)_2$, as represented by the equation

$$CaMg(CO_3)_2 \rightarrow CaCO_3 \cdot MgO + CO_2$$

$$CaCO_3 \cdot MgO + H_2S \rightarrow CaS \cdot MgO + H_2O + CO_2$$

Two natural dolomites, both supplied by the Pfizer Corp., have been half-calcined in the TGA system; these dolomites are of the same geological origin as those designated 1337 and 1341 by Bituminous Coal Research. The 1337 dolomite is nearly pure, having a Ca:Mg ratio of 1.025 and less than 1.0% other impurities; 1341 dolomite has a Ca:Mg ratio of 1.07 and contains about 2% impurity, mostly silica and hematite. In both stones, the excess Ca probably occurs as inclusions of nearly pure calcite. The two materials differ significantly in grain size. Although precise grain size measurements have not been made, the average grain size of 1337 dolomite appears to be about 30 μm, while that of 1341 dolomite is about 400 μm.

Typical results of half-calcination experiments for the two dolomites are given in Fig. 2 and 3. The data are shown as fractional conversion versus time for a series
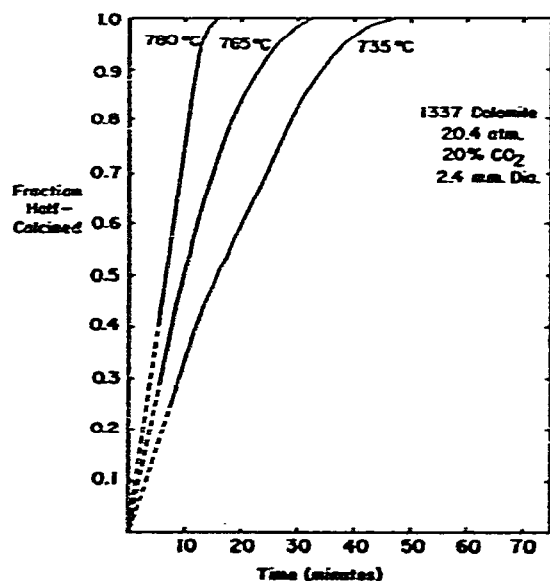

Fig. 2. Progress of the half-calcination reaction of 1337 dolomite at 20.4 atm of CO_2 in nitrogen. Flow rate: 1.14 STP l/min. Fraction half-calcined: fraction of Mg atoms converted to MgO.
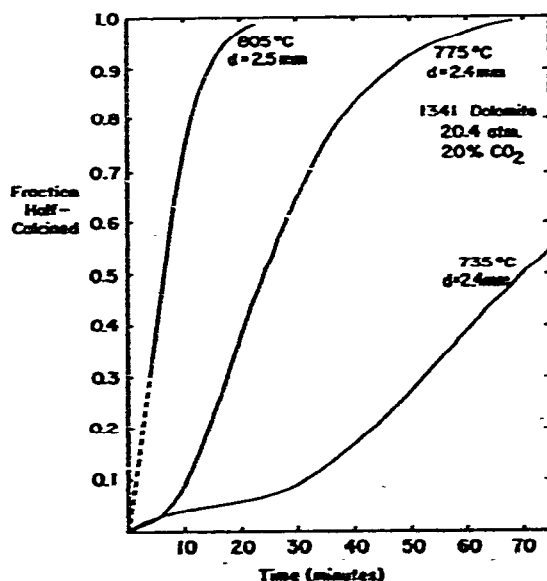
Fig. 3. Progress of the half-calcination reaction of 1341 dolomite at 20.4 atm of CO_2 in nitrogen. Flow rate: 1.14 STP l/min. Fraction half-calcined: fraction of Mg atoms converted to MgO. The diameter is that of an equivalent sphere.
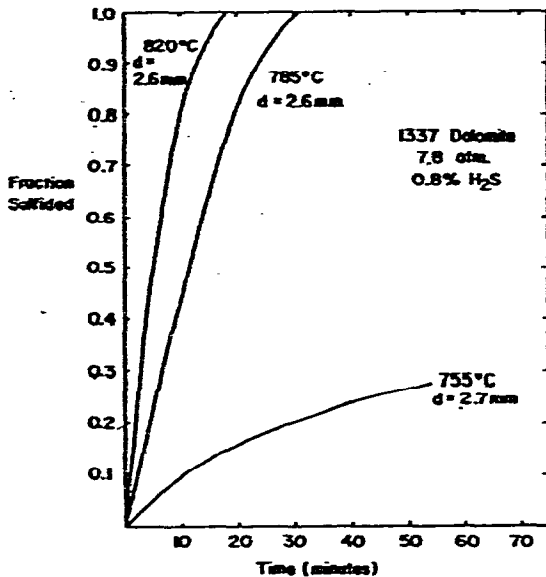
Fig. 4. Progress of the sulfidation reaction of 1337 dolomite, previously half-calcined at 785°C in 7.8 atm of 20% CO₂ in nitrogen. Flow rate: 1.33 STP l/min. of H₂S/N₂. Fraction sulfided: fraction of Ca atoms converted to CaS. The diameter is that of an equivalent sphere.

of temperatures at 20.4 atm in a 20% CO_2/N_2 atmosphere. It has not been possible, in general, to achieve isothermal conditions before the reaction begins; those portions of the mass-loss curves corresponding to this initial temperature transient were therefore obtained by extrapolation, and are shown as broken lines in the figures. Curves obtained at other pressures have similar shapes, but, at a given temperature, the reaction rate decreases with increasing pressure. As the pressure is reduced, these curves approach those obtained previously by Haul and Markus[5] and by Hubble et al.[6].

Typical results for sulfidation of half-calcined 1337 dolomite are shown in Fig. 4. No sulfidation experiments have as yet been made using 1341 dolomite. The samples were half-calcined at 785°C in a 20% CO_2/N_2 atmosphere at 7.8 atm. When the half-calcination reaction reached completion, the temperature was changed to the desired operating temperature, the CO_2 was turned off and the H_2S/N_2 mixture turned on. Due to back mixing of CO_2 and H_2S, an initial transient in gas composition may exist, the effect of which is being investigated. Although curves obtained under different conditions again have similar shapes, the rate increases with increasing temperature or H_2S concentration, but decreases with increasing pressure. The curves are qualitatively similar to those obtained by Ruth et al.[7], for sulfidation of a dolomite from the Greenfield Formation in Ohio at atmospheric pressure in $H_2S/N_2/CO_2$ mixtures, but the reaction rate in the present case is very much lower, possibly due to differences in properties of starting dolomites.

CONCLUSIONS

Spatial separation of the balance mechanism from the reaction zone is a major difference between our TGA system and others for high-pressure application in corrosive gases. This feature of the design confines hot, corrosive gases effectively in the reaction zone and permits the reactor tube to be heated externally. Steady-state values of sample temperature and of reactant gas pressure and composition can be determined to an accuracy of better than 1 %, and weight changes can be determined to better than 0.5%.

The experimental system has been successfully operated in studies of the half-calcination and sulfidation of dolomite. Tests conducted with aluminide-coated stainless steel reactor tubes have so far indicated that the mechanical strength of the system is adequate up to at least 850°C and the resistance to H_2S corrosion is adequate at 850°C in 1 % H_2S/N_2 mixtures at 20 atm. Kinetic data obtained in the system are well-behaved and the trend of the data at high pressure appears consistent with those found at low pressures by other investigations.

One serious problem is the initial transients in either sample temperature or gas composition. The extent of these transients and their effects on the measured kinetic data are currently being investigated and minimized.

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