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The fate of residual treatment water in gas shale

Terry Engelder [a,*], Lawrence M. Cathles [b], L. Taras Bryndzia [c]

[a] Department of Geosciences, The Pennsylvania State University, University Park, PA 16801, United States
[b] Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, NY 14853, United States
[c] Shell International Exploration and Production Inc., Houston, TX 77082, United States

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ABSTRACT

More than 2×10^4 m^3 of water containing additives is commonly injected into a typical horizontal well in gas shale to open fractures and allow gas recovery. Less than half of this treatment water is recovered as flowback or later production brine, and in many cases recovery is <30%. While recovered treatment water is safely managed at the surface, the water left in place, called residual treatment water (RTW), slips beyond the control of engineers. Some have suggested that this RTW poses a long term and serious risk to shallow aquifers by virtue of being free water that can flow upward along natural pathways, mainly fractures and faults. These concerns are based on single phase Darcy Law physics which is not appropriate when gas and water are both present. In addition, the combined volume of the RTW and the initial brine in gas shale is too small to impact near surface aquifers even if it could escape. When capillary and osmotic forces are considered, there are no forces propelling the RTW upward from gas shale along natural pathways. The physics dominating these processes ensure that capillary and osmotic forces both propel the RTW into the matrix of the shale, thus permanently sequestering it. Furthermore, contrary to the suggestion that hydraulic fracturing could accelerate brine escape and make near surface aquifer contamination more likely, hydraulic fracturing and gas recovery will actually reduce this risk. We demonstrate this in a series of STP counter-current imbibition experiments on cuttings recovered from the Union Springs Member of the Marcellus gas shale in Pennsylvania and on core plugs of Haynesville gas shale from NW Louisiana.

Introduction

Production of gas from shale by horizontal drilling and high volume hydraulic fracturing (HVHF) offers a suite of environmental benefits while raising other environmental concerns (Howarth et al., 2011; Jackson et al., 2013). Concerns involving water quality, the topic we discuss here, arise because as much as 2×10^4 m^3 of treatment water with additives is injected into a typical horizontal well that will tap the gas from ~83 acres of a ~45 m thick shale bed (Table 1). The additives prevent bacterial growth, prevent scaling of steel pipes, aid in rapid flow, prevent swelling of the clay minerals in the shale, and carry sand which props fractures open. This treatment water enters the gas shale via open fractures, but less than half is ever recovered as flowback or later production brine (Pagels et al., 2011; Striolo et al., 2012). In some gas shale plays, clean up and recovery of the fracture fluids prior to bringing gas on stream typically recovers only ~4–8% of the originally injected volume of water (Richard Newhart, Encana; Oklahoma Geological Survey presentation, July 2011. Norman, Oklahoma).

The water initially injected into the subsurface is fresh, typically with a TDS content of 1–5 kppm (TDS = total dissolved solids). The treatment water that does return to the surface carries back natural components of the gas shale including salt, some metals, and radionuclides. This water tends to be highly saline, often with TDS contents of as much as 200 kppm (Gregory et al., 2011). While recovered treatment water is safely managed at the surface, the water left in place, called residual treatment water (RTW), slips beyond the control of engineers. The environmental concern that we address is whether this RTW, more than 10^4 m^3 per horizontal well, could eventually flow out of the gas shale and contaminate overlying groundwater.

The possibility of such eventual leakage and ground water contamination has been raised (Myers, 2012; Warner et al., 2012). Warner et al. (2012) classified 426 water samples from shallow aquifers in an 80×160 km area of northeastern Pennsylvania where hydraulic fracturing is currently being done within the Marcellus gas shale. This classification consists of 4 groups based the Br, Cl, Na, Ba, Sr, Li concentration in the samples and isotopic

* Corresponding author. Tel.: +1 814 865 3620.
E-mail address: jte2@psu.edu (T. Engelder).

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Table 1
Examples of treatment fluid volumes. For a typical Marcellus well the approximate size of the stimulated reservoir volume assumes a 6000′ (1830 m) lateral with a stimulation reaching 300′ (91 m) on each side of the lateral (83 acres) and a vertical dimension of 150′ (45.7 m). For a typical Haynesville well single stage date are reported.

Marcellus well		
Volume of Marcellus tapped	15.3×10^6 m^3	(83 acres) (4047 m^2/acre) (45.7 m)
Volume of treatment water (83 acre well)	20,000 m^3	5,300,000 gallons
Volume of capillary-bound water	$1.5–3 \times 10^5$ m^3	(1–2% porosity) (15.3×10^6 m^3)
Vol. of free water that could leak	8035 m^3	(2.4 m/45.7 m) (1% porosity) (15.3×10^6 m^3)
Volume filled with gas	1.2×10^6 m^3	(≈8% porosity) (15.3×10^6 m^3)
Haynesville well		
Volume of treatment water (single stage)	1309 m^3	346,500 gallons
Total proppant in single stage	159,282 kg	352,257 lbs

ratios $^{87}Sr/^{86}Sr$, $^{2}H/H$, $^{18}O/^{16}O$, and $^{228}Ra/^{226}Ra$. One group with high Br/Cl and Sr/Ca but low $^{87}Sr/^{86}Sr$, their Type D waters, is interpreted to be diluted residual brine that migrated from the deep formations along cross formational pathways. Warner et al. (2012) imply that this natural migration might be ongoing today. By referring to the source repeatedly as the "Marcellus", they imply that leakage is from the Marcellus and they suggest the pathways of natural gas leakage might be areas of higher risk for leakage of RTW. The Marcellus is portrayed as leaking now without any human assistance through cross-formational pathways and the concern is raised that hydraulic fracturing in the Marcellus could make this leakage worse. If this happens for the Marcellus it would be of concern for any HVHF gas or oil development globally.

The plausibility of RTW leakage upward to groundwater was amplified in recent models suggesting that high-permeability fractures connect the Marcellus directly to the water table (Myers, 2012). Issues with such models include imbibition of RTW into the Marcellus, the interconnectivity of fractures and faults between the Marcellus and groundwater, the role of multiphase flow, and the lack of a pressure drive (Engelder, 2012; Saiers and Barth, 2012). Modeling a high-permeability pathway to groundwater suggests that RTW might climb upward to drinking water aquifers in less than 10 years. Here we examine the extent to which the Warner et al. (2012) interpretation and the Myers (2012) model, collectively called the Warner–Myers hypothesis, may or may not be plausible. We do not address issues that may arise as a consequence of engineering failures between wellbore and casing.

Brines with low Na/Cl and high Br/Cl are residual brines produced by evaporation of seawater beyond the point where halite precipitates. They are thus distinct from saline waters produced by road salt and from normal low salinity ground waters in the area (Warner et al.'s other ground water types). The heart of Warner et al.'s (2012) argument is that: (1) the low $^{87}Sr/^{86}Sr$ ratio of these distinctive brines means that they must have come from formations the same age or older and the same depth or deeper than the Marcellus because pore waters have low strontium ratios only in these strata, (2) the brines are likely coming from the Marcellus to topographically low areas because these areas are more fractured and faulted and the fractures and faults connect to the Marcellus, and (3) hydrofracturing the Marcellus could make brine leakage from the Marcellus worse by increasing the permeability of the fractures and faults.

The possibilities raised by Warner–Myers hypothesis are extremely unlikely for four reasons. First, the near-total lack of free water in gas shale means that it cannot feed a steady upward leakage of the kind proposed (Zagorski et al., 2010). Second, the fact gas shale readily imbibes water, and only a fraction of the hydrofracturing treatment water is returned, shows that the treatment waters are flowing into, not out of, the shale (Engelder, 2012). Third, the high salinities (200–300 kppm) observed in flowback brines (RTW), produce significant osmostic fluid pressure gradients. Coupled diffusion–osmosis processes and the forces associated with surface tension and adhesion (capillary forces) propel water into the matrix of gas shale and generate the high salinities observed in the recovered RTW (Bryndzia, 2012). Fourth, although there may be other environmental issues worthy of attention during gas production by high volume hydraulic fracturing, the leakage of water and gas along natural pathways from gas-filled shales like both the Marcellus and Haynesville is essentially eliminated by capillary forces which have maintained overpressuring of the gas and brines between >100 My (the Haynesville) and >250 My (the Marcellus) (Cathles, 2001).

The purpose of this paper is to elaborate on these four reasons for the implausibility of the Warner–Myers hypothesis (i.e., that frack fluid migrates out of gas shale to contaminate groundwater). The implausibility becomes apparent with an understanding of how the Marcellus was deposited and evolved, why it imbibes water when it is hydrofractured, and why capillary and osmosis forces lead to the conclusion that the Warner–Myers hypothesis is misguided. New experimental data from imbibition experiments on both Marcellus and Haynesville shale suggest that the Warner–Myers hypothesis should be viewed with great skepticism.

The geological history of the Marcellus

The Marcellus is organic rich black shale of Middle Devonian age with up to 12 wt.% total organic carbon near the maximum flooding surface at the base of the Union Springs Member. The shale was deposited 389 million years ago under euxinic conditions (Engelder et al., 2011; Kohl et al., 2013; Lash and Engelder, 2011). The Marcellus basin was filled from the SE by a river delta system carrying larger volumes of clay and fine silt, whereas a carbonate bank fed the basin at a slower rate from the NW. This difference in source material and sedimentation rate led to differences in composition of sedimentary fill in the Marcellus Basin. The Marcellus is thus more carbonate-rich, has a higher wt.% TOC, has a lower water saturation and is thinner unit on the western side of the basin.

Over the 30 million years following its deposition, the Marcellus and surrounding organic-rich shales (e.g., the overlying Geneseo/Burket, Rhinestreet, and Dunkirk/Huron) and other strata were buried to 1–2 km depths or more by sediments from either the Devonian Catskill Delta complex to the SE or the carbonate bank to the NW. During the initial phase of burial, shale porosity collapsed by mechanical compaction. This reduced the shale permeability which resulted in membrane filtration of expelled water and retention of much of the original solute load in the shale matrix. When the shales became sufficiently impermeable, compaction disequilibrium developed (Osborne and Swarbrick, 1997). The pore fluids became overpressured with respect to hydrostatic and came to support some of the overburden (Engelder and Oertel, 1985; Lash and Blood, 2007).

Temperature increased by 20–25 °C with each kilometer of burial. After the onset of compaction disequilibrium, chemical diagenesis acted to arrest mechanical compaction but contributed to further porosity reduction (Lash and Blood, 2007). Pressure solution is one of the mechanisms of chemical diagenesis which would have affected the chemistry of the remaining pore water (Weedman et al., 1992). Once the strata were heated to ~90 °C, their organic material (kerogen) started cracking to oil and some gas. The oil first displaced saline water in matrix porosity and, as more oil was generated, it was expelled and migrated upward through the overlying formations. Oil expulsion is indicated by bitumen-filled cracks in the Marcellus (Lash and Engelder, 2005) and bitumen covering concretions recovered from outcrops. When the organic material in the shales (including the retained oil) was heated beyond 110 °C these hydrocarbons were cracked to gas, which displaced most of the remaining matrix pore water, thus further reducing the water saturation in the matrix porosity.

Prior to hydrocarbon generation the initial porosity of the Marcellus that was associated with a matrix of silicate minerals gradually filled with cement to reach a porosity minimum of about 2% as indicated by comparing Upper Devonian shale with the Marcellus. Upon thermal maturation, matrix porosity was enhanced by porosity developed in the organic material due to oil and gas generation. Visible organic matter porosity (i.e., >5 nm diameter pores) begins to form at the start of hydrocarbon maturation when the vitrinite reflectance (%R_o) ~0.8. Ultimately the gas-filled porosity in the organic matter (kerogen) in gas shales can exceed 50% (Fig. 2: right tracks). Under microscopic examination, kerogen in gas shale looks like a solid froth or porous sponge (Loucks et al., 2009). The organic porosity of the Marcellus still retains much of its gas but no water. The kerogen is oil-, not water-wet, so there is no tendency for the pores in kerogen to imbibe water. Significant porosity is thus both produced by gas generation and ideal for storing it. Burial curves for the Appalachian Basin suggest that maturation and the initial development of kerogen porosity in the Marcellus started before the folding and faulting of the Alleghanian Orogeny (Evans, 1995; Zhang and Davis, 1993).

Examined in detail it can be seen that the pores in the organic matter connect in a fashion that allowed the gas to escape into the numerous joints that dissect the Marcellus (Passey et al., 2010). In fact, these joints were produced by the gas expulsion in a process of natural hydraulic fracturing that might be called gas-fracking (Engelder and Lacazette, 1990; Miller, 1995). A plumose pattern can be seen on the surface of the joints that indicate how overpressured gas broke the rock in pulses of joint propagation (Lacazette and Engelder, 1992; Savalli and Engelder, 2005). Early methane-driven joints (i.e., J_1) in the Marcellus and other gas shales of the Appalachian Basin propagated before the main phase of the Alleghanian Orogeny (Engelder and Whitaker, 2006). These joints along with an Alleghanian joint set (i.e., J_2) remained gas charged throughout the burial and exhumation cycle (Fig. 1). A gas charge prevents pervasive invasion of syntectonic fluids which passed from the Appalachian Highlands and under the Appalachian Plateau during the Alleghanian Orogeny (Oliver, 1986; Osborn et al., 2012). Yet, there is no doubt that this same basin-scale fluid migration penetrated the Marcellus along very narrow channels as indicated by J_2 joints filled with vein material. Vein filling assured that these high permeability channels were short lived. Preservation of unfilled joints, both J_1 and J_2, demonstrates the extent to which the Marcellus maintained a gas-charged fracture porosity even as water-driven fracturing cut into and maybe cross-cut the Marcellus (Evans et al., 2012). Veins above the Marcellus are much more difficult to find.

Sedimentation and gas generation continued after the onset of the Alleghanian orogeny at ~290 Ma. The Silurian Salina salt was deformed by the orogeny, and substantial quantities of residual brines were squeezed from it until about 260 Ma (Davis and Engelder, 1985). Fluid inclusions, most commonly found in veins striking in J_2 joint orientation (Evans, 1995; Evans et al., 2012), indicate this brine movement. The area of Warner et al.'s (2012) study was uplifted, unroofed, and cooled during the post-Alleghanian exhumation. Gas generation and gas expulsion and migration stopped as soon as the heating was reversed at about 260 Ma. The gas left in the Marcellus, both in the oil-wet organic matter and in the water-wet matrix porosity, was trapped in an overpressured state by capillary seals in the adjacent water-saturated strata. Gas in the Marcellus is today often quite highly overpressured (dP_p/dz > 17 MPa/km). This overpressured condition can be maintained because pressure is required to force gas into small pores in a water-saturated finer-grained shale layer. There are many such layers, and gas pushes its way through where it can until enough fine grained layers are crossed (with a pressure drop across each) that the excess pressure in the Marcellus is contained. At this point the gas cannot get out, and for this reason water cannot cross from other layers to be imbibed. The balance is extremely durable since only a change in the grain size layering can alter it (Shosa and Cathles, 2001). A little gas may leak after earthquakes, and movement on major faults may over time allow the gas to drain. By and large, however, the gas in the Marcellus and other gas shales has been stably trapped by capillary forces for more than 200 My in a kind of "permeability jail" (Spencer, 1989). In fact, the distribution of $^{87}Sr/^{86}Sr$ in basin-wide brines suggests that the Marcellus was a seal separating deep basin circulation (Osborn et al., 2012) starting at the onset of the Alleghanian Orogeny which probably takes the "permeability jail" back in time to the onset maturation at about 300 Ma when pore fluid in the Marcellus became distinctly multi-phase, thus allowing the development of a capillary seal.

The current state of the Marcellus

Log analysis

The industry has developed sophisticated downhole logging tools that yield a great deal of information about gas shales. For our purposes, these logs provide the most direct and relevant information on the current nature of the Marcellus shale. Fig. 2 shows the log of a 130 ft (39.6 m) interval between 6420 and 6550 ft (1957.3–1996.9 m) depth of a proprietary well in SW PA which cuts through an ~90 ft (27.4 m) thick portion of the Marcellus shale (Zagorski et al., 2010). Arrows identify the Union Springs and Oatka Creek Members. The left track is a gamma ray log that measures radioactivity, mostly from potassium, thorium, and uranium. Potassium and thorium are incorporated in aluminosilicate minerals, especially clays, whereas uranium is has an affinity for organic material.

The middle track of Fig. 2 indicates the shale lithology and positions of migrated hydrocarbons and free and bound water. This track shows that the Marcellus is composed of ~30 vol.% clay (illite plus chlorite), ~30 vol.% quartz, ~30 vol.% organics (kerogen, hydrocarbon, and moved hydrocarbon), 10 vol.% carbonate (calcite and dolomite), a volume percent or so pyrite and clay-bound water, and very little free water. If the gas-charged porosity is all in the kerogen, the weight percent TOC indicated by the middle track is ~7.5 wt.%. The right track shows the total porosity (dotted curve) ranges between 5 and 15 vol.% and that this porosity is almost entirely (95%) filled with gas (red shading). The red numbers indicate the gas saturation, S_{gas}, i.e., the fraction of the porosity that is filled with gas. Water saturation (S_w) is $1 - S_{gas}$. The water saturation is ~5% over most of the Marcellus interval, but in a few intervals it increases to 60%, and at 6450 ft

Fig. 1. J_2 joints in the Marcellus exposed along PA Route 35 in the vicinity of Cross Keys, PA. Their strike is in the transport direction (i.e. cross-fold) for the Alleghanian Orogeny. Other pictures of unfilled J_1 and J_2 joints cutting within the Marcellus are found in the literature (Engelder et al., 2009, 2011).

(1966.4 m) S_w = 100% through a thickness <1 m. Roughly 20% of this water saturation is capillary-bound water (grey). There is very little free water (blue), and the free water occurs only where the gas saturation is low (e.g., below the Union Springs and just above the 6450 ft depth). The water that is neither capillary-bound nor free is the immobile water captured in the crystalline structure of clay. The amount of water in the Marcellus is much less than the irreducible water saturation (i.e., water that cannot be driven out even by the injection of high pressure mercury).

The salinity dilemma

When a well, assumed to drain an area of about 83 acres, is hydraulically fractured by injecting 2×10^4 m^3 of fresh-water treatment fluid (Table 1), less than half the water returns, and it can have a salinity of 30% NaCl equivalent or more with high Br/Cl (Dresel and Rose, 2010; Haluszczak et al., 2013). The total water injected can be represented as a layer of water 6 cm thick spread over the treated area (6 cm^3-water/cm^2) as shown in Table 2. If 50% of the treatment water is returned and 50% retained, the retained treatment water (RTW) can be thought of as a layer 3 cm thick over the treated area (~3 cm^3-water/cm^2). At 10% porosity and 5% water saturation, the available formation water is equivalent to 13.7 cm^3-water/cm^2. To increase the injected water to 30% NaCl equivalent, the formation water must have a salinity of at least 43 wt.%. For a return water salinity to be increased to 20% NaCl equivalent, the required formation salinity is 28.5 wt.%. These calculated formation salinities assume that the formation water fully mixes with the injected water. They could be more if the mixing is incomplete, or less if osmotic forces expel unmixed formation brine. Since the Marcellus flowback brine salinities are commonly in the range of 200–300 kppm (i.e., salinities of 20–30%), if the porosity of the Marcellus is indeed typically ~10% and its average water saturation S_w about 5%, as suggested by the logs in Fig. 2, the formation salinities required are above halite saturation, and the brine in the shale matrix is not capable of generating the TDS loads observed in the RTW. The ion load must be derived from salt dissolution or from highly water soluble ionic complexes associated with clay mineral surfaces.

Extensive FIB-SEM examination of Haynesville shale has not observed any solid halite or other solid salts. Some solid halite has been observed in parts of the Marcellus, but it is uncommon. Thus halite dissolution is not a feasible explanation for the salinity in the returned treatment waters, and in addition, dissolved salt would have a low Br/Cl ratio rather than high ratios observed.

Is it possible that salt could be provided by ions adsorbed on clay surfaces in the shale? Due to dehydration during burial, hydrocarbon generation, and hydrocarbon expulsion, S_w in both the Marcellus and Haynesville gas shales is very low, well below irreducible ($S_w \ll S_{w,irr}$). The low water content removes the Van der Waals hydrogen bonds that usually help to maintain charge balance on clay (mainly illite) mineral surfaces, and the role of charge balance is assumed by the Na^+ and Ca^{2+} cations remaining in the shale matrix. It is beyond the scope of this paper to discuss the ionic interactions and molecular state of water in dehydrated organic rich shale source rocks, but typically in this situation water will form hydrogen bonded solvation shells around chloride ions in shale pores dominated by illite. This type of molecular moiety would help to explain why both the Haynesville and Marcellus shale appear to contain such a high, water-soluble load of Na^+, Ca^{2+} and Cl^- ions in the absence of solid mineral salts, and explain why these shales are capable of so immediately producing high salinity flow back fluids.

Quantitatively, membrane filtration could supply the needed TDS load. Because of the membrane filtration capacity of very fine grained, low permeability clay-rich rocks such as shales (Magara, 1974; Schlemmer et al., 2002), water expelled during compaction is relatively fresh. If the salinity of the water in the Marcellus is ~43 wt.%, as shown in Table 2, ~6 g/cm^2 of salt is contained in the Marcellus. If the pores of the Marcellus initially held seawater with 3.5 wt.% salinity, membrane filtration over a 10% reduction of porosity could provide >9 g/cm^2 of salt; membrane filtration of residual brine with 26 wt.% salinity could provide >71 g/cm^2 salt. The needed salt could therefore easily be provided through membrane filtration during burial and mechanical compaction.

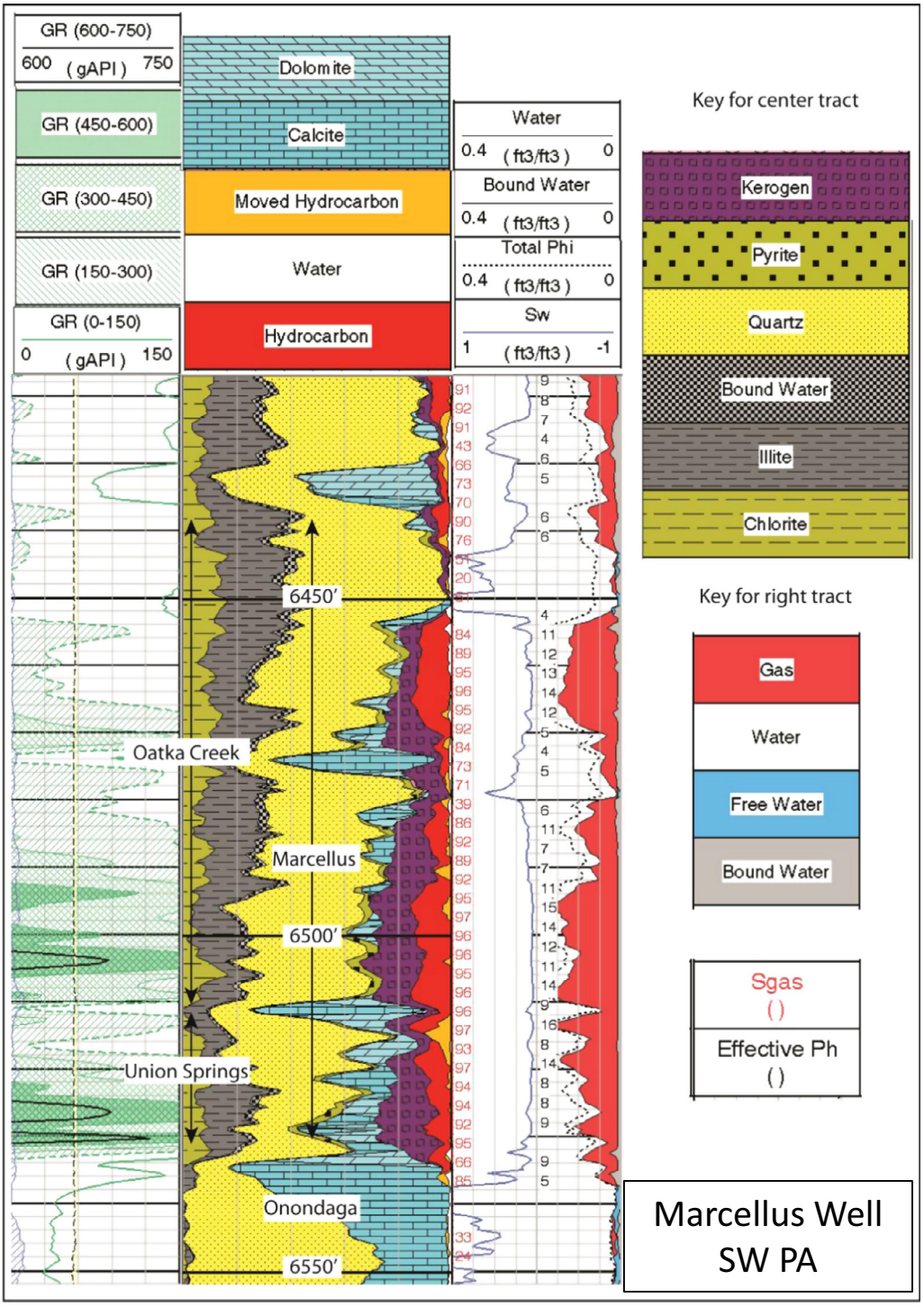

Fig. 2. A proprietary Schlumberger ELAN (Elemental Log Analysis) log from a Marcellus well in SW PA (Zagorski et al., 2010). The Marcellus is a quartz/clay mudstone with limestone stringers (middle tract), and that the pores are filled almost entirely with gas and there is very little (only a few percent) of unbound water as commonly measured using a T2 cutoff of 33 ms in NMR logs.

The Br/Cl ratio

What about the high Br/Cl and low Na/Cl ratios of the returned brines? Euxinic conditions are associated with high salinity brines ponded at the sediment interface. Due to their high salinities, and fluid densities, the brines inhibit seawater circulation which could oxygenate them, thus helping to preserve primary organic matter. Not infrequently brines evolve beyond halite precipitation before they drain into a depression or shallow sea and pond, in which case they have high Br/Cl and low Na/Cl ratios because Br is not readily taken up by salt whereas Na is easily incorporated. The Silurian Salina Group pore fluids below the Marcellus are known for their high Br/Cl and low Na/Cl ratios (Dresel and Rose, 2010) and are thus residual brines. These are the high Br/Cl brines that could have charged the Oriskany sandstone, a prolific gas reservoir in the Appalachian Basin. It is possible the Marcellus organic and silicate material was also deposited coevally with residual brines that ponded in the central basin after evolving in a restricted basin edge

Table 2
Equivalent surface volumes and masses over treated portions of a 27 m thick Marcellus Shale.

Process	Equivalent surface volume (cm^3/cm^2 plan area)
Fresh water is 1000 ft of shallow sediments with 15% porosity	4572
Surface volume of 27 m thick Marcellus shale	2740
Pore volume if average porosity of Marcellus is 10%	274
Pore volume filled with gas if gas saturation $S_g = 0.95$	260.3
Pore volume filled with water for $S_w = 0.05 = 1 - S_g$	13.7
Irreducible water	10.9
Bound water = 0.2 S_w	2.7
Free water = 0.01 S_w	0.01
Experiment-suggested imbibition in 2.5 h if fracture spacing = 100 cm	4.9
Treatment water surface volume if 2×10^4 m^3 water treats 83 acres	6
Treatment water returned if recovery >50% of injected	<3
Residual treatment water or RTW (water not returned)	>3
	Salt surface density (g NaCl/cm^2 plan area)
Salt injected if treatment water 0.5 wt.% TDS	0.030
Salt returned if return water 30% TDS	0.89
Required formation water salinity	43 wt.% TDS
Salt contained in Marcellus before treatment	5.9
Salt from membrane filtration of seawater, 10% porosity reduction	9.6
Salt from membrane filtration 26 wt.% brine, 10% porosity reduction	71.2
	Salt application rate (mg/cm^2/year)
Road salting (300 lbs salt/lane mile, 2.5 km road/km2, 3 applications/yr)	5

environment. The Middle Devonian Prairie evaporite of the mid-continent might have been just such a candidate for feeding a residual brine into deeper Devonian Basins (Wardlaw, 1968). The Prairie was deposited some distance to the north and not linked to the Middle Devonian Appalachian basin by a marine pathway as might have been the case in Upper Devonian time (Blakey, 2013). Restricted basins on the carbonate bank to the west of the Marcellus basin have not been discovered, and the source of such residual brines remains uncertain (Blauch et al., 2009).

No water contamination threat

The Marcellus does not contain enough salt to threaten the fresh water aquifers overlying it. Fresh water generally extends to about 1000 ft (305 m) below the surface. Beneath this, the pore waters are saline. Shallow sediments typically have a porosity of 10–20%, and as shown in Table 2, the water volume in the shallow subsurface at 15% porosity is ~4572 cm^3-freshwater/cm^2. If all the more-than-halite-saturated brine in the Marcellus (all 5.9 g/cm^2 worth) somehow made it through 2 km of saline-water-filled rock and into the 305 m fresh-water layer in a single year, it could increase the salinity of the pore waters there by ~1 part per thousand (ppt) NaCl equivalent. Warner et al. suggest the water in the Marcellus has been leaking out over the last 200 million years and worry that this leakage might be increased by HVHF. Spread over 200 million years, leakage of the brine that is contained in the Marcellus would be a completely insignificant and undetectable ($1/200 \times 10^6$ ppt/yr). Even if the brines were able to escape rapidly and completely, there is just not enough mobile water or brine in the Marcellus to pose a threat to the surface aquifers by steady leakage in the manner envisioned by Warner et al. (2012).

Capillary entrapment

In fact, brines are not free to escape because they are stably trapped by capillary seals, and so is the gas. The quality of the capillary entrapment of both water and gas can be appreciated when it is considered that if one 200 millionth of the gas in the Paleozoic shale leaked each year, there would be no gas left in it today. We can calculate how a thin shale bed could lose gas by analogy to heat conduction. If the thermal diffusivity is replaced by the hydraulic diffusivity $\kappa = \frac{k}{\phi_g \mu_g c_g}$, the leakage of gas from a 40 m thick shale into surrounding rock of similar properties can be estimated by the methods Lovering developed for heat diffusing into surrounding strata (Lovering, 1935). The pressure decay is controlled by a dimensionless parameter, $\frac{4\kappa t}{(H/2)^2}$. If this parameter is greater than 5, the pressure is essentially dissipated. Setting the parameter to 5, taking a gas filled porosity of $\phi_g = 10\%$ and appropriate properties for the compressibility and viscosity of gas at 100 °C and 40 MPa (and $c_g = 1.64 \times 10^{-8}$ Pa^{-1} and $\mu_g = 2.3 \times 10^{-5}$ Pa-s, respectively, (Cathles, 2007)), an $H = 40$ m thickness for the Marcellus shale, and setting time, t, to the number of seconds in 200 million years, it can be seen that unless the permeability of the shale and its surroundings is much less than 3 micro-nanodarcies (10^{-15} darcies) the gas will be lost and the gas pressure dissipated in 200 million years.

The permeability of the Union Springs Member of the Marcellus black shale is ~200 nanodarcies, and this is considered extremely low (Soeder, 1988), but it is 66 million times greater than what is required to keep the gas in the Marcellus for 200 million years. Siltstones comprise much of the surrounding strata and they typically have a permeability that is three orders of magnitude higher than the Marcellus, on the order of 100 microdarcies (Brace, 1980). They would be even less able to contain the Marcellus gas. If the permeability of the Marcellus and it surroundings were 200 nanodarcies, the above analysis indicates the present gas overpressure would dissipate in ~5 years. Capillary seals are the only way anyone has so far articulated to trap gas in either the Marcellus or Haynesville and maintain its overpressured state for the geologic periods over which we know it has remained overpressured. These seals form automatically where two immiscible fluids fill a grain-size layered pore space, and are responsible for maintaining the over- and under-pressured compartments so commonly observed in many basins for geologic periods of time (Cathles, 2001).

The impact of gas production

The final fate of the Marcellus and Haynesville gas may be its liberation by HVHF after being trapped for more than 200 million years in the case of the Marcellus (Evans, 1995) and about 100 million years in the case of the Haynesville (Torsch, 2012). If the Marcellus is hydrofractured it will be the second time this will have been done with nature doing the job the first time between 300 My and 265 My ago with the propagation of J_1 and J_2 joints (Engelder and Whitaker, 2006). Key questions being presently studied are whether the fractures produced by HVHF are new or just a re-opening of old gas-driven fractures, how the HVHF that are propped open connect to the pores in the organic material that contain most of the gas, how and by what physics the gas moves out of the very small pores, and how the two porosity systems (the water-wet porosity in the silicate parts of the shale and the

gas-wet porosity in the organic parts of the shale) interact (Bohacs et al., 2013; Passey et al., 2010; Sinha et al., 2013).

The most important points made in this section are that treatment waters will not increase contamination risks because they will be drawn (imbibed) into gas shale and stably retained, and the production of gas will reduce the risks of fluid escape because fluid over pressures will be reduced. Production will lower rather than increase risk. Industry is well aware of capillary effects and the water imbibition it causes because it can decrease gas production (Economides and Martin, 2007; Holditch, 1979). Imbibition is inversely proportional to water saturation (Kewen et al., 2002; Li et al., 2006). In tight gas sands, the formation is damaged if allowed to imbibe water because an increased water saturation decreases relative gas permeability (Spencer, 1989). Although flowback reduces this "formation damage", the tight sandstones rarely return to their original permeability. A reduction in formation permeability also takes place when imbibed water comes in contact with swelling clays (Walls, 1982). Imbibition of treatment waters in shale gas operations can harm production by greatly reducing the flow of gas to the open fractures (Cheng, 2012).

Imbibition into gas shale is a form of wicking made possible by the high capillary suction that a fine-grained, water-wet shale matrix can exert on water. Spontaneous imbibition takes place when a wetting fluid is drawn into the pore space of rock by capillary action. The wetting fluid is attracted to the solid matrix by van der Waals forces between the fluid and the solid molecules (Morrow and Mason, 2001). The amount of imbibition is inversely proportional to the saturation of the wetting phase (Li and Horne, 2004). The wetting phase will continue to advance, pushing the non-wetting phase in the direction of the advance, until the adhesive forces are balanced by gravitational forces on the wetting phase or the advance is resisted by the viscosity of the wetting phase (Morrow and Mason, 2001). In either case, the non-wetting phase is driven ahead of the advancing interface in the form of co-current flow, the process that makes water floods in declining oil fields so successful. If the non-wetting phase is trapped, it will become compressed to the limit of capillary pressure of the three-phase (solid and two immiscible fluids) system.

As water is wicked into gas shale much as into a moist sponge, the natural gas in the shale is pushed out just as air is expelled from the moist sponge (Tavassoli et al., 2005). If gas is expelled back across the same interface across which the water enters, the process is called counter-current imbibition (Hu et al., 2001; Makhanov et al., 2012; Roychaudhuri et al., 2011). In the case of gas shales, water is pumped along fractures and imbibed into the shale matrix while at the same time gas is expelled into the fracture. Early models for this imbibition predicted that the mass of water entering matrix porosity depends linearly on the square root of time (Handy, 1960). Experiments show that imbibition can cause water to invade 3 cm into a nanoDarcy permeability black shale in 3 days (Pagels et al., 2012). Imbibition is particularly effective in a gas shale with water saturations <30% (Fig. 2).

Experiments elucidating processes that occur during gas recovery

Capillary forces and coupled diffusion–osmosis processes are the reasons the brines and the RTW are not free to escape from gas shale. The most direct evidence of these forces is the observation that more than half the treatment waters are not recovered. Introducing treatment water causes gas shale to act like a sponge.

How much water can gas shale imbibe? The kerogen is oil wetting and hydrophobic and will not imbibe water. The silicate fraction of the shale is water wetting and will imbibe. The organics and silicates are complexly intertwined in the shale and so estimating imbibition is complicated, but simple experiments show that water will readily be imbibed into gas shale in quantities fully capable of sequestering the residual treatment water even where TOC in the shale is highest.

Wettability experiments on Marcellus and Haynesville shale

The relative adhesion of water and air to a solid surface can be quantitatively assessed by placing a drop of water on a shale surface and measuring the contact angle, θ, between the solid–liquid and vapor–liquid interfaces. The contact angle is measured from the solid surface under the drop to the tangent to the drop-air interface at the edge of the drop as illustrated in Fig. 3. If the angle, θ, is acute (<90°) the water wets the solid and the solid surface is hydrophyllic. If the angle is obtuse (>90°), water does not wet the shale and the solid surface is hydrophobic. The more acute the angle, the larger the force of water adhesion and the more the water will spread out along the solid surface (Vavra et al., 1992).

Fig. 3 shows a series of contact angle measurements under ambient laboratory conditions on core material from the Haynesville gas shale machined to be perfectly flat with a polished surface. The fluids tested include two different oils and three NaCl brines. The very low contact angles of the oil drops shows the Haynesville is strongly oil-wet. The brine contact angles are all less than 90°, so the Haynesville shale is also water wet and has a natural tendency to imbibe water. Expected contact angles for 'water-wet' rocks are 0–30°, so the Haynesville shale, with contact angles that vary from 40° to 50° is not as strongly water-wet as typical water-wet rocks. The contact angles measured here are for gas–oil and gas–brine wettability, where the gas phase is air at ambient conditions. Because the measurements show that, relative to gas, water is the wetting phase, if the shale under in situ conditions is at a very high gas–water capillary pressure, which it is since the in situ water saturation is less than irreducible water saturation, then exposing it to a water-filled fracture at formation pressure (zero *Pc*) will result in the spontaneous imbibition of water into the gas-filled pore space. This is also true for the Marcellus gas shale (Figs. 4 and 5).

Imbibition into the Marcellus

If the substrate upon which the drop is placed is porous, air filled, and hydrophyllic, the water of various compositions will imbibe into the substrate with air expelled from the substrate. This is called countercurrent imbibition. Countercurrent imbibition is nicely illustrated by methane bubbles appearing in chips of Marcellus gas shale that were tested within a few days at most of being recovered from the subsurface (Fig. 4).

By measuring the reduction in drop volume in excess of evaporation, we can gain an appreciation of how readily a rock can imbibe water (Fig. 5). The Marcellus measurements were performed on >1 cm chips collected from the shaker table which probably came from 2000 m depth where the drill hole turns horizontally into the shale. This proprietary well was drilled with water-based mud to within 30 m of this kick-off point. The water-based mud was then displaced with a synthetic oil-based mud having a weight of approximately 12 PPG. The well landed in the lower portion of the Union Springs. The well was then geosteered within the portion of the Union Springs Member where the gamma intensity was 300 API. The largest of the Marcellus cutting chips (>1 cm) were created during circulation as the drill string was slid back and forth 15–30 m, a procedure that takes place after the total length of the horizontal lateral has been drilled. The mud logger suggests that the larger pieces we collected were dragged off the wall of the borehole just as the drill pipe was making the

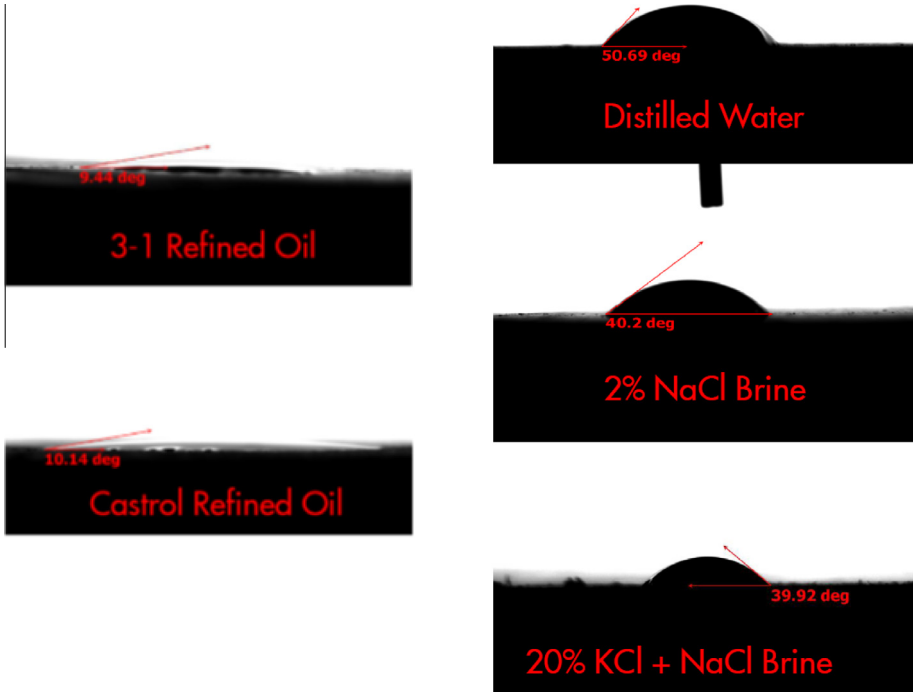

Fig. 3. Left: oil wetting experiments on samples of Haynesville gas shale with liquid oil. The measured wetting angles confirm that the Haynesville shale is a strongly oil wetting rock. Right: water and brine wettability experiments on samples of Haynesville gas shale. Note that the most wetting fluid in this series of experiments is the highest salinity brine and the least wetting is DI water.

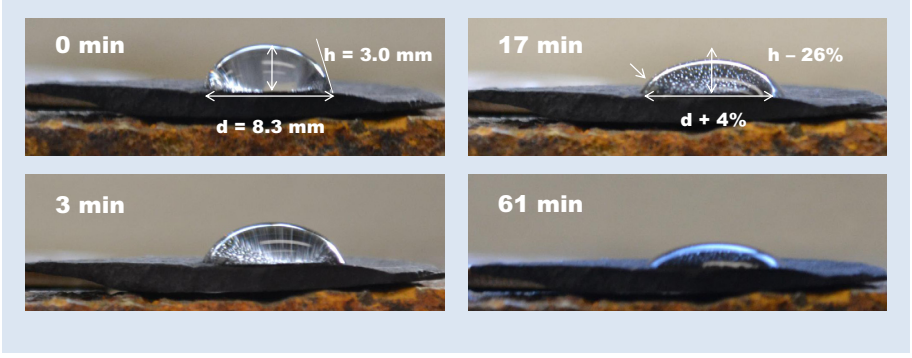

Fig. 4. Counter-current imbibition. Sixty one minutes of imbibition and evaporation of a 154 μl bead of tap water on a 2.3 g chip of the Union Springs Member of the Marcellus Formation. The drop disappeared in approximately 100 min. The initial contact angle (θ) for the water bead with the Marcellus chip is 72°. The photograph labeled 0 min was taken about 10 s after the bead was dropped on the Marcellus chip. Counter-current imbibition is indicated by methane bubbles floating up into the water bead from the Marcellus chip, starting on the left side of the bead at time = 0 min. This experiment was started 5 days after receiving fresh cuttings of the Union Springs from a horizontal well in PA.

turn up the wellbore from the landing point. We thus believe they came from the lower portion of the Union Springs at the landing point.

Chip collection from oil-based mud is important because the low surfactant energy of these oil-based drilling muds means they have little tendency to invade the chips. It also helps that the Marcellus chips have retained a water wet matrix. The cuttings were removed from the shaker table and immediately washed with mineral oil, then washed with common dish soap, placed on a paper towel, and dried with a wet vac pulling air through the towel. Marcellus cuttings continuously degas throughout the washing and drying process although the specifics of this for our as-received samples are unknown. Samples were then placed in vials and stored at room temperature a few days before our STP imbibition experiments. Samples that spent less time in these vials (i.e., are aged less) imbibed faster.

Imbibition into a 2.3 g chip of the Union Springs member of the Marcellus takes place in tens of minutes (Fig. 4). The water drop initially forms an acute contact angle of 72°, indicating the chip is somewhat hydrophilic. The drop is rapidly imbibed and disappears in about 140 min. Gas is expelled as water is imbibed, a form of countercurrent imbibition. This is indicated by the observation of a great many gas bubbles in the drop as it disappears.

Imbibition rate depends on the ratio of clay/quartz in the chip, but is strong for all Marcellus samples (Fig. 5). The imbibition must be corrected for evaporation, and the rate of evaporation was measured for all experiments by the change in volume of drops placed on a strip of scotch tape (top set of data points). The imbibition rates for two samples from the Oatka Creek member of the Marcellus (one where the drop was placed on a slickensided surface of the chip indicated by open square symbols, and one where the drop was placed on a gray, less organic rich, chip shown with

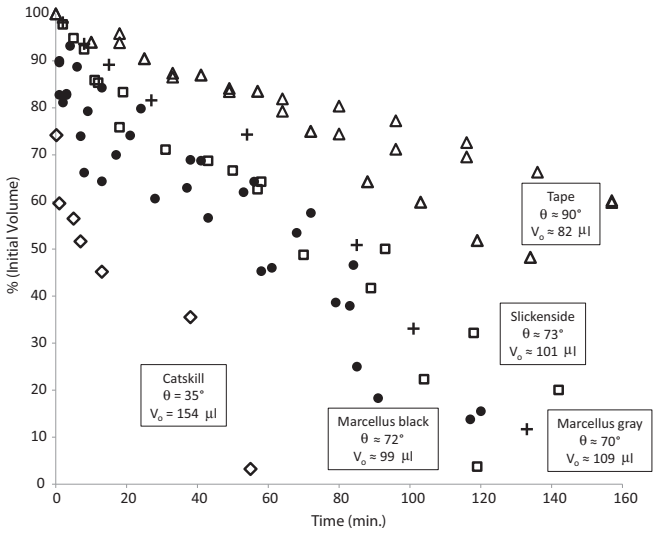

Fig. 5. Absolute volume versus time indicating imbibition into samples of the Union Springs Member of the Marcellus (solid black circles), Oatka Creek Member of the Marcellus (cross); a bed-parallel slickensides in the Oatka Creek Member of the Marcellus (open square), a sample of siltstone from the Catskill Formation (open diamond), and a hydrophobic substrate (scotch tape on glass – open triangle). True imbibition is the difference between evaporation and volume loss. As-received Marcellus cuttings from Susquehanna County, PA, have aged less than 24 days on the shelf. Countercurrent imbibition into the samples of the Union Springs ends approximately 15 minutes after the experiment starts.

cross symbols) are similar. The imbibition rate for a low-TOC sample from the Catskill formation (open triangles) is much faster than the Marcellus samples. However, a more organic rich (filled black circles) sample from the Union Springs member of the Marcellus imbibes faster than the Oatka Creek member samples. This is unexpected because organic matter is hydrophobic, but indicates importantly that the organic rich portions of the Marcellus with a lot of gas in hydrophobic pores in organic matter can nevertheless imbibe water quite strongly by way of the inorganic matrix pore network.

Imbibition into the Haynesville

Experiments by (Pagels et al., 2012) showed that imbibition can cause water to invade 3 cm into a nanoDarcy permeability black shale in 3 days. From other studies we know that imbibition is particularly effective in a gas shale when the water saturation <30%. Since imbibition slows with time, the distance from the fracture surface that treatment water will imbibe in a period of days to weeks will probably be <5 cm. Imbibition experiments were conducted on samples of mature gas shale from the Haynesville Fm. in NW Louisiana by researchers at Shell (Bryndzia, 2012). In this section we discuss the results of another set of novel experiments designed to test the interaction of water, brines and liquid hydrocarbon with the Haynesville gas shale.

A series of experiments was carried out to quantify the amount of water that could be imbibed by the Haynesville gas shale. A piece of Haynesville core was placed in a small beaker filled with 15, 60 or 120 ppm brine (Fig. 6). The mass of the core was measured every 24 h. The difference in weight of the core was taken as an indication of the volume of water imbibed. After 120 h the imbibition of the 60 kppm brine appeared to have reached a near steady state. Imbibition of the other two brines had clearly not reached steady state. The imbibition was highest for the lowest salinity brine, and lowest for the highest salinity brine. Salt crystals were observed to form on the sides of the core plug at the core/brine interface. These were wiped clean prior to weighing of the sample. Recorded imbibition volumes are therefore conservative. Water was clearly imbibed by the shale sample forcing out solutes within the shale. Steps were taken to prevent evaporation of water by covering the beaker with a water proof plastic seal. The solubility of NaCl was clearly exceeded in the water film on the outside of the core where the salt crystals precipitated. Since these were bench top experiments at 1 atm and 25 °C, they are not definitive with regard to the volume of water that can be imbibed in situ by the Haynesville. The results of these and other wetting and imbibition experiments, however, are very instructive and provide some critical insights into the origin of the high salinity flow back brines recovered after hydraulic fracturing.

Interpretation

Ionic diffusion and osmosis

The Haynesville shale is a strongly oil-wet rock (Fig. 3), yet it also imbibes water. Another curious aspect is that the most saline brine has the lowest contact angle (is most wetting) but the most strongly imbibed fluid is the least saline brine. This kind of behavior is indicative of a diffusion and osmotic process rather than an adhesion-surface tension process of classic capillary imbibition (Schlemmer et al., 2002; Simpson and Dearing, 2000; Simpson et al., 1998; Van Oort et al., 1996).

Four principal forces drive fluid/shale interactions (Al-Bazali et al., 2009). These are:

(1) A hydraulic differential between the drilling fluid pressure in the hydraulic fracture and the pore pressure in the shale matrix (ΔP).
(2) A combination of surface tension and adhesion of fluids (i.e., capilliary forces like those that make a water flood work).
(3) Osmotic pressure due to chemical osmosis, usually calculated using the activity ratio of water in the shale to hydraulic fracture fluid and,
(4) Diffusion osmosis from higher to lower concentrations for each species which is opposite to the flow of water in chemical osmosis (Fig. 7).

Although Simpson and Dearing (2000) used Fig. 7 to explain diffusion and osmosis processes between drilling fluid in a bore hole and its chemical interactions with the bore hole wall, it is equally applicable to what we envisage happens between a hydraulic fracture fluid and the shale surface freshly exposed in a hydraulic fracture. The hydraulic fracture fluid consists mostly of very low salinity surface water (low activity of ions, and high activity of water, a_w), while the shale contains high concentrations of water soluble inorganic cations and anions (high activity of ions, and low activity of water, a_w) (Fig. 7).

Based on the results of the imbibition experiments of gas shales, it is quickly appreciated that during hydraulic fracturing water is lost to the formation while inorganic cations and anions are transferred from the formation to the hydraulic fracture (Fig. 6). This is a perfect example of diffusion osmosis as illustrated in Fig. 7. Diffusion osmosis is therefore the explanation for rapid imbibition of water by the shale, the low volumes of water recovered during hydraulic fracture clean up and also the cause of the high salinities observed in flow back fluids.

Osmotic pressure associated with coupled-diffusion osmosis in gas shale

The contrast in water activity between brine and fresh water generates very substantial osmotic pressure differences that will

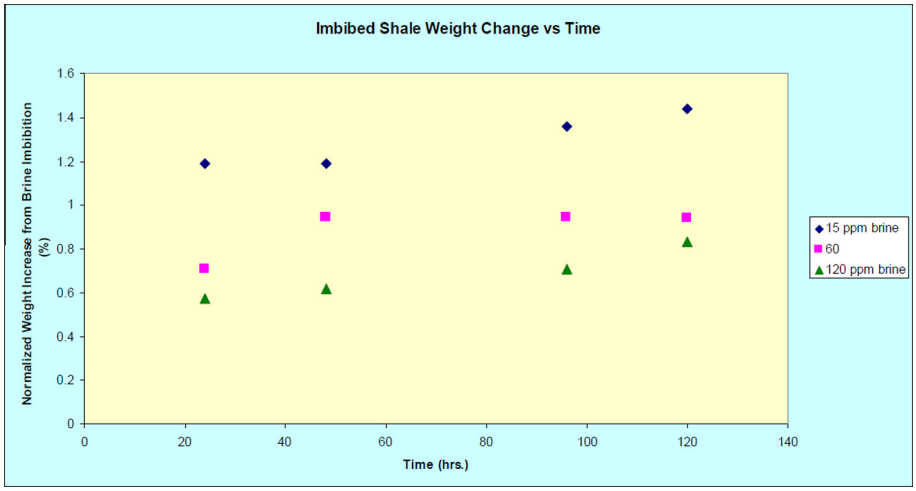

Fig. 6. Results of imbibition experiments on a sample of Haynesville shale core with brines of 15, 60 and 120 kppm NaCl. The least saline brine was most imbibed by the Haynesville shale sample.

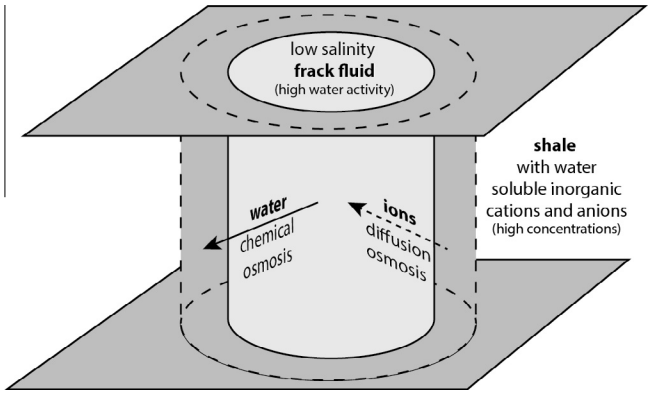

Fig. 7. Chemical and diffusion osmosis: transfer of water and inorganic ions between drilling fluid and formation when the drilling fluid is equal to the far-field formation pressure (adapted from Simpson and Dearing (2000)).

drive treatment waters into the shale matrix. Osmotic pressure is the pressure that must be applied to prevent the inward flow of water across a semipermeable membrane. The osmotic pressure of water in contact with a shale containing brine can be calculated using Eq. (1) from Schlemmer et al. (2002, 2003):

$$P_{\mathrm{osm}} = RT \ln [a_{\mathrm{w}}], \quad (1)$$

where R is the universal gas constant, 0.08206, in L atm/mol K, T is temperature in K, and a_{w} is the activity of water. At 60 °C the activity of water in a 20% NaCl or $CaCl_2$ solution (equivalent to 200 kppm), is 0.82 and 0.94 respectively (Schlemmer et al., 2003). The absolute osmostic fluid pressure required to generate such a solution through osmosis diffusion is ~2861 and 2591 psi for NaCl and $CaCl_2$ brine, respectively (Fig. 8). Mudrocks and shales are not perfect membranes and have membrane efficiencies that can vary from ~0.1 to 0.9 (Fritz and Marine, 1983; Garavito et al., 2006; Schlemmer et al., 2002). Fritz and Marine (1983) report values of 0.04–0.89 for a synthetic bentonite clay membrane while Schlemmer et al. (2003) report membrane efficiencies of 0.11 and 0.31 for NaCl and $CaCl_2$ measured in samples of Pierre 1E shale (Schlemmer et al., 2003). Garavito et al. (2006) report a membrane efficiency of 0.21 for another study on Pierre shale. We are not aware of any direct measurement of membrane efficiency made on samples of either Marcellus or Haynesville shale, but if we assume an average membrane efficiency of ~0.2 the osmotic pressure associated with the formation of a 20% NaCl brine would be 0.2 * 2861 = 572 psi. This

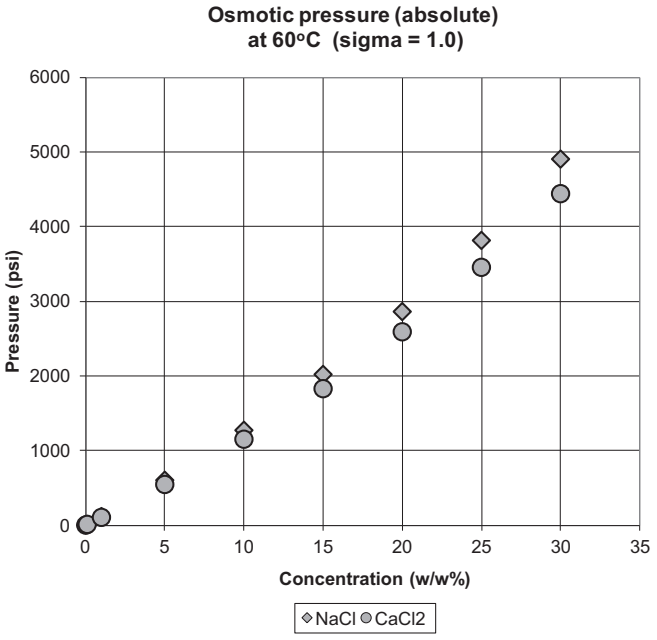

Fig. 8. Absolute osmotic pressure of NaCl and $CaCl_2$ brines as a function of solute concentration at 60 °C, calculated assuming a perfect osmotic membrane (σ = 1.0). These data show that a significant osmotic pressure difference must exist the between the shale matrix and hydraulic fracture in the Marcellus shale to reach salinities of ~20–30 w/w% in the returned fracture fluids.

hydraulic pressure drives the fresh water into the shale matrix, is opposite to the direction of gas flow, and is in addition to the fluid pressure imposed by the operator to drive the treatment water into the formation during hydrofracturing (Fig. 9). The point to be emphasized here is that this osmotic pressure pushes the hydraulic fracture fluids into the shale matrix, expelling gas and high salinity formation water in the process. It is potentially several 100 psi or greater and is in the direction opposite to the flow of gas, (Fig. 9). At the same time, ions from the formation water diffuse quickly into the treatment water that remains in the fracture.

How much treatment water can the Marcellus imbibe?

The question of how much water the Marcellus can be expected to imbibe can be answered from the drop experiment results described above. For example, the 99 mm^3, 8.3 mm in diameter

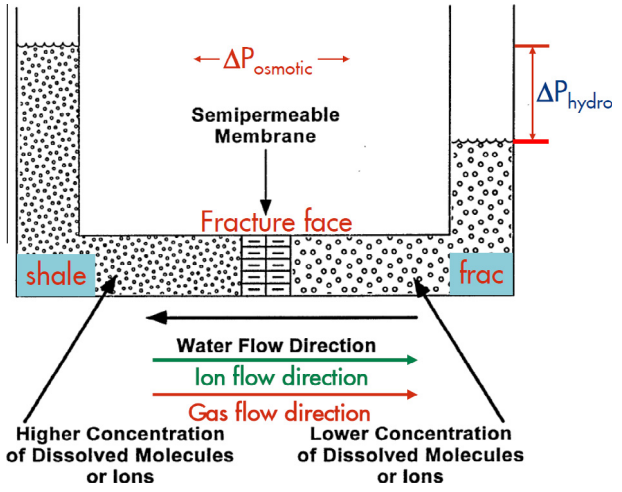

Fig. 9. Schematic model for diffusion osmosis between fresh water in the hydraulic fracture (frac) in which the $a_w = 1$, and the shale, in which the a_w is assumed to be 0.82. Due to diffusion osmosis, water flows into the shale (black arrow) in the opposite direction to the flow of gas (red arrow). Ion flow is from the shale into the hydraulic fracture. ΔP is the difference in hydraulic pressure between the shale and fracture and can be on the order of several 100 psi. Figure has been modified from Simpson et al. (1998). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

drop that was placed on the chip from the Union Springs member as shown in Fig. 4 disappeared in ~2.5 h, with about half being lost to evaporation, and about half being drawn laterally from the footprint of the drop (Fig. 5). The volume per unit area that has been imbibed under the drop, $\sigma_{2.5hr}$, is thus 99/4 mm^3 divided by the drop footprint $(4\pi\ (8.3\text{ mm}/2)^2$ or $\sigma_{2.5hr} = 0.045$ $\left[\text{cm}^3_{\text{water}}/\text{cm}^2_{\text{surface}}\right]$. If the Marcellus is considered to be fractured in a rectilinear grid of intersecting vertical fractures (so that it is split into prisms of dimension d), the internal fracture area per unit volume in the Marcellus is $S = \frac{4}{d}\left[\frac{\text{cm}^2_{\text{surface}}}{\text{cm}^3_{\text{Marcellus}}}\right]$. The volume per unit plan area that the Marcellus could imbibe in 2.5 h according to our experiment, $I_{2.5hr}$, is: $SH_{\text{Marcellus}}\sigma_{2.5hr}$, where $H_{\text{Marcellus}} = \frac{V_{\text{Marcellus}}}{A_{\text{Marcellus}}}\left[\frac{\text{cm}^3_{\text{Marcellus}}}{\text{cm}^2_{\text{Marcellus}}}\right]$ is the thickness of the Marcellus shale. Thus, $I_{2.5hr} = \frac{4\sigma_{2.5hr}H_{\text{Marcellus}}}{d}$ and for $d = 100$ cm, $I_{2.5hr} = 4.9$ cm treatment water imbibed per unit plan area of the Marcellus, which is the same as the treatment water that is not recovered i.e., the RTW. The Marcellus is certainly fractured far more intensely than a fracture spacing of 1 m at least near the wellbore. Our experiments thus indicate that the Marcellus will have no difficulty imbibing and retaining the treatment water as observed, even if the treatment waters had only 2.5 h to imbibe and they have significantly more time than this to imbibe.

Our experiments provide direct and highly visual evidence of how the Marcellus will imbibe. Many have studied this issue previously. Early models for imbibition predicted that the mass of water entering matrix porosity depends linearly on the square root of time (Handy, 1960). Hu et al. (2001) measured imbibition rates on unsaturated zone samples of the Paintbrush Formation at the Yucca Mountain nuclear repository. The Tonopah Spring Member of the Paintbrush Formation is a welded tuff with pore diameters between 19 and 53 nm (Roberts and Lin, 1997), a porosity between 8% and 16%, and a permeability between 800 nd and 64 μd (Moore et al., 1986). Tuff from the unsaturated zone of Yucca Mountain (Core A from Hu et al., 2001) has an imbibition rate of 24 μl/cm^2/100 min compared with 86 μl/cm^2/100 min for chips of Union Springs aged 24 days.

Discussion

Leakage along fractures and faults

Warner et al. (2012) found Type D brines (which they attribute to the Marcellus) were preferentially collected in topographically low areas. They ascribed the low topography to greater fracturing, and suggested that the fractures provided greater access to the Marcellus in these topographic lows. There is no doubt that topography on the Appalachian Plateau reflects systematic fracture patterns. The Finger Lake valleys of NY cut down along N–S (i.e., J_2) joint sets (Engelder and Geiser, 1980), and perhaps the same is true for the valleys of Salt Lick Creek north of Milford PA, the upper reach of the East Branch of the Susquehanna River in Bradford County PA, and stretches of Meshoppen Creek south of Montrose, PA. The E–W valleys of northeastern Pennsylvania, including Towanda, Tunkhannock, and Cowanesque Creeks follow strata that were tilted by folding during the Alleghanian tectonics. The Marcellus overburden also hosts many, many non-systematic fractures and fracture networks (Jacobi, 2002). The extent to which these are interconnected is unclear, and they must interconnect in order to enhance bulk permeability above that of the matrix. The core of Alleghanian anticlines are more heavily faulted than synclinal regions (Scanlin and Engelder, 2003). There are also suggestions that basement-related structures penetrate the Marcellus and manifest themselves in surface topography (Gold, 1999).

The simple story that more flow occurs where there are more faults is complicated, however, by the fact that most faults within the Upper Devonian section are low angle and likely to be smeared with clay gouge, making them a low permeability seal rock rather than a leakage conduit. The best examples of low angle faults are seen around Towanda PA and another near Hepburnville, PA. A careful search for evidence of large scale vertical faulting that might penetrate the Devonian section of the Appalachian Plateau finds no evidence for such features along 100+ km of road outcrops in northeastern Pennsylvania. The closest to zones of vertical permeability are joint zones, and even these tend to be relatively rare (Engelder, 1987).

While influencing landscape evolution, J_2 joints in the Upper Devonian section overlying the Marcellus ($z < 1000$ m) propagate in sand bodies and do not penetrate the interlayered shale (Fig. 10). A single systematic joint set is not a good conduit for fluid migration from depth. Too often, a weakly fractured outcrop suggests fracture interconnectivity which is actually not present. Simple geometry tells us that parallel planes, such as those of single systematic joint sets on the Appalachian Plateau, do not intersect (Figs. 1 and 10). Fracture interconnectivity matters and, if fractures are not interconnected, the bulk permeability of a section becomes that of its matrix (Hubbert, 1957). The same rule applies when sand bodies pinch out, and thus fail to interconnect, as is the case for the near-shore marine, estuarine, and fluvial rocks of the Upper Devonian section of Pennsylvania (Fig. 10). The matrix, in this case the Upper Devonian shale, determines the bulk permeability of the stratigraphic section. To further minimize the bulk permeability of the section above the Marcellus, the water saturation in the overburden shale is significantly less than 1. It is well established that as water saturation decreases, so does the water permeability (Stephens, 1996). A rule of thumb for the Appalachian Basin is that a section containing a single systematic joint set has the bulk permeability of a shale. An overburden with these properties is not likely to allow the transmission of RTW between the Marcellus and groundwater on time scales predicted by the Myers (2012) models even if capillary sealing is not a factor, which it is.

An overlay of >1000 HVHF wells in NE PA, many with laterals of nearly 2 km on topographic-scale fractures as mapped in the

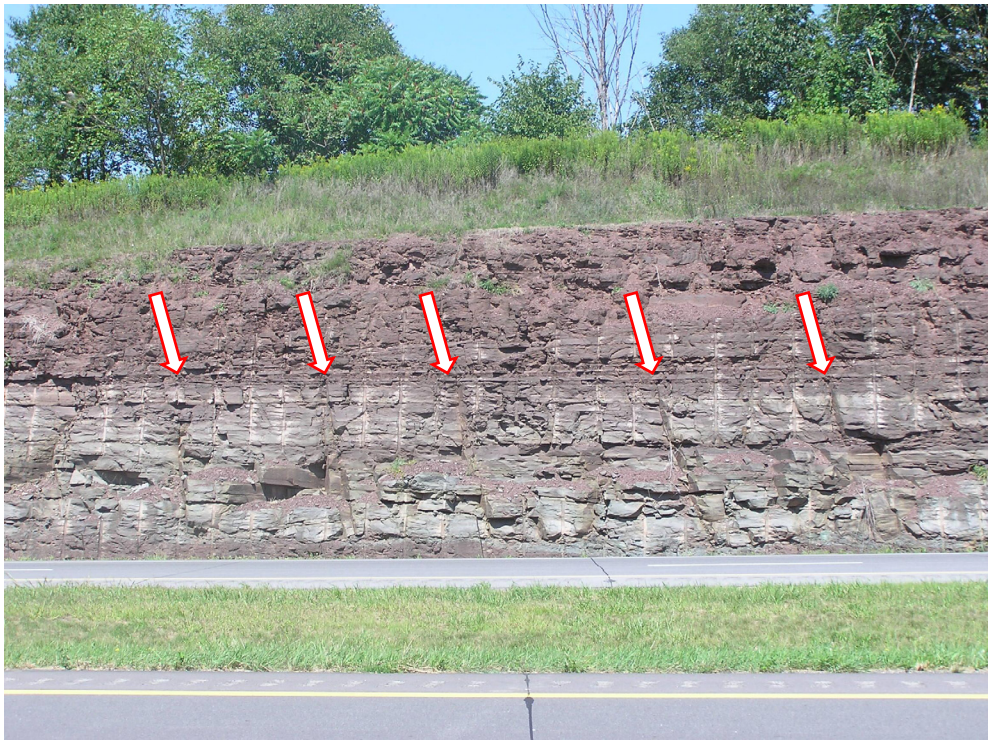

Fig. 10. A channel fill in the lower portion of the Upper Devonian Catskill Group along I-99 north of Hepburnville, PA. The channel fill has been reduced by the presence of a hydrocarbon charged fluid that may have been generated from organic material found as a lag at the base of the channel. Arrows point to a systematic set of J_2 joints cutting the channel fill without penetrating of encapsulating shale beds. These joints have a plumose markings characteristic of gas-driven natural hydraulic fractures.

southern tier of NY (Fig. 11) suggests that many Marcellus wells have cut through these surface features if they occur at the level of the Marcellus. To the best of our knowledge, none of the 4000+ HVHF wells in NE PA have encountered a Marcellus gas shale that has been drained sufficiently by these topographic-scale fractures to prevent gas-driven flowback. The point being that if these features have not bled gas on a geological time scale, they are even less likely to bleed a more viscous RTW over a few years.

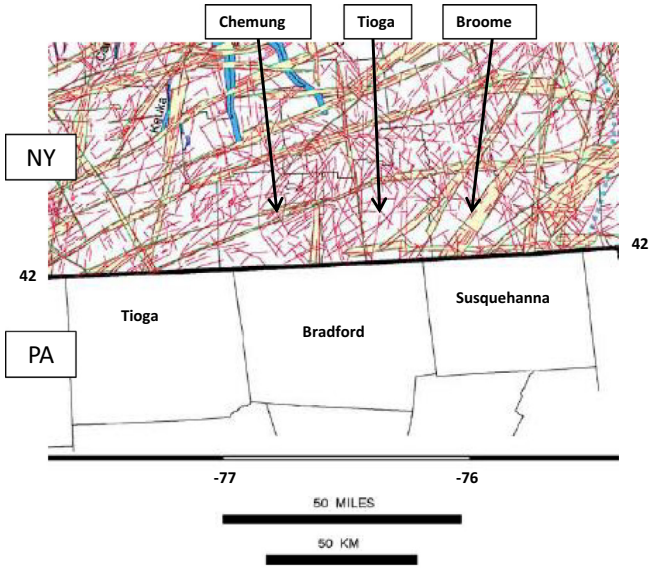

Fig. 11. Map of Landsat lineaments along the southern tier of NY (prepared by Jacobi, 2002). The scale of these lineaments, if projected into PA, suggests that dozens and dozens of lineaments occur in the three-county region that constitutes the Marcellus sweet spot in NE PA.

Methane does leak along near surface fractures as was the case for the first North American gas well in Fredonia NY and other places in the Appalachian Basin. This gas is not to be mistaken for Marcellus gas escaping from its "permeability jail", nor is this evidence for flow unrelated to the expected topographically-driven groundwater hydrodynamics (Baldassare, 2011).

The distribution of Type D waters based on hydrodynamic flow

An alternative to the Warner–Myers hypothesis (upward leakage through >2 km of Devonian section from the Marcellus shale) must be considered. A long established foundation of hydrology is the observation that the ground water table mimics topography and drives infiltrating water from uplands to rivers in valleys (Freeze and Cherry, 1979; Hubbert, 1940; Tóth, 1962). Rain falling on highlands mounds the water table, and the ground water table is pinned to rivers in the valleys. Infiltrating rainwater moves into the subsurface in the uplands, laterally at depth, and then up to feed streams in the lowlands and keep them running between rainfall events. This subsurface circulation will naturally bring the chemistry of deeper water to the surface preferentially under topographic lows. When the circulation encounters gas pockets, of which there are many in the Pennsylvania subsurface, it will dissolve some of the gas and then exsolve it near the surface, producing the gas seeps that are commonly found in streams (Molofsky et al., 2013). Such topographically-driven hydrologic flow is the conventional, parsimonious explanation of Warner et al.'s Type D water sample distribution. The Warner–Myers hypothesis is ad hoc and raises concerns which we seek to alleviate with the analyses presented in this paper.

Furthermore, the stratigraphy between the surface and the Marcellus shale was flooded with brines, oil and gas from strata at the depth of the Marcellus and below >250 million years ago when the organic material in these deeper formation matured to

hydrocarbons. Ground waters moving from upland recharge areas to lowlands (where they replenish streams and keep them flowing) pick up these old residual brines and gases, and move them to the surface in lowland areas. Methane seeps are well known in Pennsylvania and New York State. The first commercially used gas was collected and diverted for use in shops in Fredonia, New York when a shop owner noticed gas bubbling up in a nearby creek. Methane-rich ground waters and springs are common and such gas has been tapped for years by farmers and small time operators. There is even an "eternal" methane flame burning under a water fall in Chestnut Ridge County Park in Erie County New York. The gas poses a well-known explosion and fire hazard to water well drilling, when every so often a gas pocket is encountered. The distribution and origin of methane-rich ground water and methane gas seeps are nicely described (Kappel and Nystrom, 2012; Molofsky et al., 2013). The natural movements of ground water and their interaction with subsurface brines and gas is the conventional and much better explanation for the distribution of groundwater chemistry documented by Warner et al. (2012).

The contrast in strontium isotope ratios in pore waters above and below the Marcellus is central to Warner et al.'s (2012) arguments. The Marcellus pore water had a seawater salinity (≈3.5% NaCl) and an $^{87}Sr/^{86}Sr \approx 0.7085$ (Burke et al., 1982). The basis of their interpretation is Osborn et al.'s (2012) interpretation that the Marcellus is a regional seal separating different $^{87}Sr/^{86}Sr$ chemistries in the brines of the Upper Devonian Catskill delta complex from those found below the Marcellus. Osbourn et al.'s interpretation depends on the assumption that Upper Devonian sandstone pore water is highly radiogenic with low Sr concentrations ($^{87}Sr/^{86}Sr = 0.721$) in northeastern Pennsylvania as it was in northwestern Pennsylvania. This has not been established. The fact that northeastern Pennsylvania is much nearer 'uranium deposits' and the Silurian salt deposits are much thicker leaves the possibility the composition of all brine throughout the Upper Devonian of northeastern Pennsylvania has the same high Br/Cl, low $^{87}Sr/^{86}Sr$ as found in Type D groundwater samples.

Even presuming a regional Marcellus seal and contrasting strontium isotopic pore waters above and below it, the regional seal hypothesis is challenged to explain the uniformity of the isotopic ratio in the Marcellus. Regional fluids might have carried ^{87}Sr into the Marcellus during Alleghanian migration (Chapman et al., 2012). A regional flow interpretation would be supported if the Marcellus Br/Cl chemistry arises from mixing with brines expelled from the Salina salts. The homogeneity of $^{87}Sr/^{86}Sr$ across the basin points to a large scale Alleghanian flow below a Marcellus seal (Chapman et al., 2012; Osborn et al., 2012). It seems unlikely, however, that the Marcellus has fractures pervasive enough to allow an invading brine to re-write the strontium isotopic signatures as uniformly as the sampling from flowback waters in the many horizontal wells that have been drilled would suggest. Shales are not permeable and flow through them is unlikely to be uniform if it occurs at all.

The strontium isotopic signatures in the Marcellus might have been produced at burial or produced later during diagenesis. The combination of gas generation and basin-scale fluid migration could have left a Marcellus pore-water chemistry with a slightly elevated $^{87}Sr/^{86}Sr$ (=0.710–0.711) relative to its initial pore-water chemistry (Osborn et al., 2012). Smectite to illite diagenesis can cause the expulsion of ^{87}Sr from interlayers and in some layers the Marcellus can be as much as 20% illite by volume (Fig. 2). There are, however, indications that a great deal of illite in the black shales of the Appalachian Basin is detrital (Lash, 2006). High Br/Cl ratios in brines are usually attributed to halite precipitation. If the Marcellus pore waters were at least in part residual brines of this origin, the Br/Cl ratio would survive membrane filtration processes and removal of all mobile water during burial, diagenesis and hydrocarbon production and expulsion, and now be associated with residual water and solid ionic complexes on clay mineral surfaces, as observed. But again, a uniform isotopic composition over broad regions is not expected. The Marcellus pore waters could have acquired a Type D signature (in Warner et al.'s classification) in several ill-defined ways, but the uniformity of this signature and its distinctness from brines generated in the overlying stratigraphy is not as clear as Warner et al. (2012) might appear to suggest.

Summary and brief additional discussion

The samples on which we ran the Marcellus imbibition experiments had certainly been altered in many ways from collection to testing. They degassed as the pressure was reduced from at least 200 to 1 atm. They may have been invaded by water, despite precautions to minimize this, and they may have dried out slightly during cleaning and storage, although the fact that chips that were aged less imbibed more argues against drying being a major concern. The oil in the oil-based mud and the washing that removed it may have altered the wetting properties of the surface, but the alteration probably penetrated little into the chip because the oil-mud was designed not to invade and the washing was of short duration. The Marcellus imbibition tests are a poor proxy for running tests at in situ conditions, but since the controlling physics and chemistry are the same, the general results should be robust. The Marcellus is gas-filled and relatively dry in situ (Fig. 2), and it should imbibe water in a not too dissimilar fashion to that indicated in our experiments. In the near future we will know much more about the capillary properties of shales like the Marcellus because of their central importance to gas production. The Haynesville imbibition experiments were on core plugs cut from the center of a 4″ diameter core that was free of any damage or contamination by water or oil based mud drilling fluid.

In addition to pointing out that there is a simpler and better conventional explanation for the gas and brine chemistry distribution noted by Warner et al. (2012), the essential difference between our analysis and theirs is that we take into account multiphase, capillary, and osmotic phenomena and they do not. It is tempting to think that the overpressured state of the gas and brines in the Marcellus would cause them to leak if the shale is broken or disturbed by hydraulic fracturing. But this is a single phase perspective that begs the issue of how the overpressured gas and brines could have been retained in the Marcellus for such a very long time prior to their becoming of interest to us as a gas resource. The calculations we offer above show that neither the shale, much less the surrounding rock, are even close to being impermeable enough to have retained these overpressured fluids for 200 my. Rather, the overpressured fluids in the Marcellus have been retained by capillary seals. Capillary seals depend on two fluids being present (gas and water) and grain size layering. The presence of a second fluid phase completely changes the rules of subsurface fluid flow (Cathles, 2007). Anyone who has experienced gas indigestion has some insight into how gas and water can conspire to block flow. Capillary seals are very durable because it is impossible to fully remove one of the fluids or change the grain size distribution in the subsurface, and so capillary seals will continue to operate to isolate overpressured or underpressured fluids in the Marcellus long after any HVHF operations and gas recovery is finished.

Warner et al. (2012) worry that operations related to recovering gas from the Marcellus could increase the rate of brine leakage from the Marcellus and increased the risk of contamination of near-surface aquifers. The robustness of their water classification to their interpretation could be debated, as we have suggested above, but the most fundamental and really only important point is that the capillary blockage will not be changed by HVHF just

as it is not changed by earthquakes and all the other things nature has thrown at it over 200 my. Recovery of the gas in the Marcellus will, however, reduce the pressure of the gas and brines in the Marcellus to far below hydrostatic. The fluids will thus become highly underpressured and water in the surrounding strata will tend, by the dictates of single phase Darcy's law, to move into the Marcellus. This will not happen because the capillary seals surrounding the Marcellus will be as effective in preserving its underpressured state as they have been in protecting its overpressured state. But from the single phase perspective (flawed as it is by its incompleteness), the risk of brine leakage will be reduced by the reduction in gas pressure by gas production, not increased.

When the gas was expelled from the Marcellus it pushed out what little water the Marcellus still contained (pushed out or evaporatively removed from it as part of a high pressure vapor phase dominated by methane). Surrounding ground waters were prevented from imbibing back into the formation by highly durable capillary seals, which also kept overpressured gas from leaving the Marcellus. Only capillary seals with their zero permeability (like a highway you must pay the pressure toll to pass through) are capable of retaining the overpressured gas in the Marcellus for 200 million years. Capillary seals form naturally and automatically and are responsible for trapping overpressured and underpressured fluids in many basins worldwide, particularly when associated with fine grained, clay rich rocks, dominated by low aspect ratio pores as in illite rich shales such as the Marcellus and Haynesville shales. The result of all this is that such gas shales are highly water-undersaturated. It is a dehydrated sponge which will suck in water if given the chance. The fate of the residual treatment water, the HVHF water which has not returned and slipped from engineering control, is that it has been imbibed into the matrix of the Marcellus shale. It will remain there, just as the gas and small amounts of brine have remained in the Marcellus for over 200 million years. There is no plausible mechanism by which the Marcellus 'sponge' could be squeezed enough to release this water. The physics of imbibition and diffusion–osmosis force the treatment waters into the shale matrix. It is not physically possible to overcome these forces through either hydrological means or hydraulic fracturing, as has been demonstrated in most of the large shale gas plays in North America.

Perhaps the most important point of our paper is that multiphase capillary phenomena must be considered in cases where a non-aqueous fluid is present in the subsurface pore space. The vadose zone above the water table and oil and gas migration cannot be understood using single phase Darcy flow methods, and any policy insights or prescription based on single phase considerations will be fatally flawed. We hope that if nothing else this paper will communicate the importance of multiphase capillary phenomena and osmotic processes to those seeking to understand the risks associated with shale gas production.

Conclusions

Concerns that have been raised, most notably by the Warner–Meyers hypothesis, that there is a current leakage of brines and gas from gas shale which could be accelerated if that gas shale is subject to HVHF, and that residual treatment water (RTW) might also invade groundwater (Myers, 2012; Warner et al., 2012). We have demonstrated four reasons why this concern is ill-founded based on multiphase capillary phenomena. First, gas shale has a very low water saturation and the permeability of any rock decreases by orders of magnitude as the water saturation decreases from unity. Second, imbibition into a dry gas shale will sequester the RTW in a manner described by the simple imbibition experiments we describe. Third, the capillary seals which have prevented gas leakage for approximately 200 My (Marcellus) and 100 My (Haynesville), will continue to operate. Fourth, strong osmotic pressures will drive the treatment fluids into gas shale.

The hypothesis that environmentally significant leakage of brine from gas shale can be ongoing today fails completely on quantitative grounds. There is simply not enough brine in gas shale either today or in the past to produce detectable chemical anomalies in near surface samples if the leakage rate is steady. Injection of HVHF waters will not change this situation because the HVHF waters that are not returned during flow back or production are drawn into the gas shale and retained. There will still be gas and water in the surrounding strata and still be capillary seals. There are no forces to cause gas shale to discharge its brine (or gas) either before or after gas recovery. Production will in fact reduce the gas and brine pressures in the shale well below local hydrostatic levels and reduce gas or water leakage risk because there will be an additional reason (underpressure) in addition to capillarity and osmotic pressures for brines to move into rather than from the gas shale. Capillary seals will, however, prevent this inward migration just as they have prevented the escape of gas and brine for up to 200 My.

Any useful analysis of risk from recovery operations must consider multiphase capillary and osmotic phenomena. The important physics lies here, not in single phase Darcy flow as proposed by the Warner–Myers hypothesis. We will learn a great deal more about capillarity and osmotic pressures in fine grained rock because of their central importance in optimizing hydrocarbon recovery.

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