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# Chloride Concentration Gradients in Tank-Stored Hydraulic Fracturing Fluids Following Flowback

Pamela J. Edwards  
Linda L. Tracy  
William K. Wilson



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## Abstract

A natural gas well in West Virginia was hydraulically fractured and the flowback was recovered and stored in an 18-foot-deep tank. Both in situ field test kit and laboratory measurements of electrical conductivity and chloride concentrations increased substantially with depth, although the laboratory measurements showed a greater increase. The field test kit also underestimated chloride concentrations in prepared standards when they exceeded 8,000 mg L<sup>-1</sup>, indicating that laboratory analyses or other more accurate methods of detection should be used to determine chloride concentrations in flowback when they may be approaching West Virginia regulatory levels (12,500 mg L<sup>-1</sup>) that disallow disposal by land application. The gradation of chloride with depth also has implications for procedures used to collect flowback samples from reserve pits or tanks before disposal to ensure the resulting composite chloride concentration is representative of the total volume.

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## Cover Photo

William Wilson uses a field kit to determine the chloride concentrations of a flowback sample. Photo by Pamela Edwards, U.S. Forest Service.

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## INTRODUCTION

Production of natural gas generally involves a process known as hydraulic fracturing, which is more commonly called hydrofracing or fracing (sometimes spelled fracking). As its name implies, hydraulic fracturing creates fractures that extend from the well bore hole out into adjacent geology; these fractures then act as conduits through which the natural gas held in the geologic formation can flow back to the well. Fracing typically is accomplished by injecting a mixture of acids, water, gases, and additives under high pressure through the bore hole (Agbaji et al. 2009). Nitrogen and carbon dioxide, typically in their liquid phase (Agbaji et al. 2009), have become a relatively recent component of fracing fluids (Reidenbach et al. 1986) and are used to reduce the volume of needed water (Agbaji et al. 2009), which can range from several tens of thousands to several millions of gallons (Weston 2008).

The exact composition of fracing fluids depends upon the geologic layer to be fractured and the availability of the individual acids, water, gases, and additives (Agbaji et al. 2009); however, fracing additives fall into a variety of applications, and each application has a specific purpose during the fracturing process (Table 1). Additives may not be needed for every application and therefore would not be included in all fracing fluid formulations (URS 2009). Typically, most of the chemicals involved are in low concentrations because large volumes of water are used in the fracing process (URS 2009). Proppants, which are used to “prop” open fractures and voids to allow gas to flow to the well, are often present in substantially higher concentrations than the other additives in fracing fluids (Arthur et al. 2009). Sand is the most common proppant (GWPC and ALL Consulting 2009).

Once fracing is completed, a portion of the fracing fluid is recovered through a process called flowback (Sullivan et al. 2004, URS 2009, Woodroof et al. 2003a). The recovered fluid (also called flowback) typically is stored temporarily in open pits near the well called reserve pits (Deuel et al. 1999, Leuterman et al. 1988) or sumps (French 1980). These pits also may hold drill cuttings, drilling fluids, lubricants and soaps, rig wash, wastes from casing cement operations, and precipitation (Thurber 1992, Veil 2002). In some situations, flowback is stored in tanks (Agbaji et al. 2009), but this is more typical in wells that undergo refracing (after the pit has been emptied and reclaimed) or in locations that have restrictions on the use of open pits for storing drilling-related fluids.

### *The Authors*

*PAMELA J. EDWARDS, research hydrologist, currently is engaged in research on the effects of forest management and energy development on hydrology and water quality, and on the development of new techniques and tools for assessing the implementation and effectiveness of best management practices used within forested landscapes. She works at the Northern Research Station's Timber and Watershed Laboratory in Parsons, WV.*

*LINDA L. TRACY, geologist, has managed the minerals and geology program on the Monongahela National Forest for 33 years. Her office is located in Elkins, WV.*

*WILLIAM K. WILSON, mineral assistant, has 19 years of minerals administration experience. He currently oversees and administers the mineral operations on the Monongahela National Forest and works out of the Greenbrier Ranger District Office in Bartow, WV.*

**Table 1.—Applications and purposes of additives used in hydraulic fracturing for natural gas production (Adapted from URS 2009)**

Application	Purpose
Proppants	“Props” open fractures to allow produced gas to flow to the well
Acids	Helps create fractures
Breakers	Reduces viscosity of fracing fluid to release proppant into fractures and to improve recovery of fracing fluids in flowback
Bactericides	Prevents the growth of organisms that could generate gases that would contaminate produced natural gas. Also prevents growth of organisms that could reduce proppant flow into fractures
Clay stabilizers	Prevents clay swelling and release and movement of clays associated with the formation that could clog pores and fractures
Corrosion inhibitors	Used with fracing fluids that include acids, to reduce oxidation of steel tubing, casings, tools, and storage tanks
Iron controls	Inhibits the metal oxide precipitation in the formation to keep fractures open
Crosslinking agents	Increases the viscosity of the fracing fluid to allow greater amounts of proppants to flow into the fractures
Gelling agents	Increases the viscosity of the fracing fluid to allow greater amounts of proppants to flow into the fractures
Friction reducers	Reduces friction to allow more optimal injection of fracing fluid
Scale inhibitors	Prevents precipitation of carbonate and sulfate compounds that could clog pores and fractures
Surfactants	Reduces the surface tension of fracing fluids to improve recovery of flowback

Fluids held within the reserve pit are disposed of in several ways. The more common techniques are recycling, onsite treatment, treatment at a publically owned treatment plant, treatment at an industrial treatment plant, injection into depleted wells or deep safe formations through permitted Underground Injection Control wells, or land disposal (Nesbit and Sanders 1981, URS 2009). Recycling is done only on a limited basis (GWPC and ALL Consulting 2009) because the chemistry of flowback is not entirely suitable for fracing, so fresh additives and water need to be added to the mixture before it can be reused (URS 2009). A primary reason for recycling is to reduce the amount of freshwater needed (GWPC and ALL Consulting 2009, URS 2009, Weston 2008). Onsite or offsite treatment is expensive so both are uncommon, and onsite treatment typically occurs only at the largest well sites (Al-Harthy and Al-Ajmi 2009, URS 2009). Flowback is generally considered industrial wastewater (Gaudlip et al. 2008, URS 2009), so treatment is regulated and permitted as such. Only a small subset of privately or publically owned facilities is equipped to treat flowback fluids (URS 2009). Underground injection has been the most common

method of flowback disposal (Burnett 2008, GWPC and ALL Consulting 2009), and it is sometimes used in combination with treatment for disposing of residual chemicals (URS 2009). Injection has the negative consequence of removing the fracing water from the hydrologic cycle (Agbaji et al. 2009). Land disposal can occur by either burial (French 1980, McFarland et al. 1994, Nesbit and Sanders 1981) or surface application (Bauder et al. 2005, Nelson et al. 1984). Land disposal is allowed only in some states. Where allowed, however, land disposal may be common because it is economical.

There are environmental implications associated with the chemical composition of fracing fluids and their disposal, but research on these issues has been outpaced by research and development of extraction techniques. The proprietary nature of newer fracing chemicals can make it difficult to find out their exact chemical content (Soeder and Kappel 2009). But even when the chemical content can be determined from material safety data sheets (MSDS), the differences in concentrations between the raw chemicals and the much more diluted concentrations present in fracing fluids (and thus flowback) limit the

**Table 2.—Additives contained in the initial fracing fluid mixture used May 23, 2008, for gas well B-800<sup>a</sup>**

Product trade name/Additives contained in product	Application	Concentration
Sand – premium/Crystal silica, quartz (60-100%)	Proppant	1,300 lb/1,000 gal
SP Breaker/Sodium persulfate (60-100%)	Breaker	0.25 lb/1,000 gal
WLC-6 Fluid Loss Additive/Tallow soap (60-100%)	Surfactant	150 lb/100,000 gal
HC-2/Sodium chloride (5-10%) + inner salt of alkyl amines (10-30%)	Scale inhibitor	2 gal/1,000 gal
Clayfix-II Material/Alkylated quaternary chloride (30-60%)	Clay stabilizer	1 gal/1,000 gal
GBW-30 Breaker/Hemicellulase enzymes (5-15%) + carbohydrates (85%)	Breaker	1 lb/1,000 gal
BC-140/Monoethanolamine + ethylene glycol + boric acid solution (10-30% for each)	Crosslinker	2.5 gal/1,000 gal
OPTIFLO-HTE/Walnut hulls (60-100%) + crystalline silica (quartz) (10-30%)	Breaker	0.25 lb/1,000 gal
LGC-35 CBM/Paraffinic solvent (30-60%) + polysaccharide (30-60%)	Gelling agent	5.75 gal/1,000 gal
BE-3S Bactericide/2-mononbromo-3-nitrilopropionamide (1-5%) + 2, 2 dibromo-nitrilopropionamide (60-100%)	Biocide	1 lb/10,000 gal

<sup>a</sup>Four thousand (4,000) gallons of hydrochloric acid were introduced into the well bore under pressure; mixture of approximately 70,350 gallons of water obtained from a local stream, proppant, and fracing chemicals was forced into the well bore following the hydrochloric acid.

usefulness of the MSDS information for projecting biological effects (Bishop 2009). Available studies show fluids can impact plant growth negatively because of high concentrations of salts or toxic metals (e.g., McFarland et al. 1992, 1994; Miller and Pesaran 1980; Miller et al. 1980; Nelson et al. 1984; Younken and Johnson 1980), and there is a broader concern about how reserve pit chemicals may affect ground water and surface water quality (Harrison 1983, Hudak and Blanchard 1997, Soeder and Kappel 2009). More information about the chemical characteristics and behavior of fracing fluids and flowback would be valuable for better deciding upon treatment or disposal options or for developing more thorough science-based recommendations for land applications, such as establishing maximum allowable loadings for the most concentrated and/or toxic chemicals present.

## Background of this Study

In 2008, a natural gas well (well B-800) was drilled by a private oil and gas lessee on the Fernow Experimental Forest in Tucker County, West Virginia. This experimental forest is part of the Monongahela National Forest (MNF) and is administered by the U. S. Forest

Service, Northern Research Station. The well is 7,882 feet deep and was drilled into the Oriskany Sandstone and Huntersville Chert geologic formations. After drilling was completed, the bedrock at that depth was prepared for release of gas by fracing with a 70,350-gallon mixture of fracing fluids (Table 2) injected into the well bore hole under high pressure. When fracing was completed, flowback was stored temporarily in an open pit just downslope of the well pad that also contained drilling fluids and drilling waste. Pit fluid was treated with activated carbon to bring fluids into compliance with the general water pollution control permit (GP-WV-1-88) requirements for land application, and it was mixed by circulating fluid within the pit using pumps. Land application of the pit fluid began after 2 days of settling time.

In accordance with West Virginia minerals laws, fracing fluids may be land applied if the Cl concentration of the pit-stored fluid is less than 12,500 mg L<sup>-1</sup> ([http://www.wvdep.org/Docs/16150\\_General%20Water%20Pollution%20Control%20Permit%20.pdf](http://www.wvdep.org/Docs/16150_General%20Water%20Pollution%20Control%20Permit%20.pdf)). The Cl concentration of the pit fluid on the Fernow was determined using the procedure required by state

regulations: the well owner's contractor obtained a single composite sample collected by mixing equal volumes of six equally distributed grab samples taken from various locations in the pit and then determined the chloride (Cl) concentration in the field using a color-indicator field test kit on the day of, but prior to, land application. There is no formal explanation in the state regulations of what is meant by six equally distributed samples from various locations in the pit, but the individual who collected the samples stated they were collected from around the edge of the pit, just below the layer of floating scum (pers. comm., Charles Krushansky, Action Environmental, Jan. 26, 2010). The field test kit Cl concentration of that composite sample was approximately 7,500 mg L<sup>-1</sup>, so land application proceeded.

The fluids were pumped through a hose and hand sprayed onto two previously approved areas. During the 12-day application period in June 2008, additional fracturing fluid samples were taken at the hose nozzle by Forest Service personnel. Several of these samples were analyzed for Cl by ion chromatography at the Forest Service's Timber and Watershed Laboratory, using EPA-approved procedures (Edwards and Wood 1993).

The results from these samples indicated that Cl concentrations applied to the land varied temporally, ranging from 10,200 to 14,200 mg L<sup>-1</sup>. Consequently, there was speculation that the Cl concentrations in the pit fluids may have become spatially nonhomogeneous between treatment and mixing and the start of land application 3 days later. Therefore, well refracing in October 2009 to improve gas production was seen as an opportunity to examine Cl characteristics of flowback during short-term storage. Well refracing was done in the Sycamore Grit Formation in the hopes of reaching more gas with less associated water. This formation lies above the Oriskany Sandstone and Huntersville Chert Formations that were originally fraced, so the well was plugged beneath the Sycamore Grit to better confine fracturing within that formation.

This paper describes the Cl results associated with flowback obtained from the Sycamore Grit Formation.

## METHODS

### Refracing and Recovery Processes

The 2009 fracturing process differed from the original operation in 2008. First, 500 gallons of hydrochloric acid (30-60%) were injected into the well under pressure on September 27, 2009, several days before the other fracturing fluids were injected. An unknown percentage of this acid was recovered into the well's production tank (not the tank where flowback was collected) and then transported offsite.

On October 7, 2009, refracing was accomplished using a chemical formulation that involved a relatively high percentage of foam to reduce the volume of water needed (pers. comm., David Berry, October 7, 2009). The refracing process began by introducing approximately 840 gallons of fresh water into the well bore. This was followed by a foam mixture composed of approximately 1,000 gallons of water and 1,197,110 standard ft<sup>3</sup> of liquid nitrogen. The remaining fracturing additives were then combined using the following mixture and injected under pressure into the well bore:

- 14,406 gal of water, 242 lb WG-35 gelling agent, and 28.8 gal BC-140 crosslinker
- 6,429 gal of water and 108 lb WG-35 gelling agent
- 750,000 lb of premium sand
- 20 lb of GBW-30 breaker
- 3 lb of BE-3S bactericide
- 7 gal of LOSURF-300M surfactant
- 31 gal of Clayfix-II material organic salt additive
- 12 gal of GasPerm 1000 surfactant
- 3 gal of HC-2 salt additive

Another approximately 4,200 gallons of fresh water with no chemical additives were introduced into the well bore to push the fracturing fluids into the formation for hydraulic fracturing. Based on the total volume of water used (~26,875 gallons), the final concentration of each of the fracturing additives is given in Table 3.

**Table 3.—Additives contained in the fracturing fluid mixture used for the October 7, 2009, refracturing of well B-800**

Product trade name/Additives contained in product	Application	Concentration
Sand – premium/Crystalline silica (quartz) (60-100%)	Proppant	2,787 lb/1,000 gal
BC-140/Monoethanolamine + boric acid + ethylene glycol (10-30% for each)	Crosslinker	1.70 gal/1,000 gal
BE-3S Bactericide/2-mononbromo-3-nitrilopropionamide (1-5%) + 2, 2 dibromo-nitrilopropionamide (60-100%)	Biocide	1.12 lb/10,000 gal
Clayfix-II Material/Alkylated quaternary chloride (30-60%)	Clay stabilizer	1.15 gal/1,000 gal
GBW-30 Breaker/Hemicellulase enzymes (5-15%) + carbohydrates (85%)	Breaker	0.744 lb/1,000 gal
HC-2/Sodium chloride (5-10%) + inner salt of alkyl amines (10-30%)	Scale inhibitor	0.112 gal/1,000 gal
WG-35 Gelling Agent/Guar gum (60-100%)	Gelling agent	13.02 lb/1,000 gal
LOSURF -300M/1,2,4 Trimethylbenzene (0-1%) + Naphthalene (0-1%) + Poly(oxy-1,2-ethanediyl), alpha-(4-nonylphenyl)-omega-hydroxy-, branched (5-10%) + heavy aromatic petroleum (10-30%) + ethanol (30-60%)	Surfactant	0.26 gal/1,000 gal
GasPerm 1000/Isopropanol (10-30%) + terpenes and terpenoids of sweet orange-oil (10-30%)	Surfactant	0.558 gal/1,000 gal

Approximately 11,000 gallons of fracturing fluid were recovered during flowback, which were stored in two 18-foot-tall metal tanks brought to the site for short-term storage (Fig. 1). One tank was filled and the second held the remaining ~500 gallons. Initially, the well owner’s

contractor intended to land apply this fluid (excluding the hydrochloric acid) at a site mutually agreed upon with the Forest Service. However, because the volume of fluid was relatively small, the contractor transported all of the fracturing fluid offsite for disposal.



Figure 1.—The tank on the right is the one from which the flowback was sampled following refracturing of well B-800 on the Fernow Experimental Forest. The access inlet is on the top of the tank between the top of the ladder and the person preparing for sampling. The valves for emptying or sampling fluid are located near the base of the ladder; there are two valves on each of these tanks and they are visible on the second tank from the right, just above the buckets on the ground. Photo by William Wilson, U.S. Forest Service.



Figure 2.—The capped PVC pipe attached to the conductivity cell cable contains water that was used to provide extra weight to the cell to keep it from becoming buoyant when lowered into the flowback fluid in the tank. Photo by Frederica Wood, U.S. Forest Service.

Had land application occurred, the fluid would have been mixed by recirculating it among tanks using a pump. Following state regulations, a 10-day waiting period would have been required to allow solids to settle before the Cl concentration was tested. However, in the current situation, the contents of the tanks were not mixed because the operator decided against land application. Therefore, the measurements described in this report were made on fluids that received no additional mechanical mixing other than what occurred during chemical preparation, high pressure injection, and flowback.

## Field Methods

The current investigation of the Cl concentrations took place on October 14, 7 days after the fluid was pumped into the storage tanks. Only the single tank that held the ~10,500 gallons of fluid was included in the study.

Access to the tank was through a covered inlet on top of the tank (Fig. 1). To obtain some initial immediate information about the tank contents, a YSI EcoSense® EC300 conductivity cell was lowered into the tank and conductivity measurements were taken every 2 feet,

beginning at 0 feet (i.e., just below the fluid surface). Intervals of 2 feet were chosen somewhat arbitrarily, but the authors believed this spacing would be sufficient to define the general characteristics and variability of the tank's contents. A weight constructed of 0.75-inch-diameter x 11.5-inch-long PVC pipe filled with water was attached to the conductivity cell cable just above the cell (Fig. 2) to reduce the buoyancy of the conductivity cell in the fracing fluid. Two-foot intervals were delineated on the cable (measured from the contact points of the cell) using permanent marker. The conductivity cell provides temperature-adjusted readings and can shift automatically between  $\mu\text{S cm}^{-1}$  and  $\text{mS cm}^{-1}$  units as needed, depending upon the conductivity of the solution.

After the conductivity measurements were taken and the cell was removed from the tank, fracing fluid samples were collected from 4-, 8-, 12-, and 16-foot depths (measured from the top of the fluid level) using a model 3700 ISCO® automatic water sampler with 25 feet of uptake tubing with 1-foot intervals marked on the tubing. The pump motor was disconnected from the case for use (Fig. 3). The strainer was retained on the end of the tubing to provide weight to reduce the





Figure 3.—An ISCO® 3700 sampler removed from its housing was used to obtain flowback fluid samples from the tank at 4-, 8-, 12-, and 16-foot depths. The strainer (i.e., intake) of the sampler is the perforated tube on the left front of the photograph. Photo by Frederica Wood, U.S. Forest Service.

buoyancy of the tubing (Fig. 3). An approximately 1-L sample was collected at each of the four depths using the manual setting on the ISCO® sampler. Only one sample was collected from each of the four depths because the small tank opening and flexibility of the uptake tubing made it difficult to take multiple samples from different locations at those depths. To avoid carryover between samples, after the tubing was lowered to the 8-, 12-, and 16-foot depths, a volume of sample that exceeded the bore volume of the 25 feet of tubing was pumped into a refuse container. After all sampling was completed, the fluid in the refuse container was poured back into the storage tank.

A subsample of each of the four samples was analyzed in the field for Cl concentration using a model CD-51 Hach® High Range Chloride Test Kit. The analysis is colorimetric and uses silver nitrate as the titrant, and chloride measurements are estimated in 500-mg L<sup>-1</sup> increments for concentrations up to 10,000 mg L<sup>-1</sup>. The field measurements were made by the MNF geologist,

using the same techniques and equipment normally used on the MNF for assessing Cl concentrations in fracturing fluids before land application. This brand of kit also is used commonly in West Virginia to make field assessments of Cl concentrations in reserve pits.

## Laboratory Methods

The fracturing fluid samples were returned to the Timber and Watershed Laboratory for laboratory determinations of electrical conductivity and Cl concentrations. Electrical conductivity was measured because there was some concern that the field measurements made at 0-, 2-, 4-, and 6-foot depths were incorrect because the conductivity values were extremely low and the readings were unstable (described later). Laboratory measurements of electrical conductivity were determined using a Radiometer® CDM 83 conductivity meter with a platinum cell. The conductivity cell was calibrated at a single value, 995  $\mu\text{S cm}^{-1}$ .

Chloride concentrations were determined in the laboratory using a Dionex® DX500 ion chromatograph to obtain more accurate readings than the field tests because those tests estimate Cl concentrations only to the nearest 500 mg L<sup>-1</sup>. Each sample was vacuum filtered through 0.45-µm glass microfiber filters. Two to three hours were required to filter approximately 50 ml because of the high viscosity of the fracturing fluid. Three replicate dilutions were prepared for each sample using 1:1,000 dilutions for the 4- and 8-foot samples and 1:5,000 dilutions for the 12- and 16-foot samples. The required dilution levels needed to obtain results within the instrument's calibration range were determined from the field-measured results (described later).

Because of the limited amount of data collected in this study, analyses are limited to descriptive statistics of means, standard deviations, and coefficients of variation (Sokal and Rohlf 1994). Those statistics were calculated using Microsoft® Office Excel® 2007 software.

## RESULTS

Field conductivities increased markedly with depth (Table 4). At depths ≤6 feet, they were very low and seemed suspect because of the continuous drift of the readings and general inability to obtain a stable measurement. Such drift had not occurred during previous use with this meter in low ionic strength stream water. These shallow readings became even more suspect when the deeper values showed much higher conductivities (Table 4) that did not drift. Indeed, the laboratory-measured conductivity values (Table 4) for the 4- and 8-foot depth samples were much greater than those obtained in the field. We believe the ≤6-foot-deep field-measured values were in error because there was poor contact between the fluid and conductivity cell, perhaps due to particles that partially blocked the sensor contacts or gas bubbles in the cell that became dislodged as the head increased with depth.

The field-measured conductivity readings below 6 feet in combination with the four laboratory measurements of conductivity suggest that the Cl concentrations increased to about a depth of 14 feet (Table 4). Deeper than 14 feet, conductivity varied much less, suggesting that Cl

**Table 4.—Field-measured and laboratory-measured electrical conductivities of fracturing fluids**

Distance below fluid surface in tank (ft)	Electrical conductivity	
	Field	Laboratory
0	4.1 µS cm <sup>-1</sup>	--
2	7.0 µS cm <sup>-1</sup>	--
4	11.9 µS cm <sup>-1</sup>	3.490 mS cm <sup>-1</sup>
6	26.3 µS cm <sup>-1</sup>	--
8	1.375 mS cm <sup>-1</sup>	8.770 mS cm <sup>-1</sup>
10	4.330 mS cm <sup>-1</sup>	--
12	21.00 mS cm <sup>-1</sup>	23.20 mS cm <sup>-1</sup>
14	23.09 mS cm <sup>-1</sup>	--
16	23.26 mS cm <sup>-1</sup>	23.70 mS cm <sup>-1</sup>
18	23.30 mS cm <sup>-1</sup>	--

concentrations also stabilized. Differences in the physical appearances of the shallow (4- and 8-foot) and deeper (12- and 16-foot) samples also suggested the overall chemistry of these samples was quite different. The two shallower samples were a whitish opaque color, while the deeper samples were a darker orange or rust (Fig. 4).

Field and laboratory determinations of Cl confirm the gradient suggested by the conductivity results. The field-measured Cl concentrations in the 12- and 16-foot samples were 7,500 and 8,500 mg L<sup>-1</sup>, respectively, which were about 2 to 4 times greater than the concentrations at the shallower depth (Table 5). The concentration gradient was even more striking for the laboratory-measured values. The average laboratory-measured Cl concentrations at 12- and 16-foot depths were between 11,000 and 13,000 mg L<sup>-1</sup> and were 4 to 10 times greater than the 927 and 3,463 mg L<sup>-1</sup> averages at 4- and 8-foot depths, respectively. The largest increases in concentrations for both types of Cl measurements occurred between 8 and 12 feet; the concentrations from 4 to 8 feet increased by about 1,000 to 2,000 mg L<sup>-1</sup>, depending upon whether the analysis was in the field or in the laboratory. The concentrations from 12- to 16-foot depths increased by 1,000 mg L<sup>-1</sup> for field testing while the average decreased by about 1,000 mg L<sup>-1</sup> for laboratory measurements (Table 5).

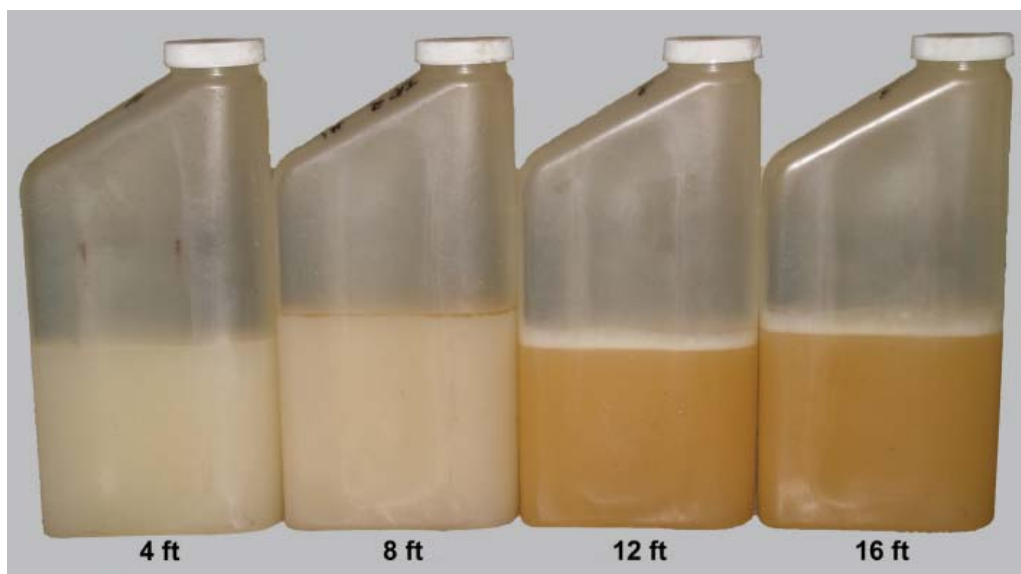


Figure 4.—Four flowback samples collected for laboratory analyses, showing the color differences between the shallow (4- and 8-foot) and deep (12- and 16-foot) samples. Photo by Pamela Edwards, U.S. Forest Service.

Not surprisingly, the largest standard deviations for the laboratory measurements of Cl were associated with the two samples containing the greatest Cl concentrations and involving the 1:5,000 dilutions (Table 5). However, the largest coefficient of variation, 24.8 percent, corresponds to the 4-foot-deep sample that had the lowest replicate and average Cl concentrations. The coefficient of variation for the 12- and 16-foot-deep samples ranged from about 11 to 14 percent and was only 2 percent for the 8-foot-deep sample.

Field and laboratory testing yielded similar concentrations of Cl for the two shallowest samples. The 4- and 8-foot samples had lower laboratory-measured concentrations than obtained by field testing, but the

8-foot field measurement was essentially equal to all three laboratory replicates and the average. By contrast, as the Cl concentrations increased, the deviation between the field and laboratory measurements increased substantially. For 12- and 16-foot-deep samples, the laboratory averages were approximately 3,000 to 5,000 mg L<sup>-1</sup> greater than the field values, and the individual replicate values were 2,000 to 6,650 mg L<sup>-1</sup> greater than the field-measured values.

## DISCUSSION

Before sampling, we were uncertain whether the flowback fluid would have elevated Cl concentrations because the primary source of Cl was the hydrochloric acid in the fracturing fluids, which had been recovered separately

**Table 5.—Field-measured Cl concentrations determined using model CD-51 Hach® High Range Chloride Test Kit and laboratory-measured Cl concentrations determined using ion chromatography**

Depth (ft)	Field measurement	Laboratory measurement				
		Replicate			Mean ± 1 std. dev.	Coefficient of variation
		1	2	3		
		mg L <sup>-1</sup>				
4	2,000	1,160	700	920	927 ± 230	24.8
8	3,000	3,530	3,470	3,390	3,463 ± 70	2.0
12	7,500	11,900	11,700	14,150	12,583 ± 1,360	10.8
16	8,500	11,300	13,200	10,050	11,517 ± 1,586	13.8

before the other additives were introduced. There were Cl-containing compounds in the fluids, but they were generally in relatively low concentrations (Table 3) so their influence on flowback chemistry was not expected to be substantial.

Both the field and laboratory data show that Cl concentrations present in the flowback were substantial. Carryover of chemicals from the storage tank from use at other sites is not believed to be an important source of the Cl because tanks are emptied and the inside surfaces are hosed out to remove residual material before removal from a site. While reactions between the entire suite of fracturing chemicals and the geology may have released some Cl, it is likely that much of it was attributable to unrecovered hydrochloric acid. We do not have data to estimate the percent of recovery of the hydrochloric acid, but flowback recoveries are never complete (Sullivan et al. 2004; Woodroof et al. 2003a,b). Recovery data are largely unavailable on a broad scale (Sullivan et al. 2004), but recovery from wells drilled in the Marcellus Shale in Pennsylvania averaged 35 to 40 percent, with a maximum recovery for a single well of 62 percent (URS 2009). This average approximates the post-acidized recovery of fluid found in the non-Marcellus Shale in this investigation; if it is representative of the percentage of hydrochloric acid recovered in the earlier, separate acid flowback, about half or more of the acid would have remained in the geologic formation. Thus, residual hydrochloric acid was a likely source of much of the Cl recovered in the post-acidized flowback.

Samples from the tank showed that the Cl concentrations increased with depth, and differences in fluid characteristics with depth also were evident visually. But it is impossible to know whether this gradation occurred after flowback was complete or if the fluid delivered to the tank had variable chloride concentrations during the delivery period that resulted in the increasing concentrations with depth. The composition of flowback has been documented to change during flowback recovery (URS 2009); limited data from drilling in the Marcellus Shale in Pennsylvania showed increases in total dissolved solids, chloride, and barium concentrations over time through flowback processes (URS 2009). In the current study, the tank was filled from the top,

so decreasing Cl concentrations through the flowback process would have been required for the gradation we observed. Even if some Cl differences existed during flowback, substantial mixing within the tank would be expected due to the 18-foot-deep tank being filled from the top and the resulting turbulence from fluid falling into the tank. These pieces of evidence suggest that Cl gradation occurred following flowback and not as the result of temporal differences in flowback chemistry.

The occurrence of Cl gradation has several potential implications with respect to land application of fracturing fluids. For tank-stored fluids, depending on how the composite sample is taken before land application, very different Cl concentrations could result. If the composite sample is taken from the valves at the bottom of the tank (Fig. 1), based on our findings this sample would be expected to approximate the highest Cl concentrations in the tank. By contrast, a composite sample taken from the top of the tank could grossly underestimate both the maximum and the average Cl concentrations in the tank.

Because a tank is physically different from an open pit, and pits are used to hold both drilling fluids and fracturing fluids, there is some uncertainty about how these results apply to pit-stored fluids. However, Cl concentrations in the samples collected during 2008 land application following the original well fracturing support either that gradation occurred or that Cl chemistry in the pit was spatially nonhomogeneous even after mixing. Because the field conductivity data and the Cl results showed that the greatest change in Cl concentrations occurred between 10- and 12-foot-depths, concentration differences may be most evident in pits that are at least that deep. If Cl differences can occur through time, the samples taken from near the surface and edges of reserve pits may not adequately represent the Cl chemistry present, and further study on reserve pit chemistry is warranted.

The comparisons of the field and laboratory results currently have only limited implications because only one test kit was used and only four samples were tested. However, we also compared known Cl concentrations of standards prepared from sodium chloride mixed in deionized water to measurements of those standards made with the Hach® kit. Using the manufacturer's

**Table 6. —Chloride concentrations of known standards determined by CD-51 Hach® test kit**

Hach® method	Cl standard concentration	Hach® test-kit concentration
	-----mg L <sup>-1</sup> -----	
High Range Cl Test	500	1,000
	1,000	1,500
	2,000	2,500
	5,000	5,000
	8,000	8,500
	10,000	10,000
Expanded High Range Cl Test	10,000	15,000
	12,000	15,000
	15,000	15,000
	20,000	25,000
	25,000	30,000

instructions, the Hach® High Range Cl Test method was used for determining concentrations up to 10,000 mg L<sup>-1</sup>, and the Hach® Expanded High Range Cl Test (also a titration with silver nitrate) was used for concentrations of 10,000 to 25,000 mg L<sup>-1</sup>. In the expanded range, the Hach® test estimates concentrations only to the nearest 5,000 mg L<sup>-1</sup>.

The Hach® methods routinely overestimated Cl concentrations in the range of 500 to 25,000 mg L<sup>-1</sup> (Table 6). That the Cl concentrations in the flowback samples were underestimated in only the highest concentration samples (Table 5) suggests chemicals were present in those flowback samples that interfered with the titration results. Therefore, simple calibration of this type of field kit to conventional “clean” standards may be insufficient to understand how their results will compare to more rigorous laboratory measurements.

Because it would be difficult and expensive to develop calibration standards that contain similar chemical constituencies to those found in flowback, it may be easier to use laboratory analyses to determine Cl concentrations in flowback for assessing allowable disposal methods. It would obviously take longer to obtain results from laboratory procedures than field test kits, but the results would be more accurate. The field test

kit is useful as a filter, so if Cl concentrations are reasonably low subsequent laboratory testing would not be necessary; for this particular kit, concentrations of approximately 8,000 mg L<sup>-1</sup> appear to be in the range that would not require additional laboratory testing and could be assumed to be less than 12,500 mg L<sup>-1</sup>. Because analysis with the field test kit requires use of the Expanded High Range Cl Test for concentrations above 10,000 mg L<sup>-1</sup>, even if this brand of field kit had a 1:1 relationship with laboratory results, it would be necessary to default to laboratory procedures or some other type of more sensitive field analysis to determine actual concentrations (since results for the Expanded High Range Test are reported only to the nearest 5,000 mg L<sup>-1</sup>).

Laboratory results also have some level of error associated with them, and preparation of dilutions can add to that variability. Because only small amounts of flowback fluid were pipetted for the dilutions, very small differences in delivered volumes can lead to relatively large differences in calculated concentrations, especially for the 1:5,000 dilutions. The high viscosity of the fracturing fluid also may affect the efficacy and repeatability of pipette delivery.

The variability among replicates of an individual sample ranged from tens to thousands of milligrams per liter, with the greatest absolute variability associated with concentrations that were above 10,000 mg L<sup>-1</sup> (Table 5). In both the 12- and 16-foot-deep samples, one of the replicates exceeded the 12,500-mg L<sup>-1</sup> maximum concentration for land application (had land application been considered), while the other two replicate values and the average of all three values were below that concentration (Table 5). Therefore, even if laboratory procedures are used to determine Cl concentrations, it may be prudent to analyze 2 or 3 replicates of a sample when the Cl concentrations are within 2,000 to 3,000 mg L<sup>-1</sup> of the threshold value (12,500 mg L<sup>-1</sup>) and use the average concentration to determine whether land application is appropriate.

It is important to note that the results presented here are from a single tank at a single point in time, and the data result from fracturing a specific geologic layer using a specific fracturing technique and additive mixture. However, these limitations do not make the data inconsequential

because there are few data of this type in the literature. Different Cl concentrations or differences in their spatial relationships may result if different fracing additives, fracing techniques, and/or geologic layers are involved or if flowback efficiencies are substantially different. Consequently, much more research is needed to build relevant databases from which the physical and chemical conditions associated with flowback can be characterized and the associated environmental impacts of holding and disposing of those fluids can be better understood.

## CONCLUSION

Following refracing of a natural gas well in West Virginia, flowback was recovered and stored in a 10,500-gallon tank. In situ electrical conductivity and laboratory analyses of electrical conductivity and Cl concentrations made after 7 days of storage showed that the Cl concentrations in flowback increased substantially with depth. This finding suggests that Cl associated with flowback stored in reserve pits also has the ability to become graded with depth. In West Virginia, land application of flowback is permitted only if the Cl concentration of a representative sample is less than 12,500 mg L<sup>-1</sup>. Thus, if samples collected to make that assessment are not representative of the pit or the tank in which they are stored, the selected disposal method may be inappropriate or unnecessary relative to state regulations.

Chloride concentrations in the tank-stored flowback were underestimated by a common type of colorimetric field test kit at concentrations above 3,000 mg L<sup>-1</sup>. For field measurements of approximately 8,000 mg L<sup>-1</sup> or greater, reanalysis of the sample using laboratory procedures is recommended to ensure that more accurate results are obtained on which to base decisions about fluid disposal. Calibration of the field unit to typical “clean Cl” standards will not be sufficient to compensate for differences between laboratory and field kit test results, because flowback fluid may have chemicals that interfere with colorimetric tests. Additionally, we recommend that replicate laboratory analyses be used so an average of those results is employed to represent the Cl concentration of flowback, whether stored in pits or tanks.

This study examined the contents of only a single tank of flowback. However, there is surprisingly little information in the literature on flowback chemistry, and substantial additional research is needed to fully understand the character and environmental effects of fracing fluids and flowback. This information becomes increasingly important as the Nation turns to its own natural gas reserves for energy independence.

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A natural gas well in West Virginia was hydraulically fractured and the flowback was recovered and stored in an 18-foot-deep tank. Both in situ field test kit and laboratory measurements of electrical conductivity and chloride concentrations increased substantially with depth, although the laboratory measurements showed a greater increase. The field test kit also underestimated chloride concentrations in prepared standards when they exceeded 8,000 mg L<sup>-1</sup>, indicating that laboratory analyses or other more accurate methods of detection should be used to determine chloride concentrations in flowback when they may be approaching West Virginia regulatory levels (12,500 mg L<sup>-1</sup>) that disallow disposal by land application. The gradation of chloride with depth also has implications for procedures used to collect flowback samples from reserve pits or tanks before disposal to ensure the resulting composite chloride concentration is representative of the total volume.

**KEY WORDS:** natural gas, unconventional well development, hydraulic fracturing, flowback recovery, chloride concentrations, specific conductivity

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