Rotating Disk Apparatus for Reaction Rate Studies in Corrosive Liquid Environments

D. R. BOOMER AND C. C. MCCUNE
Chevron Oil Field Research Company, La Habra, California 90631

AND

H. S. FOGLER
Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48104

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This paper describes the design and use of a rotating disk apparatus for studying reactions between fluids and solid surfaces. The apparatus is capable of operation in extremely corrosive liquid environments under controlled pressures and temperatures up to 70 atm and 150°C. The design includes a unique magnetic drive assembly that allows the disk to be rotated in the high pressure reactor vessel without the need of a stuffing box seal. All parts that contact corrosive fluids are fabricated from Hastelloy alloys and Teflon. A special feature of the reactor vessel is its ready conversion to a high pressure visual cell.

INTRODUCTION

The rotating disk is increasingly being applied in the laboratory for studying reactions between fluids and solid surfaces.[1,2] Litt and Serad[2] point out that a disk spinning in a fluid has the following advantages over the traditional system of the fluid flowing over a flat plate: (1) No flow tunnel is required because the fluid motion is induced by the disk; (2) large fluid volumes are not required; (3) end effects are minor, whereas with a flat plate they can be a major factor; (4) a disk rotating in an infinite fluid volume represents a three-dimensional flow system for which there exists an exact solution to the Navier–Stokes equations; and (5) the heat and mass transfer coefficients are constant over the surface of the disk, whereas they decrease down the flat plate. The spinning disk surface is "uniformly accessible," i.e., for laminar flow there are no radial temperature or concentration gradients.

This paper describes a rotating disk apparatus with the design capability of operating in extremely corrosive liquid environments up to 70 atm and 150°C. The apparatus uses a unique magnetic drive assembly that allows the disk to be rotated from outside the reactor without the need of a troublesome stuffing-box seal. The equipment is assembled in an insulated box using an air bath for temperature control. An added feature of the apparatus is that the rotating disk reactor vessel can be readily converted to a high pressure visual cell.

BASIS OF DESIGN

According to Levich[3] the mass flux of a solute from a fluid to the surface of a disk rotating under laminar conditions, i.e., with a Reynolds number no greater than 10^4–10^5, is given by the relation

$$j=0.62D^{\frac{2}{3}}\nu^{-\frac{1}{6}}\omega^{\frac{1}{2}}C_{02}\ \mathrm{g\cdot mole/cm^2\cdot sec}, \qquad (1)$$

where D is the diffusion coefficient of the solute (square centimeters per second), ν is the fluid kinematic viscosity (square centimeters per second), ω is the angular velocity of the disk (radians per second), and C_0 is the solute concentration (gram·mole per cubic centimeters). Therefore, the diffusional rate constant may be defined as

$$k=0.62D^{\frac{2}{3}}\nu^{-\frac{1}{6}}\omega^{\frac{1}{2}}\ \mathrm{cm/sec} \qquad (2)$$

and the diffusion boundary layer may be approximated by

$$\delta\simeq\frac{DC_0}{j}=1.61\left(\frac{D}{\nu}\right)^{\frac{1}{3}}\left(\frac{\nu}{\omega}\right)^{\frac{1}{2}}\ \mathrm{cm}. \qquad (3)$$

Equations (2) and (3) are the basis for the design and operation of a rotating disk system for studying the reaction of a fluid with a solid surface. However the conditions specified in the theory must be adhered to. The flow in the vicinity of the disk must be laminar; the Reynolds number, $\omega R^2/\nu$ (R= the disk radius), must not exceed 10^4–10^5. The theory assumes the disk is an infinite plane. Therefore, the disk diameter must be much larger than the thickness of the diffusion boundary layer. In the case of a liquid the boundary layer thickness is approximately 10^{-3} cm, and for a gas it is in the order of 10^{-1} cm. The disk diameter and angular velocity should be chosen to satisfy the Reynolds number and boundary layer restrictions. The theory also assumes that the disk is spinning in an infinite fluid volume. However, Gregory and Riddiford[4] demonstrated in a liquid system that if the vessel diameter was at least double the disk diameter, the observed transport rate was independent of the vessel diameter. They also showed that a 5.3 cm disk rotating at 146 rpm could be as close as 0.5 cm from the vessel bottom without causing interference with the flow.

The use of the rotating disk system to study the relative importance of diffusion and reaction rate controlling effects in the reaction of a fluid with a solid can be illustrated with the aid of Eq. (2) and Fig. 1, which is a plot of the rate constant as a function of the square root of the disk angular velocity, for a hypothetical case. It is assumed that the angular velocity is the only variable

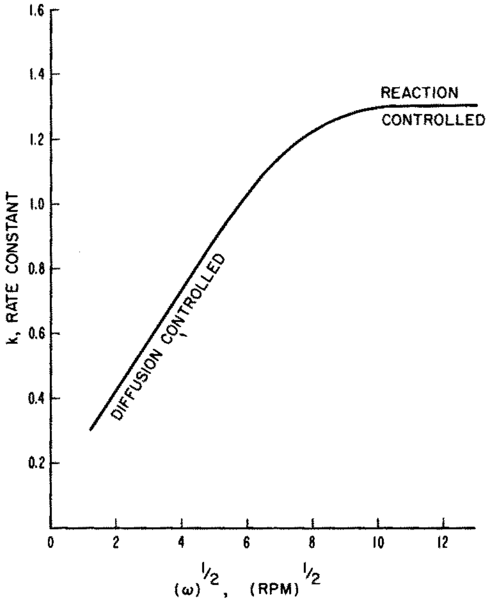

FIG. 1. Plot of rate constant vs square root of disk rotation speed for hypothetical case indicating regions of reaction rate and diffusion control.

and laminar conditions are maintained. As predicted by Eq. (2), a constant positive slope is obtained in the region of diffusion control. However, at higher velocities the effect of velocity decreases as chemical reaction rate control begins to take effect. Finally, a region is reached where increasing angular velocity has no effect and the chemical reaction completely controls. Thus the relative importance of the two control mechanisms can be analyzed.

APPARATUS

General

An over-all layout of the rotating disk apparatus is shown schematically in Fig. 2 and illustrated in Fig. 3.

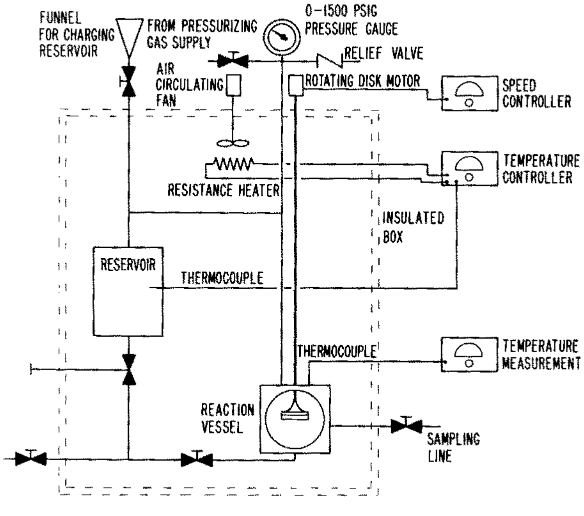

FIG. 2. Schematic diagram of over-all layout of rotating disk apparatus.

The principal components are a reaction vessel and a liquid reservoir. They are mounted in an insulated, double walled, stainless steel box enclosure. The reaction vessel, liquid reservoir, and liquid flow lines were fabricated from Hastelloy B. The flow lines that contact gas only are Hastelloy C. All other parts of the reactor that come in contact with the reacting liquid were fabricated from Teflon. Consequently, very corrosive liquids including concentrated hydrochloric acid (37 wt%–38 wt% HCl) and hydrochloric–hydrofluoric acid mixtures (up to 15% HCl–5% HF) can be used in the system up to a pressure of 70 atm and a temperature of 150°C.

The temperature within the insulated box is maintained by the forced circulation of air over electrical resistance heaters, which are wired to a temperature controller. The pressure of the reactor and reservoir is controlled from an external, regulated gas supply. A valved funnel is available for charging the reservoir with liquid.

At the start of a test a sample of the solid to be reacted is mounted in the reactor and the reservoir is charged with the reacting liquid. When the temperature and pressure have become stabilized at their required levels rotation of the disk is begun and the valve below the reservoir is opened. The liquid flows by gravity from the

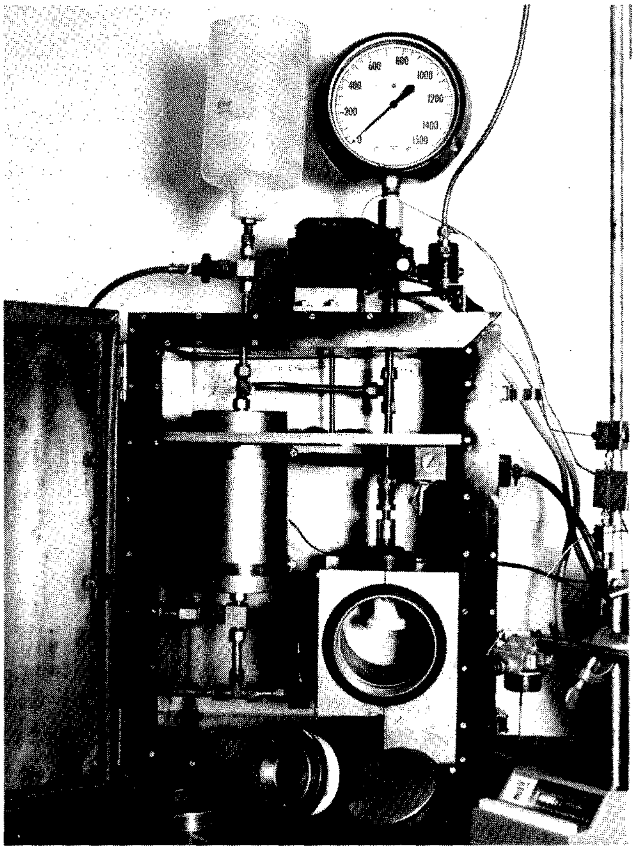

FIG. 3. Photograph of rotating disk apparatus.

reservoir into the reactor. During the course of the test liquid samples can be drawn from the reactor. Lines and valves are available to allow the system to be drained and flushed out at the termination of the test.

INSULATED BOX ENCLOSURE

The insulated box enclosure has double walls of 304 stainless steel with the walls separated by Micarta and the 3.9 cm space between the walls filled with fiberglass. Removable doors are mounted on the front and back of the box. The doors also are double walled stainless steel filled with fiberglass. Silicone rubber gaskets provide a seal when the doors are closed. A 10 cm×10 cm viewing window is installed in the front door. This window is double glazed, hermetically sealed Pyrex with a 1.3 cm gap between the two sheets of glass.

Heating within the box is accomplished with two 600 W, 110 V resistance heaters wired in series giving a net of 300 W of power. A baffle divides the enclosure into an upper and lower compartment. Each heater is mounted in a 10 cm diam opening in the baffle. A fan is located above one of the heaters. With the fan on, air circulates within the enclosure, across the two heaters, and over the reaction vessel and reservoir.

REACTION VESSEL

A scale drawing of the rotating disk reactor vessel is shown in Fig. 4. The vessel was fabricated from a 19 cm section of schedule 40 Hastelloy B pipe (11.4 cm o.d., 10.2 cm i.d.). The vessel is mounted horizontally. The two end plates, also fabricated from Hastelloy B, are held in position by threaded retainer rings. Ethylene–propylene O-rings provide a seal between the end plates and reactor wall. A thermowell and liquid sampling line (not shown in Fig. 4) are also welded on the wall of the vessel. The inside distance between the two end plates is 12.5 cm, and the capacity of the reactor vessel is about 975 cc.

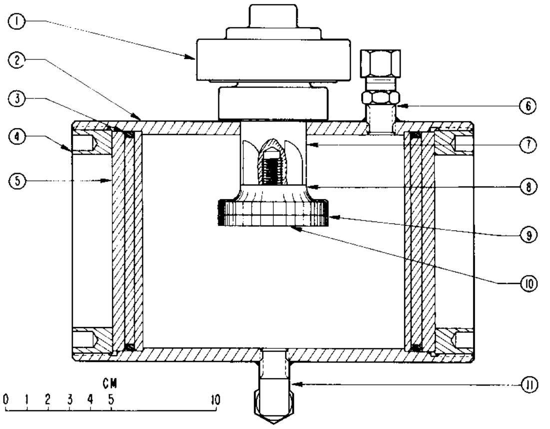

Fig. 4. Scale drawing of rotating disk reactor vessel. 1—Magnetic coupling; 2—reactor body (Hastelloy B); 3—O-ring seal (Parker #2-241, ethylene–propylene); 4—threaded retainer ring (Hastelloy B); 5—end plate (Hastelloy B); 6—gas line connection (Hastelloy B); 7—sample holder base and impeller (Teflon); 8—sample holder (Teflon); 9—shrinkable tubing (Teflon); 10—sample disk; 11—liquid inlet (Hastelloy B).

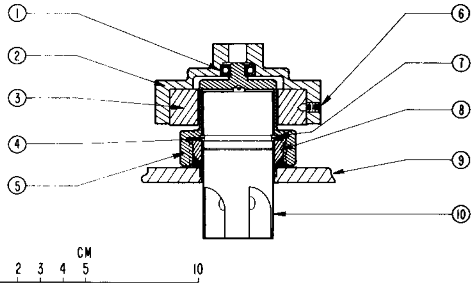

Fig. 5. Scale drawing of magnetic drive. 1—Bearing (Norma-Hoffman #R4PP); 2—aluminum holder for magnet; 3—ceramic magnet; 4—O-ring seal (Parker #2-28, ethylene–propylene); 5—barrier, threaded to welded collar (Hastelloy B); 6—set screw; 7—retaining ring; 8—collar, welded to reactor body (Hastelloy B); 9—reactor body (Hastelloy B); 10—rotor (Teflon).

Magnetic coupling through the reactor wall was chosen to connect the rotating sample holder and rotor to the shaft from the electric drive motor. This eliminated the need for a stuffing box with its inherent sealing and corrosion problems. The diagram of the magnetic drive, drawn to scale, is shown in Fig. 5. The magnetic coupling was the drive assembly from a Teel #1P676 pump and modified for the use described herein. Because of the difference in thermal expansion between the aluminum holder and the ceramic magnet, set screws were required to retain the magnet in the holder. The holder is connected by a shaft to an electric motor (Bodine NSE 11R motor with a 36:1 gear reducer head) and rotates on an antifriction bearing that is mounted on the top of a corrosion proof barrier between the inside of the reactor vessel and the magnetic drive. The cap is screwed onto a Hastelloy collar, which is welded to the vessel wall. An ethylene–propylene O-ring provides a seal.

The rotor and driven magnet of the coupling are shown in detail in Fig. 6. The magnet (actually an eight-pole, torus shaped magnet) is enclosed in a Hastelloy B cap. An O-ring seals the cap to the Teflon rotor base to protect the magnet from corrosion. A Hastelloy B screw joins the cap to an aluminum insert, which in turn is threaded into the Teflon base. The Teflon base is notched and drilled with two holes so that it can function as an agitator for the fluid in the reactor. A spring retainer, fitting in a groove in the Hastelloy cap, was provided to hold the rotor in place. Because of the weight of the rotor, the drive magnet is not strong enough to hold the rotor in place when there is no liquid in the reactor vessel.

The disk-shaped, Teflon sample holder screws into the rotor base. The sample disk, 5.1 cm in diam, is attached to the sample holder by means of shrinkable Teflon tubing, which is capable of shrinking with the application of heat

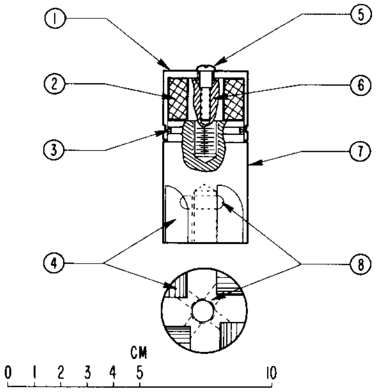

FIG. 6. Scale drawing of rotor assembly. 1—Protective cap (Hastelloy B); 2—magnet (from Teel #1P676 pump); 3—O-ring seal (Parker #2-008, comp. E540-8; 4—milled notches; 5—screw (Hastelloy B); 6—aluminum insert for joining protective cap to base; 7—base (Teflon); 8—0.5 cm holes drilled through base.

from an initial diameter of 5.5 cm down to a minimum of 4.1 cm. The Teflon is cleanly cut off with a razor blade at the edge of the sample.

The design of the reactor vessel permits it to be readily converted to a high pressure visual cell as shown in Fig. 7. The magnetic coupling is used as before except the sample holder is removed from the rotor, and the rotor then only serves as an agitator. A window assembly consisting of a tempered plate glass window, 2.54 cm thick and 7 cm in diam, held in place by a Teflon clamp screwed to a Hastelloy B end plate is mounted at each end of the vessel. The seal between the window and end plate is an ethylene–propylene O-ring. The same sample holder used for the rotating disk sample is inverted and mounted on a Teflon base attached to the window assembly to become a stationary disk sample holder. The capacity of the reaction vessel when used as a visual cell is decreased to 650 cc. The design operating conditions for the visual cell are the same as for the rotating disk reaction vessel, i.e., 70 atm and 150°C. Corrosion resistance is the same except the use of hydrofluoric acid is not permitted because it would react with the glass windows. The cell is viewed through the double glazed window in the front door of the insulated box enclosure. The cell interior is illuminated by the light mounted on the back door. For safety reasons the cell is normally viewed by means of a mirror mounted at the door window for this purpose.

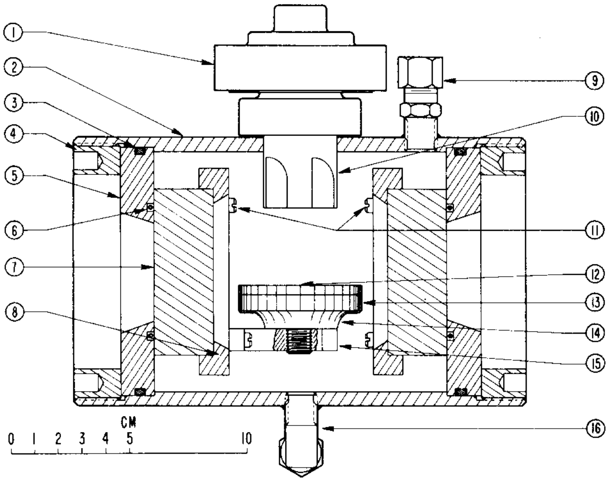

FIG. 7. Scale drawing of high pressure visual cell. 1—Magnetic drive; 2—reactor cell body (Hastelloy B); 3—O-ring seal (Parker #2-241, ethylene–propylene); 4—threaded retainer ring (Hastelloy B); 5—window end plate (Hastelloy B); 6—O-ring seal (Parker #2-137, ethylene–propylene); 7—tempered plate glass window, 2.54 cm thick; 8—window retainer ring (Hastelloy B); 9—gas line connection (Hastelloy B); 10—impeller (Teflon); 11—window mounting screws (Hastelloy B); 12—sample; 13—shrinkable tubing (Teflon); 14—sample holder (Teflon); 15—sample holder base (Teflon); 16—liquid inlet (Hastelloy B).

LIQUID RESERVOIR

The liquid reservoir was fabricated from a 21.6 cm length of schedule 40 Hastelloy B pipe. End plates, retainer rings, and O-rings similar to those described for the reaction vessel were used to close the ends. The reservoir is mounted vertically in the insulated box enclosure, and inlet and outlet lines are installed in the center of the end plates. The capacity of the reservoir is 1200 cc.

FLOW LINES AND VALVES

Pressure tubing was not readily available in Hastelloy B. Consequently, all flow lines that contact hot liquid had to be fabricated from 1.11 cm Hastelloy B solid rod. The rod was drilled out to 0.64 cm and the ends of each piece were machined to be compatible with commercially available high pressure, Hastelloy B tubing fittings. Hastelloy C tubing, which was available, was used wherever only gas contact was expected. Hastelloy B needle valves were installed throughout the system. In some cases it was necessary to lengthen the stem to permit the valve to be operated from outside the closed insulated box.

MISCELLANEOUS

The required power switches and instruments used for control of temperature, pressure, and disk rotational speed were mounted on a special control panel. Temperature is controlled with a Wheelco 293 controller, which was modified to allow the desired temperature to be set on a digital dial. An iron–constantan thermocouple attached to the side of the liquid reservoir supplies the temperature signal to the controller. A second thermocouple located in the thermowell of the reactor vessel is used to read the temperature with a potentiometer.

The liquid reservoir and reaction vessel are always at equal pressures because a gas line interconnects the tops of the two vessels. A regulated external gas supply connected to that line is used to control the pressure within the system. A choice of gaseous atmospheres is provided depending on the gas supply that is chosen. An adjustable pressure relief valve is installed for safety. The entire system was pressure tested at 1.5 times the rated maximum.

The speed of the rotating disk or agitator is set with a Minatrol model M22 motor speed controller and measured with a Zero-Max model B-215 tachometer with a range of 0–500 rpm.

EXAMPLE OF AN EXPERIMENT USING APPARATUS

A series of experiments was carried out using the rotating disk apparatus in which calcium carbonate disks were reacted with hydrochloric acid. The disks, 5.1 cm in diam and 0.64 cm thick, were cut from a white Vermont marble, which analyzed as 98%–99% calcium carbonate.

In each experiment a disk, supported on the sample holder by shrinkable Teflon tubing, was placed in the reaction vessel, and the reservoir was charged with 1 liter of 1*N* hydrochloric acid. The system was pressurized under 55 atm of nitrogen, and the temperature was set at 25°C. When the pressure and temperature were stable, disk rotation was started and the valve below the reservoir was opened to allow the acid to flow into the reactor. During the course of the run small liquid samples, about 2 ml each, were periodically drawn from the reactor. The samples were later analyzed for calcium by atomic absorption spectroscopy. At the termination of the experiment the pressure was released and the system drained and flushed with distilled water.

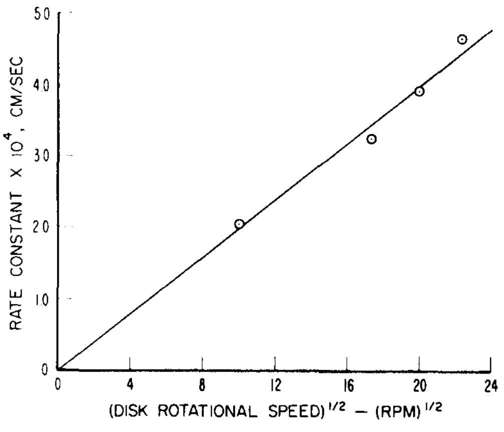

FIG. 8. Plot of rate constant vs square root of disk rotational speed for white Vermont marble in 1*N* HCl.

The calcium content of the collected samples was used to determine the rate of reaction and the rate constant. The results of four experiments are shown in Fig. 8 in which the rate constant is plotted as a function of the square root of the disk rotational speed. The resultant approximate linear relationship agrees with that predicted by Eq. (2) for a diffusion controlled reaction. Therefore the reaction of the acid is much faster than its rate of diffusion from the bulk of the liquid to the surface.

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[1] F. G. Blake, D. Landolt, and C. W. Tobias, Rev. Sci. Instrum. **39**, 1753 (1968).

[2] M. Litt and G. Serad, Chem. Eng. Sci. **19**, 867 (1964).

[3] V. G. Levich, *Physicochemical Hydrodynamics* (Prentice-Hall, Englewood Cliffs, N. J., 1962), p. 69.

[4] D. P. Gregory and A. C. Riddiford, J. Chem. Soc. **1956**, 3756.