Fluid Flow in Porous Media Studied by a Nuclear Magnetic Resonance Technique

Abstract. *A nuclear magnetic resonance technique was used to determine the hydrocarbon content of a porous material during its displacement by an oil-miscible but hydrogen-free liquid (CCl_4). After displacement of heptane by an amount of carbon tetrachloride equal to 1.5 times the pore volume, about 10 percent of the heptane remained, presumably in "dead-end" pores.*

The influence of pore structure on fluid velocity distribution during the flow of fluid through porous media is still largely unknown. Most studies on sedimentary rock indicate that for materials such as sandstones all pores conduct fluid when only a single fluid phase is present. When, however, two immiscible fluids are present, one of the two may trap the other either in single pores or in isolated large fingers, resulting in "dead-end" pore volume (*1*). The phase contained in these dead-end pores is stagnant and communicates with the flowing phase only through molecular diffusion; therefore, not all of the fluid-filled pores contribute to the flow of that fluid.

Careful studies by Coats and Smith (*2*) now indicate that during the flow of a single-phase fluid in a Torpedo sandstone, unconsolidated sand, and sintered alundum, there is a stagnant volume of 2.4 to 10 percent of the total pore volume. This result has sufficient importance in hydrology, soil physics, and petroleum technology to warrant further study. We investigated this phenomenon by an entirely different method and on another sandstone.

Our method depends upon the observation that a liquid that chemically incorporates hydrogen atoms (such as water or hydrocarbon) will absorb electromagnetic energy from a radiofrequency (rf) field when the liquid is in a d-c magnetic field corresponding to the resonant frequency of the hydrogen nucleus (*3*).

We encased a 15-cm long Boise sandstone (permeability, 1.7 darcies; porosity, 26 percent) core of 1.9 cm diameter in a heat-shrunk plastic tube which also held brass nipples to each end so that liquid could pass through the sample. This sample was placed vertically inside the sample coil (2.5 cm in diameter, 2.5 cm long) of the NMR (*4*) apparatus.

The coil, mounted in the gap of a 30-cm Varian electromagnet, was connected to a marginal oscillator which provided rf energy at 34 Mc/sec. At this frequency, hydrogen nuclei in water or in a hydrocarbon absorb energy when the d-c magnetic field is 8000 gauss. In operation, the frequency of the rf field was held constant and the d-c magnetic field was varied a few gauss above and below the value for maximum absorption, in order to observe the energy absorption from the oscillator. The NMR spectrometer developed for this work is described by Timur *et al.* (*4*); the experimental arrangement of the NMR apparatus is explained in (*5*).

The rock sample, before being placed in the magnetic field, was saturated with n-heptane by evacuating the pore space and then allowing the liquid to enter under atmospheric pressure. The nuclear resonance absorption spectrum was then recorded. The derivative of the NMR absorption curve so obtained is given in Fig. 1*a*. Carbon tetrachloride was then forced upward through the sample, with a frontal velocity of 0.971 × 10^{-3} cm/sec, until an amount equal to approximately double the pore-volume was injected. After injection of about 1.5 times the pore volume, no further decrease in amplitude of the NMR absorption signal was observed. The derivative of the NMR absorption curve corresponding to injection of carbon tetrachloride to 1.525 times the pore volume is given in Fig. 1*b*. The derivative of the NMR absorption curve obtained for a dry sample is presented in Fig. 1*c*.

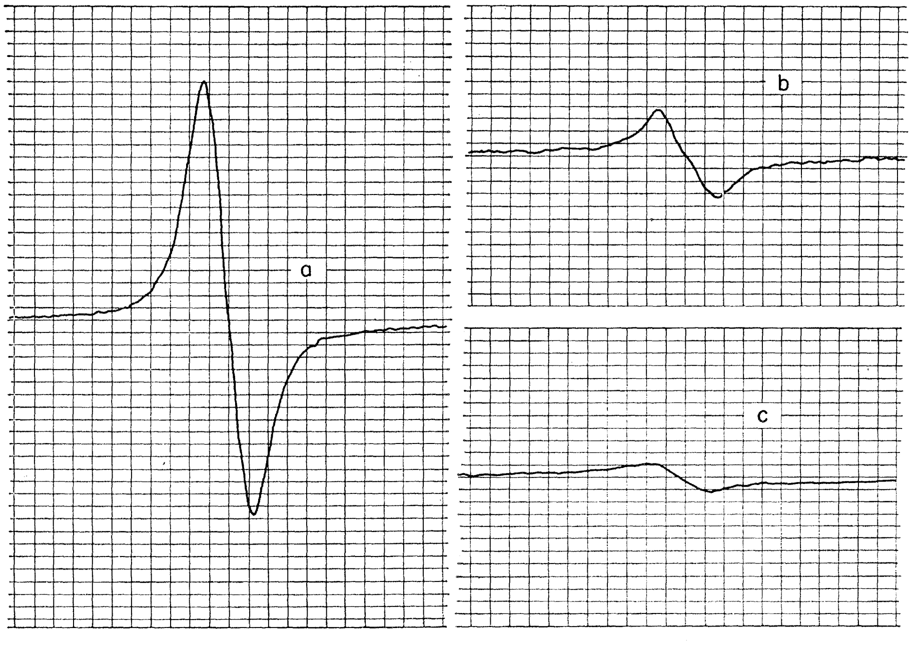

Fig. 1. Derivatives of the NMR absorption curves: (*a*) 100 percent heptane saturation; (*b*) after injection of 1.525 times the pore volume of carbon tetrachloride; (*c*) 0 percent heptane saturation. The amplitude of the NMR absorption signal (in arbitrary units) is 132.0 in *a*, 29.4 in *b*, and 17.4 in *c*.

A separate series of measurements of NMR absorption-signal amplitude on samples of Boise sandstone of known heptane content had established that there was a straight line proportionality between these parameters. Figures 1*a* and 1*c*, corresponding to a heptane content of 100 percent and 0 percent, respectively, permit the proportionality content to be calculated for the heptane-carbon tetrachloride system. Using this proportionality constant, we calculated from Fig. 1*b* that the heptane content of the sample, after 1.525 pore volumes of carbon tetrachloride had passed through, was 10.5 (± 0.4) percent of the pore volume (*6*). This result indicated that, in spite of the favorable viscosity and density ratio between *n*-heptane and carbon tetrachloride, 10.5 percent of the heptane was trapped in pores which did not contribute to the flow. It is unlikely that the trapped heptane observed by the NMR technique diffused downward from the front into dead-end pores. The concentration, *C*, of heptane in the carbon tetrachloride resulting from diffusion downward from the front is given approximately by

$$C = C_0 \operatorname{erfc} (l / 2\sqrt{Dt})$$

where *l* is distance from the front, *D* is the diffusion coefficient of heptane in carbon tetrachloride, and t is time (*7*). For the parameters involved ($l \simeq 5$ cm, $D \simeq 10^{-5}$ cm^2/sec) there can be only 0.06 percent heptane, even after 30 hours, in the carbon tetrachloride as a result of diffusion from the front.

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References and Notes

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6. The uncertainty is from the standard deviation of the mean of the proportionality constant which in turn is based on six calibration runs.
7. The abbreviation erfc refers to a complementary error function.

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High-Pressure B-Type Polymorphs of Some Rare-Earth Sesquioxides

Abstract. *New high pressure forms of the sesquioxides of holmium, erbium, thulium, ytterbium, lutetium, and yttrium have been obtained by exposure of the C-type sesquioxides to pressures between 25 and 40 kilobars and temperatures between 900° and 1020°C. X-ray diffraction analysis shows that these new high-pressure phases are of the monoclinic B-type which is known for several of the lighter rare-earth sesquioxides (samarium through dysprosium).*

The crystal chemistry of the rare-earth sesquioxides was first studied in a systematic manner by Goldschmidt, Ulrich, and Barth (*1*). They found that these compounds could exist in three polymorphic forms, which were denoted as A, B, and C. This classification is still in use. The crystal structure of these polymorphs has been determined in a number of investigations (*2*). According to these, the A-modification is hexagonal (space group $P\bar{3}m1$), the B-modification is monoclinic (probably $C2/m$), and the C-modification is cubic ($Ia3$).

In their study of the stability relationships of the sesquioxide polymorphs (*1, 3*) Goldschmidt and his coworkers considered all phase transformations to be reversible. Subsequent studies (*4*) showed that for pure oxides the C → A and C → B transformations could be produced but not reversed, and no conclusive proof could be found for any transition between A and B modifications. Roth and Schneider (*5*) concluded that the C-modifications observed for some of the lighter rare earth oxides are metastable with respect to either the A- or B-form and that each rare earth sesquioxide is stable in only one of the three polymorphic forms.

Other recent investigations have modified this conclusion concerning the C → B transformation. Thus, the change has been shown to be reversible for pure Dy_2O_3 and Tb_2O_3 (*6, 7*), for Gd_2O_3, Eu_2O_3, and Sm_2O_3 in the presence of water as a catalyst (*8*), and is rendered reversible in Eu_2O_3 by stabilization of the C phase with ThO_2 (*8*). From these observations Warshaw and Roy (*6*) concluded that the sesquioxides of samarium through dysprosium exist in two stable enantiotropic forms with a transformation temperature that increases almost linearly with decreasing ionic radius. The apparent irreversibility of the B → C transformation in pure dry samarium, europium, and gadolinium sesquioxides is most likely due to unfavorable kinetics at the equilibrium temperatures.

At the present time the sesquioxides of yttrium, holmium, erbium, thulium, ytterbium, and lutetium have been found in only one crystalline form, the C type. Extrapolation of the temperature curve of the C → B transformation predicts conversion to the monoclinic phase above their melting points with the possible exception of yttrium sesquioxide.

In all previous investigations, the primary object has been the study of temperature effects on the crystal chemistry of the rare-earth (R) sesquioxides; the role of pressure has not been systematically investigated. From the fact that there is a decrease in volume per mole of R_2O_3 in going from C → B → A (Fig. 1) one expects that high pressures should favor the B- and A-forms over the C-form, and the A-form over the B-form. Since these transformations are of the reconstructive type, it can be expected that new high-pressure modifications could be retained by temperature and pressure quenching to ambient conditions.

In our investigation the influence of pressure on the C-type phases of the heavy rare-earth sesquioxides has been studied at elevated temperatures. Rare-earth sesquioxides of the C-type (99.9+ percent purity) which had been annealed in air at 1000°C for several hours to remove H_2O and CO_2 were used as starting material. Terbium sesquioxide was prepared by reduction of Tb_4O_7 with hydrogen.

For the high-pressure experiments a tetrahedral anvil apparatus (*9*) was used. In the pressure calibration a value of 25.3 kb was assumed for the Bi (I → II) transformation (*10*) and 40 kb for the Yb transformation (*11*).

Oxide samples (about 0.4 g) were placed in Pt envelopes (2 mil) and pressed to pellets at 0.4 kbar. Several pellets, separated by pyrophyllite spacers, were then placed in a pyrophyllite tube which fitted the graphite heater inside the pyrophyllite tetrahedron. Graphite disks were inserted at both ends of the heater to assure good contact with molybdenum tabs through which the power connections were made. The temperature was measured by a ceramic-coated thermocouple consisting of Pt and Pt containing 13 percent Rh encased in a stainless steel sheath (0.1 cm outside diameter). The thermocouple bead, coated with alundum cement, was located in the pyrophyllite tube containing the sample pellets. Temperatures could be read to ±1°C; fluctuations during a run were usually kept to within ±10°C, in some cases ±20°C. After the treatment at high pressure and high temperature,

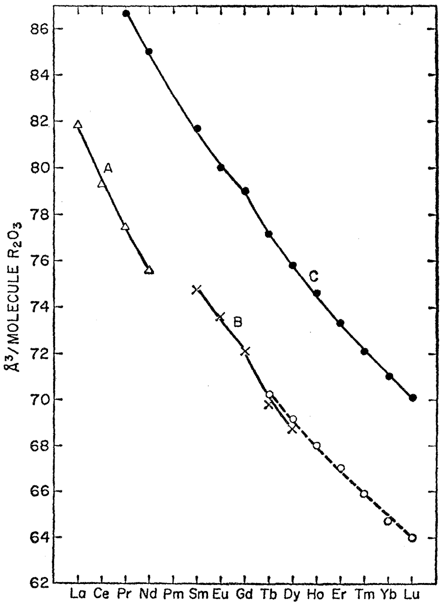

Fig. 1. Molecular volume of rare earth sesquioxide crystal modifications. Solid line, previous work; broken line, this work.