

A DIFFERENTIAL REACTOR FOR HIGH-TEMPERATURE GAS-SOLID REACTIONS

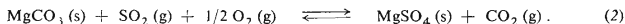
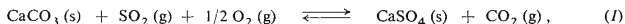
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A differential reactor is described in the paper for a single passage of gas through a fixed bed of solids. The reactor has proved useful for the kinetic study of the reaction between limestone and sulphur dioxide in flue gases. The combustion gases were generated by catalytic combustion of propane and subsequent addition of sulphur dioxide. The dependence is indicated in the paper of the temperature attainable in the reactor on the power input of the electric heating coil. With the aid of a ion-exchange resin the reacted solids were dissolved and the content of sulphate was determined by titration with 0.005M-Ba(ClO₄)₂ solution using thiorine and methylene blue as indicators. The obtained results agree well with those from direct gravimetric analysis described also in the paper.

Both in this country and abroad considerable attention has been focused on the problem of air pollution by sulphur dioxide. Despite of the efforts no success has been achieved in the removal of sulphur dioxide from flue gas of power plants which has become the major source of sulphur dioxide air pollution. A possibility of capturing sulphur dioxide at high temperatures is offered by reaction with calcium or magnesium carbonate



The former proceeds from left to right at the temperature between 750 and 1000°C; the latter between 600 and 850°C.

This paper describes a laboratory differential reactor for a single passage through a fixed bed of solids designed to obtain kinetic data for the reactions (1) and (2). The reactor may also be well suited for the study of numerous other heterogeneous gas-solid reactions. The above type of the reactor has been chosen in view of the fact that the over-all reaction rate between SO₂, O₂ and solid CaCO₃ (MgCO₃) or CaO (MgO) particles may be affected both by the rate of the reaction itself as well as the rate of diffusion of gas components within the particles. The reactor enables the data on the reaction rate to be obtained directly serving in turn as a basis for proper choice of the kinetic equations. Under defined conditions one can find out the

attainable degree of carbonate-to-sulphate conversion and thus provide efficiently valuable information regarding practical feasibility of dry methods of desulphurization with limestone, magnesite or dolomite.

EXPERIMENTAL

The Reactor

The reactor was designed so as to meet the following requirements: Heat up considerable volume of gases, low pressure drop, the option of long-term operation at 1000°C, easy handling of the samples, wide ranging power input control, temperature control deviating only a few degrees from the required temperature, ample thermal capacity.

The arrangement of the reactor is shown in the diagram in Fig. 1. The reactor was made of two heat-resistant coaxial steel tubes 46 X 3 (steel 17251) and 22 X 2 (steel 17255). The gas is fed at the bottom into the 850 mm long annular space between the tubes to heat up. At the top the gas is diverted into the inner tube to contact the sample of limestone placed about half-ways in the tube in a cup. The cup is supported by a rod mounted retractably by means of a nut and a high-lead thread on the outer tube of the reactor. The cup was also made of heat-resistant steel and provided with openings uniformly distributed over the bottom. The walls of the cup are 15 mm high and fit the inner wall of the tube forcing thus the gas to pass through the openings. The samples of limestone were uniformly spread over about 5 mm thick layer of quartz gauze in the cup.

In order to eliminate the effect of mass transfer to the surface of the solid phase a relatively high velocity of the gas phase was chosen. The superficial velocity of gas in the inner tube was 2.5 m/s at 850°C. In this region the gas film resistance is negligible¹.

To approximate a differential reactor, *i.e.* only small changes in gas composition, the weight of the samples was confined to 50 mg of limestone or magnesite. Estimating the volume of the sample to 0.1 cm³ the space velocity of the gas phase at 850°C amounts to 2.3 · 10⁷ hour⁻¹. Erdős and coworkers^{2,3} consider the magnitude of space velocity of the order of 10⁶ hour⁻¹ to be sufficient for reactive samples. Later measurements with the most reactive sample indicated that even for the maximum reaction rate the concentration of sulphur dioxide did not drop by more than 2% rel.

Reactor Heating

The reactor was heated by an electric resistance coil made of kanthal A—1 wire 3 mm in diameter. The coil was designed and made in accord with manufacturer's (The Kanthal Corp.) recommendations⁴ for the maximum power input of 4 kW. The coil was supported by a 95 cm long ceramic tube fitting the outer diameter of the reactor. The temperature inside the reactor was measured and controlled by a calibrated temperature controller connected to a PtRh—Pt thermocouple. As a very good means of temperature control proved a circuit with two adjustable-ratio auto-transformers supplying necessary power input on a signal of the controller. The necessary power input and hence the voltage on the coils was estimated in advance from the chosen operating temperature. The differences in pre-set inputs amounted to about 10% of the mean value. The temperature within the reactor was maintained constant to within a few degrees of centigrades. The thermocouple was mounted with its joint reaching about 1 cm above the cup with the sample. The reactor was shielded by a 25 cm diameter jacket 100 cm high. The space between the ceramic tube supporting the coil and the jacket was filled with ground corundum. The metal sheet jacket was insulated by a 10 cm thick layer of glass wool.

Preparation of Combustion Gases

The combustion gases were generated by combusting propane in a moderate excess of air. Sulphur dioxide was continuously added to the gases from a pressure cylinder.

Air and propane after purification pass through flow-meters 1 and mixed enter a catalytic combustion reactor 2. The temperature within the reactor is measured by a Ni—NiCr thermocouple 3. The combustion chamber is equipped on its outside with a resistance coil 4. The gas leaving the reactor is mixed with sulphur dioxide metered by a calibrated capillary 7. The piping has two stainless-steel valves 5 to sample the gases. The combustion gas containing sulphur dioxide passes through the reactor 6 to be vented later in the atmosphere.

The combustion reactor was made of 170 mm long heat-resistant 17251 steel 46×3 . The gases are fed axially through the upper flange. The thermometer well is parallel with the axis and reaches the lower third of the reactor height. The whole volume of the reactor was packed with porous alumina spheres 2.5—3.5 mm in diameter. Before use the spheres were impregnated with saturated aqueous solution of cobaltum nitrate, dried and roasted at 950°C . An oxidizing catalyst was used in order to ensure complete combustion of propane.

On the outer surface of the combustion chamber there was a resistance coil (Kanthal A-1) with controlled input 0—2 kW. To start the combustion reactor up the packing was heated to $420\text{--}440^\circ\text{C}$ and the flow rate of the reaction mixture gradually increased. The used propane was drawn from a pressure cylinder. 20% stoichiometric excess of air was used. The combustion temperature was recorded and was found fluctuating between 780 and 800°C . A chromatographic analysis of the combustion products confirmed complete combustion. The combustion gases

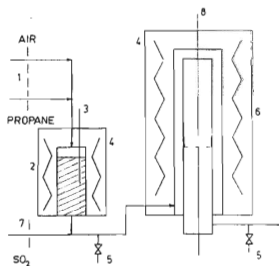


FIG. 1

Sketch of Experimental Set-Up

1 Flowmeters, 2 catalytic combustion chamber, 3 Ni—NiCr thermocouple, 4 heating resistance coil, 5 stainless steel valves, 6 reactor, 7 capillary, 8 PtRh—Pt thermocouple.

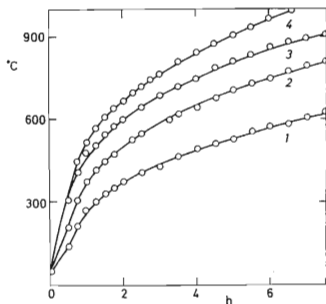


FIG. 2

Reactor Temperature as a Function of Heating Time and Power Input

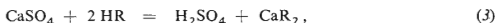
Power input: 1 1.5 kW, 2 2.0 kW, 3 2.5 kW, 4 3.0 kW.

consisted of 10.1% CO₂, 3.5% O₂, 12.6% H₂O, 73.8% N₂. The amount of sulphur dioxide added was controlled so as to keep its content in the combustion gases between 0.05 and 0.30% by vol. Carbon dioxide and oxygen were determined by volumetric analysis in the Orsat apparatus; water vapour by absorption in sulphuric acid. Sulphur dioxide was analyzed by absorption in diluted H₂O₂ solution and subsequent titration by 0.1M-KOH solution.

Analysis of Solid Phase

The samples of limestone or magnesite exposed in the reactor to the combustion gases containing sulphur dioxide were analyzed on the content of sulphate.

To dissolve the sample the reacted particles were first ground to a fine powder and heated with a strong acid cation-exchange resin (Wofatit KPS 200) in distilled water on a steam bath. Calcium sulphate⁵ as well as calcium oxide⁶ are slightly soluble in water. By trapping the calcium ions on the hydrogen form of the resin according to the following reactions



the equilibrium is shifted in the desirable direction. The sulphate ions are transferred into the solution with simultaneous trapping of the cations which might interfere with the determination of sulphate by titration⁷. With the aid of the cation-exchange resin one can avoid harsh methods of dissolution such as *e.g.* trituration with concentrated acids or fusion.

The capacity of the wet activated ion-exchange resin according to the manufacturer is 1.6 · 10⁻³ g equiv./g. Approximately triple excess of ion-exchange resin over calcium was used to dissolve the sample.

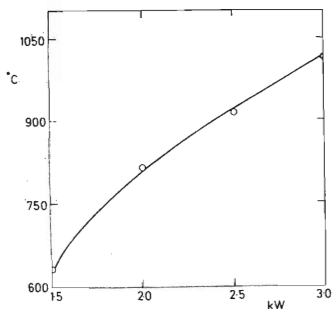


FIG. 3

Attainable Reactor Temperature as a Function of Power Input

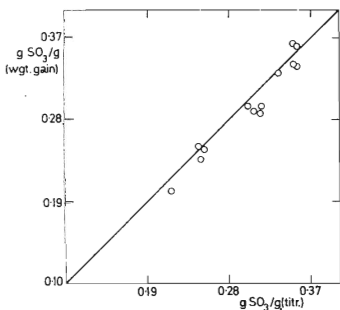


Fig. 4

Comparison of the Titration and the Weight Gain Method of Sulphate Determination

The content of sulphate was determined by titration with 0.005 M-Ba(ClO₄)₂ solution in 80% isopropyl alcohol. The indicator was a mixture of thorine and methylene blue in 5 : 2 ratio whose originally bright yellowish green colour first dimmed and turned violet with the last drop indicating the end of the titration. The colour transition of the indicator was tested by a series of known samples of dilute solutions of sulphuric acid. The concentration of the indicator was in all titrations identical and all analyses were carried out at daylight.

Phosphates and fluorides present in higher concentrations⁸ interfere with the determination.

The results of the test analyses of known samples of CaO and CaSO₄ were within the accuracy of weighing.

Measurement

Having established the preselected temperature and having steadied the whole system (the flow rates of gases, temperatures) the weighed sample of dried limestone was placed into the reactor. The weight of the sample was in all cases about 50 mg. The time of exposure of the sample to the combustion gases was measured by a stop watch.

The sample removed from the reactor was partially cooled and transferred quantitatively from the quartz gauze into a small weighing bottle. To eliminate the effect of air moisture the sample was weighed immediately after removal from the reactor. The degree of conversion of limestone to calcium sulphate was determined from the amount of sulphate and calcium in the sample.

RESULTS

The Effect of Power Input on the Reactor Temperature

These results are presented because they are thought to be useful for an estimate of the power input in design of similar reactors. Before starting the experiments the effect was examined of the power input and the time of heating on the temperature within the reactor. No gas was passing through the reactor in these measurements. The power input was calculated from the current and the resistance (4.37 ohm) of the heating coil. The power input ranged between 1.5 and 3.0 kW and the maximum time of heating at a selected power input was 7 ½ hours.

From the curves in Fig. 2 it is apparent that after more than 7 hours of heating the temperature within the reactor has not yet levelled off. The effect of the power input on the temperature within the reactor after 7 hours is apparent from Fig. 3. The curve in this figure indicates that a power input corresponding to 1000°C amounts to 2.9 kW and that the available input of the heating coil was designed sufficiently conservatively.

A Comparison of the Titration Method with the Weight Gain

The amount of sulphates in a reacted sample may be determined also by direct weighing because at high temperatures and in the presence of oxygen calcium sul-

phate is the sole product of sulphatation. All sulphur found by analysis in solid samples exposed to the combustion gases in the reactor was present as sulphate.

This method applied to a sample of limestone exposed to the combustion gas free of sulphur dioxide provides information about the loss due to calcination. As the next step another sample of the same limestone is exposed to the combustion gas containing sulphur dioxide under identical conditions. The difference of the sulphated and calcined sample gives the weight of captured sulphur trioxide.

In a series of experiments the sulphates were determined for comparison both by direct weighing and the titration method. The results of both methods are shown in Fig. 4. Of the thirteen samples the largest difference amounts to 10.2 or 7.1% and the smallest difference was 0.9 or 1.2% rel. The average difference was 4.3% rel. The agreement of both methods can be rated as good and both methods as equivalent. The method of the weight gain is generally somewhat less laborious but cannot be applied to samples of fine particles.

It can be concluded that the design, the heating and the temperature control of the reactor proved useful. The apparatus has been in permanent operation for more than two years. The above procedure provided valuable information about the reaction between limestone and sulphur dioxide in flue gas. The results will be published subsequently.

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