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Characterization of the surface properties of epoxy-type models used for multiphase flow studies in fractured media and creation of a new model

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[1] Epoxy models have been used as analogs for fractured rock surfaces in many laboratory investigations of multiphase flow processes. However, there is no agreement on how well or poorly such an analog replicates the surface chemistry of geologic materials, nor is there a satisfactory analysis of the surface properties of epoxy. This paper addresses the issue of accurately characterizing the surface chemistry of a typical epoxy used in laboratory multiphase flow studies and comparing that surface to a polystyrene surface and a radio frequency glow discharge treated polystyrene surface. Surface properties were determined using direct contact angle measurements of polar and apolar liquids on flat test samples. The epoxy was determined to have surface properties as follows: $\gamma = 62.3$, $\gamma^{LW} = 39$, $\gamma^{AB} = 23.3$, $\gamma^{\oplus} = 0$, and $\gamma^{\ominus} = 23.3$ mJ/m^2, where γ is the total surface tension of the solid, γ^{LW} is the Lifshitz-van der Waals (LW) surface tension component, γ^{AB} is the Lewis acid base (AB) surface tension component, $\gamma^{\ominus}$ is the electron-donor (negative) parameter, and $\gamma^{\oplus}$ is the electron-acceptor (positive) parameter. Values of $\gamma^{\ominus} < 27.9$ mJ/m^2 indicate a hydrophobic surface, which means that epoxy is not a good analog for most geologic materials. This study also explores the use of radio frequency glow discharge plasma to add hydroxyl functionality to polymer surfaces producing a material with alterable surface properties and the same optical and casting properties as epoxy. Using this method, the degree of alteration of the surface chemistry of polymer fracture models can be controlled, allowing the creation of models with a variety of different wettabilities. The resultant models were found to be durable, long lasting, and a potentially very useful alternative to the more typical epoxy models. *INDEX TERMS:* 5104 Physical Properties of Rocks: Fracture and flow; 1829 Hydrology: Groundwater hydrology; 1045 Geochemistry: Low-temperature geochemistry; 5199 Physical Properties of Rocks: General or miscellaneous; *KEYWORDS:* fracture mechanics, hydrogeology, surface chemistry

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1. Introduction

[2] Nonaqueous phase liquids (NAPLs), composed of one or more organic liquids which exist as a stable separate phase in equilibrium with water, have long been recognized as serious and persistent groundwater contaminants [*Mercer and Cohen*, 1990; *Pankow and Cherry*, 1996]. Owing to their extremely low solubilities in water, NAPLs are able to travel substantial distances through the subsurface as a separate liquid phase and create complex multiphase cleanup problems [*Feenstra and Cherry*, 1988; *Hunt et al.*, 1988a, 1988b]. While frequently described as immiscible fluids, the solubilities of NAPL in water are, in fact, sufficiently high to create significant groundwater contamination [*Pankow and Cherry*, 1996].

[3] Over the past decade a substantial body of work has been done on characterizing the behavior of NAPLs in various geologic media [*Kueper*, 1989; *Schwille*, 1988] (see *Pankow and Cherry* [1996] for an overview). Even with an extensive body of work in the field, understanding of the flow behavior and residual distribution of NAPLs in fractured media is still under development, with many unresolved issues. The migration of NAPLs through fractured bedrock has been recognized as a widespread problem at sites throughout North America. Not only do fractures provide both horizontal and vertical conduits for extensive

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NAPL migration, they also allow NAPL migration to occur in pathways entirely unassociated with the local groundwater flow [*Reitsma and Kueper*, 1994].

[4] Two key properties greatly influence NAPL flow and residual distribution in fractures: the void geometry of the fracture network and the surface wettability of the fracture material. Significant research has gone into establishing the statistical distribution of apertures within fractures [e.g., *Hakami and Barton*, 1990; *Vickers et al.*, 1992; *Brown et al.*, 1986], but there has been little research into the effects of different surface properties on NAPL flow and residual distribution. As experimental data are lacking in this area, when modeling two liquid systems, most researchers assume "perfect wettability" of rock surfaces with respect to water (i.e., water contact angles of zero) or very low contact angles (10° or less) [*Mendoza*, 1992; *Kueper and McWhorter*, 1991; *Pruess and Tsang*, 1990; *Steele and Lerner*, 2001].

[5] There have been several studies of flow in actual fractured rock, but given the opaque nature of the material, it is not possible to visually track fluid pathways during the course of the experiment [*Reitsma and Kueper*, 1994; *Longino and Kueper*, 1999; *Chown et al.*, 1997]. In order to directly observe flow behaviors several researchers have used translucent epoxy models, the surface properties of which have been very poorly characterized [*Gentier*, 1986; *Gentier et al.*, 1989; *Hakami and Barton*, 1990; *Persoff and Pruess*, 1993, 1995; *Cox et al.*, 1995; *Geller and Pruess*, 1995; *Hakami*, 1995; *Su*, 1995; *Geller et al.*, 1996; *Brown et al.*, 1998]. To understand the results of these multiphase laboratory flow studies, it is imperative to accurately characterize the surface properties of the material used and understand how it compares to geologic material.

[6] When two immiscible fluids are in contact with a solid surface, one of those two fluids will be preferentially attracted to that surface and will spread out over a greater contact area, i.e., it will "wet" the surface [*Adamson*, 1990]. This behavior is determined by the interfacial tensions of the fluids and solid involved. Wettability is determined from measurement of the triple-point contact angle at the fluid-fluid-solid interface. For two fluids, NAPL and water, for example, in contact with a solid, Young's equation describes the relationship between the contact angle at the three-way interface and the interfacial tension between the components:

$$\cos\theta = (\gamma_{ns} - \gamma_{ws})/\gamma_{nw} \tag{1}$$

where γ_{ns} is the interfacial tension between the NAPL and the solid, γ_{ws} is the interfacial tension between the water and the solid, γ_{nw} is the interfacial tension between the two fluids and θ is the contact angle measured in degrees at the triple point through the wetting fluid [*van Oss*, 1994]. The contact angle indicates which of the two fluids preferentially wets the surface and varies between 0° and 180°. In the NAPL literature, if the contact angle through the water is $\leq 70°$, the system is considered water-wet; if the water contact angle is $\geq 110°$, the system is considered NAPL-wet or oil-wet, and if the contact angle is between 70° and 110°, it is considered a neutral system [*Dullien*, 1988; *Mercer and Cohen*, 1990].

[7] This terminology however is nonstandard outside of the NAPL research community. In a two liquid system, surface chemists consider the term "water-wet" to mean a water contact angle of 0°, and "oil-wet" to mean an oil contact angle of 0° [*Adamson*, 1990]. In this paper, the terms oil-wet and water-wet will be used to refer specifically to near-zero contact angles. The term hydrophobic will be used for systems in which water is not the preferential wetting fluid, and the term hydrophilic will be used for systems in which water is the preferential wetting fluid. These terms are purely descriptive and do not connote any specific degree of wetting, just the general relationship for the system under discussion.

[8] With only rare examples, such as mercury, liquids will preferentially wet solid surfaces with respect to air [*Mercer and Cohen*, 1990]. Therefore, in the vadose zone, this means that a liquid, either NAPL or water, will preferentially coat the solid surface with respect to air. In NAPL-water systems below the water table, the behavior is much more complex, depending on the mineralogy of the solid surface, the aqueous chemistry, the NAPL composition, the amount of organic material present, the saturation history of the medium and the duration of contact. Generally, with the exceptions of organic rich matter (such as coal, peat, humus, biofilms and some black shale), graphite, sulfur, talc and talc-like silicates, and many sulfides, most natural media will be preferentially wet by water [*Mercer and Cohen*, 1990; *Anderson*, 1987]. However, the existence of oil-wet reservoirs, particularly those in limestones and dolomites, is well documented in the petroleum literature [*Nutting*, 1934; *Benner and Bartell*, 1941; *Leach et al.*, 1962; *Craig*, 1971; *Salathiel*, 1973].

[9] Adsorption and deposition of NAPL components on organic matter can significantly increase the likelihood that NAPL will be or will become the wetting fluid, and NAPL contact angles have been shown to decrease with duration of contact. In the NAPL research literature, however, it has been commonly assumed that nearly all geologic material is water-wet or "perfectly wetting"; that is, water has a near-zero contact angle [*Nicholl and Glass*, 1994; *Nicholl et al.*, 1994; *Reitsma and Kueper*, 1994; *Mendoza*, 1992].

[10] Good characterization of the wetting characteristics of the geologic material under investigation is of great significance because the wetting behavior of the liquids greatly influences both flow behavior and physical distribution in the subsurface. The wetting fluid is at a lower pressure and will coat the surface of the solid occupying the smallest apertures while the nonwetting fluid, which is at a higher pressure, will be isolated inside the areas of largest aperture. The pressure difference between the two phases, called the capillary pressure (P_c), can be related to the size of the aperture invaded by the nonwetting via the Young-Laplace equation:

$$P_c = P_n - P_w = n\gamma\cos\theta/b \tag{2}$$

where P_n and P_w are the nonwetting and wetting fluid pressures, respectively, n is a shape factor that ranges from 2 (for a parallel plate opening) to 4 (for a circular opening), γ is the interfacial tension between the fluids, and θ is the triple-point contact angle as measured through the wetting fluid [*Kueper and McWhorter*, 1991]. Capillary pressure, which is inversely related to aperture size, must be overcome for a nonwetting fluid to invade saturated media. This threshold capillary pressure is generally referred to as the entry pressure. This means the flow behavior and distribution of a secondary, immiscible phase is determined by the surface tension interactions between the two fluids and between the

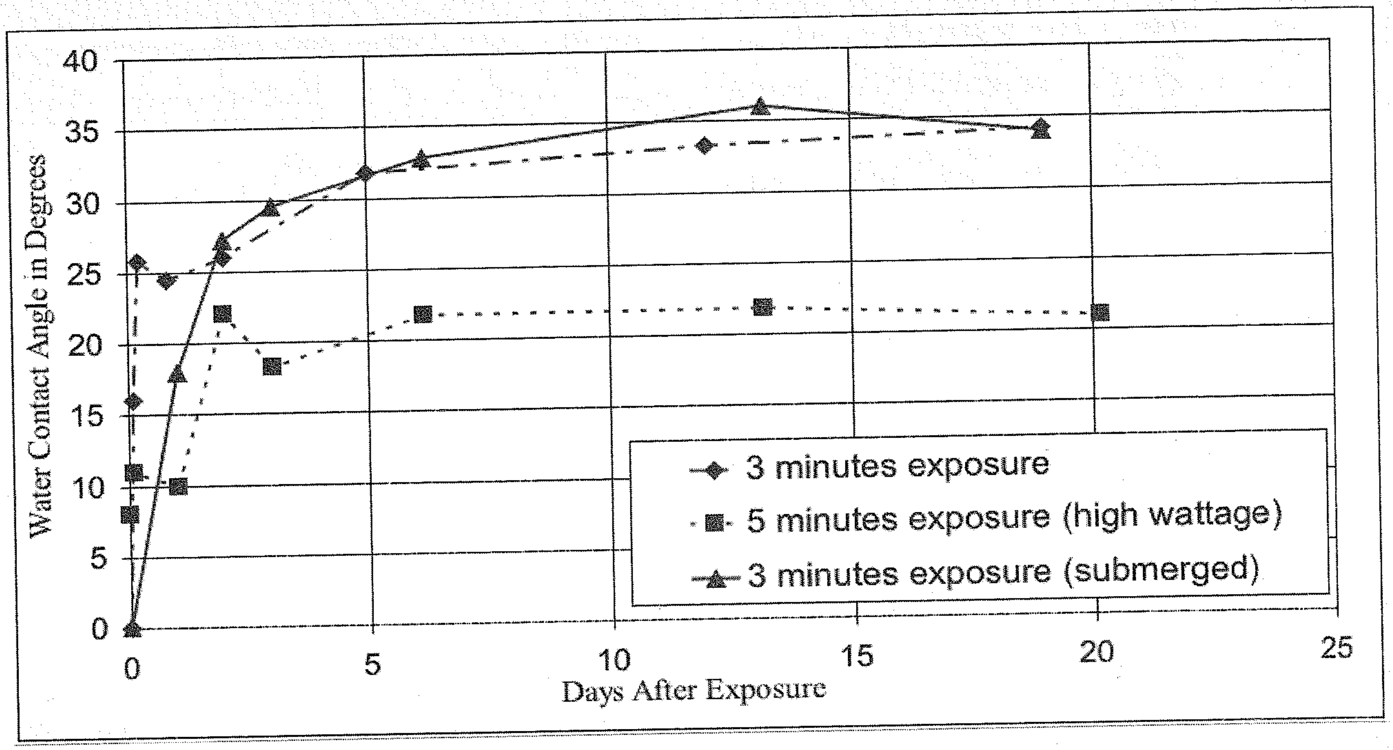

Figure 2. Acclimatization of various exposures of polystyrene surfaces to the atmosphere.

confirmed both the longevity and stability of RFGD plasma treatment though use and time.

3. Surface Properties

[25] An extensive program of surface characterization was performed on the three solid surfaces described above. The Lifshitz-van der Waals (LW) and Lewis acid base (AB) surface tension components (γ_S^{LW} and γ_S^{AB}), and the electron-donor (negative) and electron-acceptor (positive) parameters (γ_S^- and γ_S^+) of each of the solids (identified with subscript s) were determined using sessile drop measurement of fluids of known character (where γ_L^{LW}, γ_L^{AB}, γ_L^- and γ_L^+ are known) on the solids (Table 2). Teflon and glass

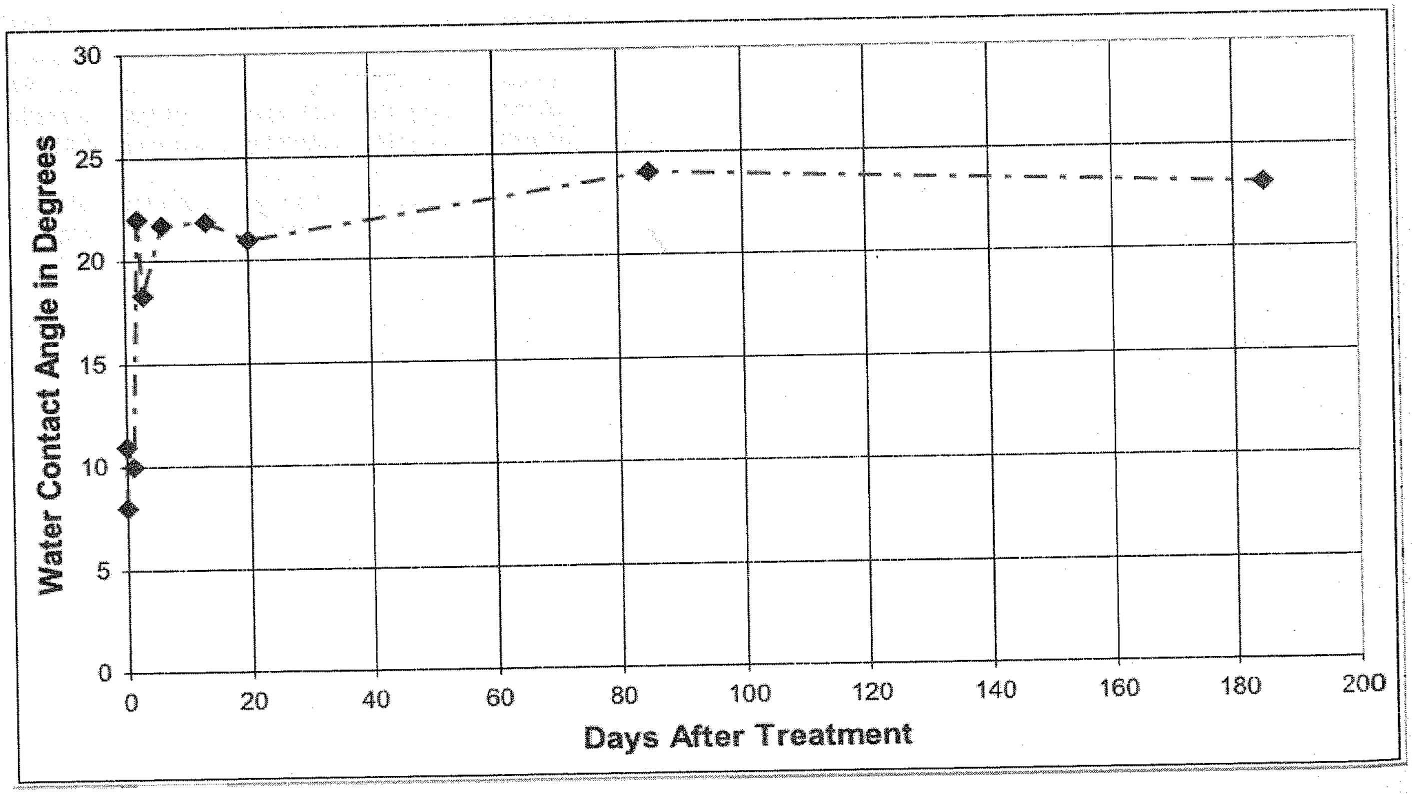

Figure 3. Long-term persistence of treated polystyrene surface.

Table 2. Surface Tension Components and Parameters for the Test Liquids Used for Measurements[a]

	γ	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}
Diiodomethane	32.2	32.2	0	0	0
α-Bromonapthalene	44.4	44.4	~0	~0	~0
Glycerol	64.0	34.0	30.0	3.92	57.4
Water	72.8	21.8	51.0	25.5	25.5
Formamide	58.0	39.0	19.0	2.28	39.6

[a]Values are given in mJ/m^2 and are from *van Oss* [1994].

syringes with stainless steel flat-tipped Luer-lock hypodermic needles were used to place the liquid drops onto the test surfaces, and the contact angles were measured on the solid surfaces using a telemicroscope equipped with a goniometer (Gaertner Scientific Corporation). Surface tension components and parameters were determined by measuring θ for each liquid on the selected solid, entering the known values for each liquid and applying the following relationship [*van Oss*, 1994]:

$$(1+\cos\theta)\gamma_L = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_L^{-}\gamma_S^{+}} + \sqrt{\gamma_S^{-}\gamma_L^{+}}\right) \qquad (3)$$

where γ_L is the total surface tension of the liquid, θ is the contact angle measured at the air-liquid-solid interface in degrees, γ_S^{LW} is the Lifshitz-van der Waals parameter of the solid surface tension, γ_L^{LW} is the Lifshitz-van der Waals parameter of the liquid surface tension, γ_L^- and γ_L^+ are the electron-donor and electron-acceptor parameters of the liquid surface tension, and γ_S^+ and γ_S^- are the electron-acceptor and electron-donor parameters of the solid surface tension [*van Oss*, 1994] (Table 2). The values for each of the liquids were taken from *van Oss* [1994] and verified for the test liquids in-house following procedures described by *van Oss* [1994]. For each solid, measurements of contact angle using a series of both polar (where γ_L^+ and/or $\gamma_L^- > 0$) and nonpolar (where γ_L^+ and $\gamma_L^- = 0$) fluids were collected The γ_S^{LW} value is determined first using the contact angle measurements from nonpolar liquids, and simultaneous equations are solved to determine γ_S^+ and γ_S^- for each of the solids in question (Table 3).

[26] Three different test liquids were also characterized for later use in two-phase flow studies: dodecane, a light (L) NAPL, perfluorocompound FC-75, a nontoxic dense (D) NAPL, and water dyed with known amounts of Liquitint Blue HP (Milliken Chemcial). Dodecane dyed with 0.05 g/L Sudan IV was also used for visualization experiments because small amounts of dye appeared to have only a small affect on the fluids surface tension as measured using the techniques described below (Table 6). It should be noted that the addition of an organic dye often has a profound affect on the surface tension and resultant interfacial tension behavior of a fluid [*Tuck et al.*, 2003; *Jeong et al.*, 2002]. Experiments have demonstrated that as little as 0.508 g/L of Sudan IV in tetrachloroethene (PCE) decreased the solvents interfacial tension with water by approximately 15% [*Tuck*, 1999]. As noted in the above referenced articles, very few NAPL-dye combinations have been investigated to date, and the potential side effects of using a dye in any NAPL study should be appraised on a case-by-case basis.

[27] The flow studies described in the literature have typically been performed using air, an inert gas, or an LNAPL as the nonwetting fluid because the commonly available DNAPLs are toxic and will dissolve the epoxy used to create the transparent models [*Gentier*, 1986; *Gentier et al.*, 1989; *Hakami and Barton*, 1990; *Persoff and Pruess*, 1993, 1995; *Cox et al.*, 1995; *Geller and Pruess*, 1995; *Hakami*, 1995; *Su*, 1995; *Geller et al.*, 1996; *Brown et al.*, 1998]. For this study, a commercially available perfluorocarbon that has low toxicity, would not damage the polymers used in model creation, and has properties similar to common DNAPL contaminants was selected (Material safety data sheet for perfluorocompound FC-75, 8 pages, 3M, St. Paul, Minnesota, 2003, hereinafter referred to as 3M, 2003) (Table 4). Dodecane was used in order to allow future comparison of the flow behaviors of a LNAPL and a DNAPL.

[28] Basic surface tension and interfacial tension for each of the fluids used in this study was determined using the ring method, also called the du Noüy's method, on a Fisher Scientific Surface Tensiomat 21 [*Adamson*, 1990]. In this method, the force required to detach a horizontal ring of platinum-iridium wire from the surface (or liquid-liquid interface) is measured. This force measurement is related to the surface tension (or interfacial tension) via the following equations [*American Society for Testing and Materials International*, 1991; 3M, 2003]:

$$S = P \times F \qquad (4)$$

$$F = 0.7250 + \sqrt{\frac{0.01452P}{C^2(D-d)} + 0.04534 - \frac{1.679r}{R}} \qquad (5)$$

where S is the absolute surface tension in mJ/m^2, P is the apparent surface tension (the dial reading) in mJ/m^2, F is a correction factor, R is the radius of the ring, r is the radius of the ring wire (R/r ~ 54), D is the density of the lower phase, d is the density of the upper phase, and C is the

Table 3. Surface Tension Components and Parameters for Study Solids[a]

	γ	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}
Polystyrene	42	42	0	0	0
Epoxy	62.3	39	23.3	0	23.3
RFGD-treated polystyrene (5 min experiment)	56.1	48	8.1	0.3	54.8

[a]Values are given in mJ/m^2 and are laboratory measurements.

Table 4. Physical Properties of Study Fluids and Some Common DNAPLs[a]

	Density, g/cm^3	Solubility	Surface Tension, dyn/cm	Absolute Viscosity, cP
Perfluorocompound FC-75[b]	1.76	11 ppm	15	1.408
n-Dodecane[b]	0.75	3.4 μg/L	25.35	1.35
Tetrachloroethene (PCE)	1.63	150 ppm	32	0.93
Trichloroethene (TCE)	1.46	1100 ppm	29.5	0.566
1, 1, 1-Trichloroethane (TCA)	1.35	757 ppm	25	0.91

[a]Sources are *Mercer and Cohen* [1990] and 3M (2003).
[b]This is a study fluid.

Table 5. Surface Tension Components and Parameters of the Test Solids Used for Measurements[a]

	γ	γ^{LW}	γ^{AB}	γ^+	γ^-
Parafilm	26.8	26.8	0	0	0
Teflon	18.3	18.3	0	0	0
Glass slide	51.7	33.7	18	1.3	62.2

[a]Laboratory measurements and measurements from *van Oss* [1994] are given. Values are given in mJ/m^2.

circumference of the ring (~6 cm). The surface tension components and parameters of each of the test liquids were determined using sessile drop measurement of the unknown fluids on solids of known character, applying equation (3), and solving simultaneous equations (Tables 5 and 6).

[29] In the case of perfluorocompound FC-75, which has a zero contact angle with respect to air for all tested surfaces, a two-liquid method was used to determine the surface tension components and parameters. A solid surface of known surface tension components and parameters was placed into a vessel filled with water (subscript L) and drops of the FC-75 (subscript O) were then placed at the solid-water interface. The equation for determining the properties of the liquid is [*van Oss*, 1994]:

$$\gamma_L\cos\theta_L - \gamma_{OL}\cos\theta_{OL} = -\gamma_O^{LW} + 2\left(\sqrt{\gamma_S^{LW}\gamma_O^{LW}} - \sqrt{\gamma_O^-\gamma_O^+} + \sqrt{\gamma_O^-\gamma_S^+} + \sqrt{\gamma_S^-\gamma_O^+}\right) \qquad (6)$$

where θ_L is the contact angle water makes on the solid with respect to air, γ_{OL} is the interfacial tension between the two liquids, θ_{OL} is the contact angle at the water-NAPL-solid interface measured through the wetting fluid, and the remainder of the symbols are the same as those used for equation (3).

4. Sessile Contact Measurements

[30] For comparison, the contact angles of sessile drops of the test fluids were measured on the test surfaces. The sessile water drop contact angles measured in air on the epoxy used in this study ranged between about 59° and 64°, agreeing with the findings of *Geller et al.* [1996]. Measurement of the triple-point contact angle of water in dodecane on epoxy, which averaged ~92° through the water, seemed to indicate that epoxy is very slightly hydrophobic (Table 7). However, in an examination of the results for the perfluorocompound FC-75-water-epoxy system this interpretation is contradicted (Table 8). Here the contact angle measured through the water averaged 63°. Clearly, in this case the perfluorocompound is the nonwetting fluid on the epoxy surface. These finding demonstrate that surfaces should only be declared to be hydrophilic or hydrophobic with respect to a specific chemical system to be examined.

Table 6. Surface Tension Components and Parameters for Study Liquids[a]

	γ	γ^{LW}	γ^{AB}	γ^+	γ^-
Dodecane	25.35	25.35	0	0	0
Dodecane with Sudan IV	25	25	~0	~0	~0
0.5 mL Liquitint in 1 L water	58.6	34	24.6	7.7	19.6
FC-75[b]	15	15	~0	~0	~6.37

[a]Laboratory measurements are given. Values are given in mJ/m^2.

[b]Tentative results are given (see text).

Table 7. Measurements of Sessile Contact Angle on Various Surfaces in a Dodecane-Water System

Surface	Water-Air Contact Angle, deg	Dodecane-Air Contact Angle, deg	Dodecane-Water Triple-Point Through Water, deg
Untreated polystyrene	90	~0	139.4
Epoxy	62	~0	92
Treated polystyrene (aged)	25	~0	57

[31] There are, however, difficulties in directly comparing these results. To measure contact angles in the water-dodecane system, each of the solids had to be immersed in the dodecane (which is less dense than water) and the water drops deposited onto the surface. This means that the solid surface is not clean and may, in fact, be significantly altered by its contact with the dodecane. This might account for the epoxy's slightly hydrophobic behavior. One of the major unresolved issues of this study is the relationship between "clean" laboratory measurements and the actual behavior of "dirty" flow systems. It is unclear exactly how the behavior of the fluids changes through time with prolonged contact.

[32] Certainly, the contact angles measured when the fluid interface is fresh will not be the same as the contact angles found when the fluids dissolve into one another as interface ages. For example, the interfacial tension between pure dodecane and pure water after 1 hour of contact is 50 mJ/m^2. After 24 hours of contact the fluid will have dissolved slowly into each other, dropping the interfacial tension to 43 mJ/m^2. This situation is complicated even further when considering the fluids interfaces found in active systems, where one or both of the liquids is in motion. While this leaves an obvious area for further research, the methodology discussed in this paper provides a way to quantify end-member surface chemical systems.

[33] Also of interest in Table 8 are the triple-point contact angle measurements of the dolomite surface in comparison to the other surfaces examined. Chips of dolomite were prepared using an Isomet diamond-edge low speed rock saw and precision positioning knobs to ensure the creation of smooth parallel edges (Buehler, Ltd.). The triple-point contact angle measurements taken through the water averaged ~15°, which compares favorably to the results for the

Table 8. Measurements of Sessile Contact Angle on Various Surfaces in a Perfluorocompound FC-75-Water System

Surface	Water-Air Contact Angle, deg	Perfluorocarbon-Air Contact Angle, deg	Water-Perfluorocarbon Triple-Point Through Water, deg
Untreated Polystyrene	85–90	~0	138
Epoxy	60–65	~0	63
Dolomite	14–18	wicks into rock	15.25
Treated polystyrene (fresh)	0	~0	13.3
Treated polystyrene (aged)	33	~0	27

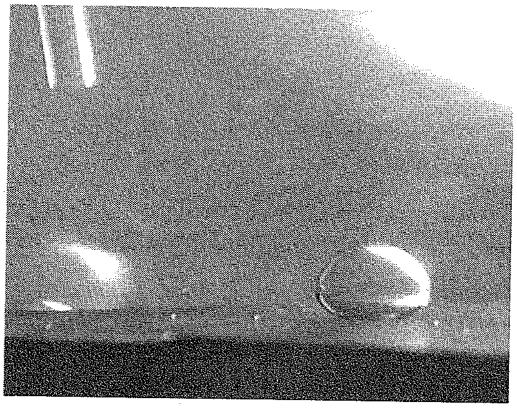

Figure 4. Perfluorocompound in water on dolomite with $\theta_{avg} \approx 12°$ through water.

RFGD plasma-treated polystyrene surface, which ranged between ~14° and 30° depending on the age of the surface and duration of exposure. Certainly, this behavior is significantly different from the behavior demonstrated by both the untreated polystyrene and epoxy surfaces. FC-75 drops on both the treated polystyrene surface and the dolomite chip tended to ball-up and actually roll off the surface, something which did not occur on either of the other two solid surfaces. It is easier to compare the behavior of these surfaces by inspection of actual photographs of the perfluorocompound FC-75 in water on each of them (Figures 4–7).

[34] This comparison strongly suggests that the RFGD-treated polystyrene surface is demonstrably a better physical analog for the natural dolomite system than the untreated epoxy surface, while the other surfaces have significantly different surface free energies than those common to natural geologic media. It is important to note, however, that for each of these FC-75-water triple-point contact angle measurements the solid surface was completely submerged in water, so once again the surface is "dirty," and its behavior could change completely if FC-75 were to be introduced first. The other complexity in interpretation here is that dolomite is made up of a network of mineral surfaces, while the polymers used in this study are all "monocrystals." Single crystals of dolomite will behave differently than a dolomite rock surface, and a smooth, artificially created surface will also behave differently than a rough naturally fractured surface. However, the highly hydrophilic behavior of the dolomite chip indicated by the low, but nonzero, contact angle measurement at the dolomite-water-FC-75 triple-point, which was measured on a water-saturated chip of dolomite, is probably a good indication of the potential behavior of a saturated dolomite aquifer prior to contamination, i.e., a low but nonzero water contact angle with respect to the invading NAPL.

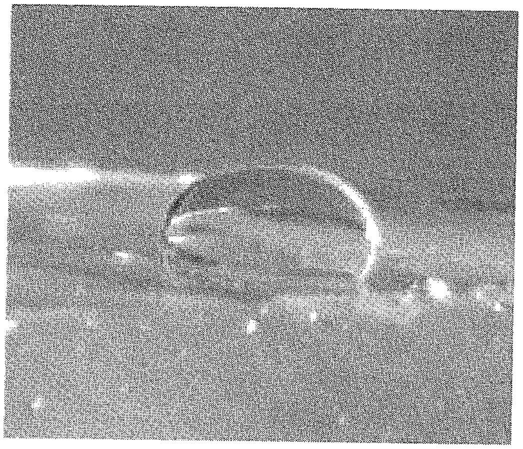

Figure 6. Perfluorocompound in water on untreated epoxy with $\theta_{avg} \approx 64°$ through water.

[35] The surface of dolomite rock would actually have two separate components (discounting impurities in the rock), the dolomite mineral surface and "water surface" created by the existence of water in the saturated pore spaces. The approximate nature of this aggregate surface could potentially be determined using some variant of Cassie's law:

$$\cos\theta_A = f_1\cos\theta_1 + f_2\cos\theta_2 \tag{7}$$

where θ_A is the aggregate contact angle measured on the multicomponent surface, θ_1 and θ_2 are the contact angles expected on a solid surface composed solely of materials 1 and 2, respectively, f_1 and f_2 are the fraction of the surface composed of materials 1 and 2, respectively, with $f_1 + f_2 = 1$ [*van Oss*, 1994]. Unfortunately, in this study, there is a small drawback with this approach, in that preliminary calculations of the contact angle of FC-75 on dolomite crystals suggest that this liquid would have a zero contact angle with respect to air on the mineral surface. It is also unclear

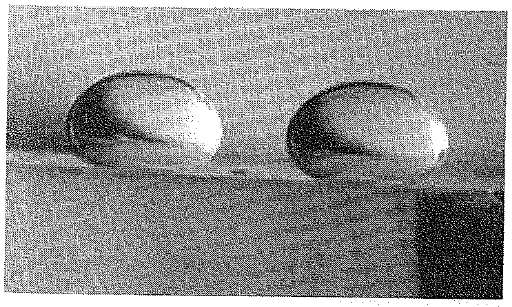

Figure 5. Perfluorocompound in water on polystyrene exposed to RFGD plasma for 80 s with $\theta_{avg} \approx 14°$ through water.

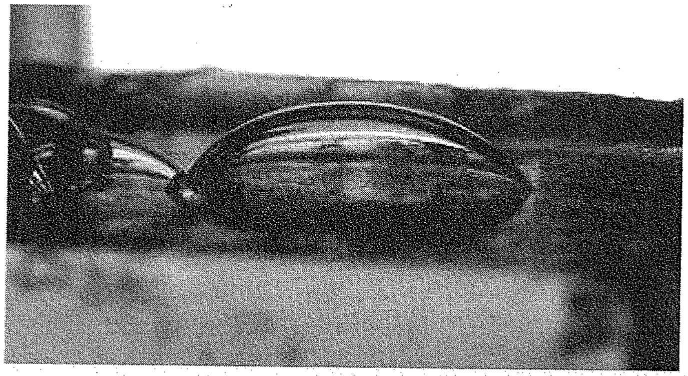

Figure 7. Perfluorocompound in water on untreated polystyrene with $\theta_{avg} \approx 123°$ through water.

Table 9. Surface Tension Components and Parameters for Test Solids and Various Geologic Media[a]

	γ	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}	Source
Epoxy	62.3	39	23.3	0	23.3	laboratory measurements
Polystyrene	42	42	0	0	0	laboratory measurements
Treated Polystyrene (5 min exposure)	56.1	48	8.1	0.3	54.8	laboratory measurements
SiO_2, Fisher Scientific, Pittsburgh, Pennsylvania	50.7	39.2 ± 2.4	11.5	0.8 ± 0.3	41.4 ± 3.0	*Giese et al.* [1996]
Ground calcite	37.0	29.1 ± 3.5	7.9	0.5 ± 0.4	31.6 ± 2.6	*Giese et al.* [1996]
Dolomite	42.5	37.6 ± 1.6	4.9	0.2 ± 0.2	30.5 ± 1.8	*Giese et al.* [1996]
Muscovite	59.9	40.6 ± 2.4	19.3	1.8 ± 1.0	51.5 ± 6.0	*Giese et al.* [1996]
Kaolinite	43.3	35.9 ± 3.2	7.4	0.4 ± 0.2	34.3 ± 0.9	*Giese et al.* [1996]

[a] Values are given in mJ/m^2.

exactly how to define the contact angle of FC-75 on water. Thus development and testing of the validity of this approach awaits further study.

[36] It should also be noted that measurement of air-perfluorocompound contact angles on the dolomite chips is impossible. The FC-75 wicks directly into the rock. For comparison with these results, *Arthur D. Little*, Inc. [1981] reported Lockport dolomite-tetrachloroethene contact angle measurements in air of 171° and in water of between 16° and 21°. Also reported were S-Area DNAPL a solvent mixture measurements on Lockport Dolomite in air, which ranged between 164° and 169°, and in water, which ranged from 16° to 19°.

5. Conclusions

[37] The results of this study indicate that standard epoxy surfaces are not very good analogs for most geologic media with regard to multiphase flow studies and that the results of laboratory multiphase flow studies which utilized epoxy models should potentially be reexamined. Values of $\gamma^{\ominus} < 27.9$ indicate a hydrophobic surface, which suggests that epoxy is not necessarily a good analog for most geologic materials [*van Oss and Giese*, 1995]. This is most easily seen in a comparison of the surface tension components and parameters of epoxy with those of various typical geologic media (Table 9). Epoxy and untreated polystyrene are the only solids where $\gamma^{\ominus}$ is less than 27.9. In contrast, RFGD-treated polystyrene has surface tension components and parameters very similar to those of the listed geologic media.

[38] This study is an initial step in addressing the issue of surface characterization of geologic and modeling materials, and their potential importance in accurately modeling multiphase flow in the subsurface. These results make clear the importance of accurately characterizing the geologic system to be modeled. A great deal of work potentially remains to be done in both the characterization of geologic materials and in examination of the effects of time and contact on the flow behaviors of multiphase systems. The conclusions drawn here are the best available with the existing data and provide a first step toward characterizing very complex systems.

[39] The importance of the effects differences in wettability on flow behavior can be demonstrated by a visual evaluation of the simple flow shown in Figure 8. On the untreated epoxy surface, the invasion of NAPL occurs in well-developed channels which flow freely through the model. Through time the resident water is almost completely displaced, with few significant zones of residual water remaining. This is patently not the case for the RFGD plasma-treated hydrophilic models. When capillary pressure is controlling invasion of a nonwetting fluid into the replicas with RFGD plasma-treated surfaces, flow does not initially occur as a continuous stream forming into well-developed channels. Instead, invasion occurs as a series of stringers or discrete blobs which are cut into sections by zones of narrow aperture. This type of flow involves a series of pulses though the zones of narrow aperture and migration of discrete blobs in the zones of large aperture. Depending on the amount of NAPL invading and the duration of the experiment, stable channels may or may not eventually develop. This clearly demonstrates that surface wettability indeed plays a key role in determining the flow characteristics and ultimate residual distribution of NAPL. A future paper will address the

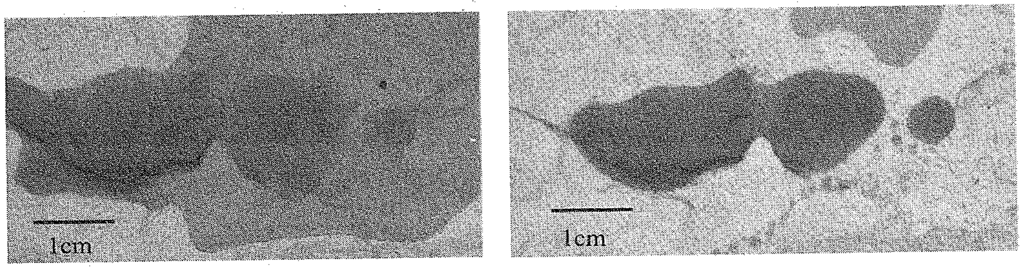

Figure 8. Invasion of Sudan IV dyed-dodecane (dark fluid) into (left) an untreated water-saturated epoxy replica and (right) a RFGD plasma-treated replica. The models are lying horizontally with the inlet to the right and outlet to the left.

importance of the effects of wettability on flow behavior in more detail.

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