Analytical Considerations During Natural Gas Fracturing Activities

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Overview

- Introduction
  - Intense Scrutiny, Important Factors, Fracturing Solutions, Data Validation
- Hydraulic Fracturing
- Fracturing Fluids
- Case Study 1
  - Investigation and Summary
- Case Study 2
  - Investigation and Summary
- Recommendations and Corrective Actions

Introduction: Intense Scrutiny

Natural Gas E&P activities under intense scrutiny from public, media, and regulatory agencies

Rising Shale Water Complicates Fracking Debate

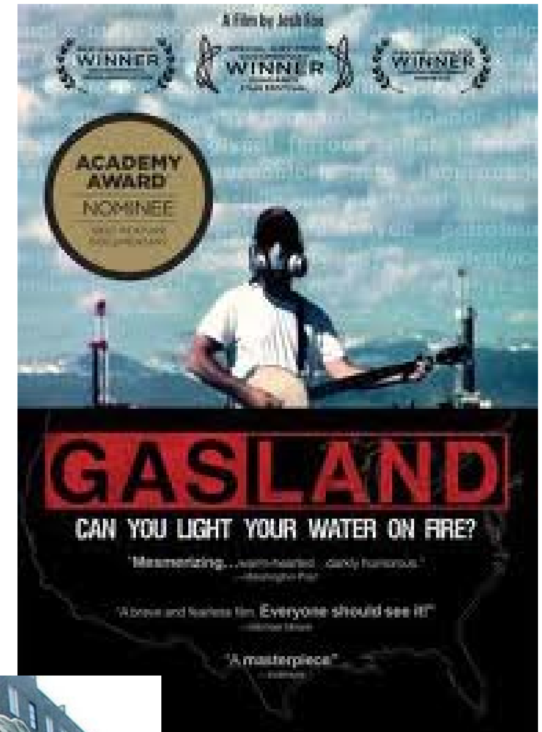
(7/9/12, NPR)

New Fracking Research Disputes A Fundamental Industry Claim

(7/10/12, businessinsider.com)

Natural gas gold rush: Is your state next?

(7/2/12, USA Today)



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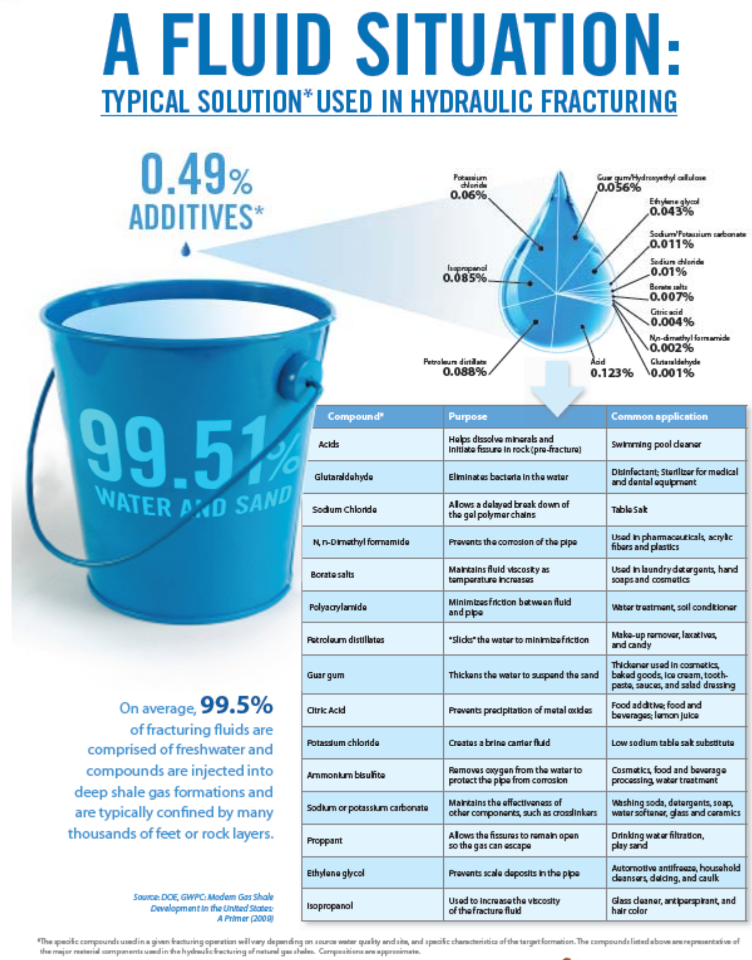
Introduction: Important Factors

- High-quality analytical data before, during, and after production processes is increasingly important to document baseline and post-drilling groundwater quality
- Equally important is the characterization and analysis of unusual analytes which may be present in fracturing solutions

Introduction: Fracturing Solutions

- Fracturing solutions typically contain
  - 98-99% water and sand (proppants)
  - about 1% chemical additives (*e.g.,* gelling agents, friction reducers, surfactants)
- Many additives are not routinely tested for by laboratories
- Where laboratory methods do not exist for unusual analytes, a robust method development process is necessary to ensure that a complete characterization of groundwater is achieved



Compound*	Purpose	Common application
Acids	Helps dissolve minerals and initiate fissure in rock (pre-fracture)	Swimming pool cleaner
Glutaraldehyde	Eliminates bacteria in the water	Disinfectant; Sterilizer for medical and dental equipment
Sodium Chloride	Allows a delayed break down of the gel polymer chains	Table Salt
N, n-Dimethyl formamide	Prevents the corrosion of the pipe	Used in pharmaceuticals, acrylic fibers and plastics
Borate salts	Maintains fluid viscosity as temperature increases	Used in laundry detergents, hand soaps and cosmetics
Polyacrylamide	Minimizes friction between fluid and pipe	Water treatment, soil conditioner
Petroleum distillates	"Slicks" the water to minimize friction	Make-up remover, laxatives, and candy
Guar gum	Thickens the water to suspend the sand	Thickener used in cosmetics, baked goods, ice cream, tooth-paste, sauces, and salad dressing
Citric Acid	Prevents precipitation of metal oxides	Food additive; food and beverages; lemon juice
Potassium chloride	Creates a brine carrier fluid	Low sodium table salt substitute
Ammonium bisulfite	Removes oxygen from the water to protect the pipe from corrosion	Cosmetics, food and beverage processing, water treatment
Sodium or potassium carbonate	Maintains the effectiveness of other components, such as crosslinkers	Washing soda, detergents, soap, water softener, glass and ceramics
Proppant	Allows the fissures to remain open so the gas can escape	Drinking water filtration, play sand
Ethylene glycol	Prevents scale deposits in the pipe	Automotive antifreeze, household cleansers, deicing, and caulk
Isopropanol	Used to increase the viscosity of the fracture fluid	Glass cleaner, antiperspirant, and hair color

*The specific compounds used in a given fracturing operation will vary depending on source water quality and site, and specific characteristics of the target formation. The compounds listed above are representative of the major material components used in the hydraulic fracturing of natural gas shales. Compositions are approximate.

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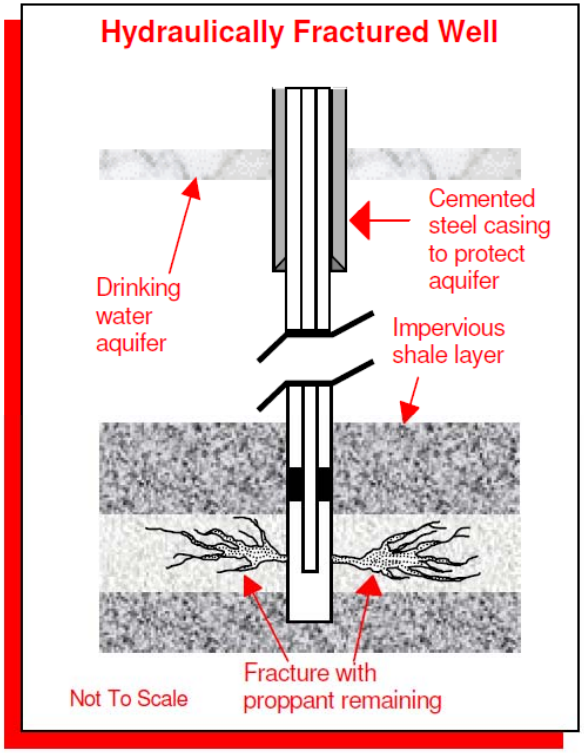
Introduction: Data Validation

- Proper evaluation of data validity requires:
  - Thorough knowledge of the pre-existing conditions
  - Thorough documentation
    - sampling and handling processes
    - bottleware used for sampling
    - instrumentation and methodology used for testing

Hydraulic Fracturing

- Propagation of fractures in a rock layer caused by the presence of a pressurized fluid
- Hydraulic fractures form naturally
  - one means for gas and petroleum from source rocks to migrate to reservoir rocks
- Oil and gas companies may attempt to accelerate this process in order to release petroleum, natural gas and coal seam gas for extraction
- Energy from injection of a highly-pressurized fracturing fluid creates new channels in the rock which increases the extraction rates and recovery of fossil fuels
- Operators maintain fracture width or slow its decline by introducing a proppant into the injected fluid
  - Grains of sand, ceramic, or other particulates
  - They also prevent the fractures from closing when the injection is stopped



Independent Petroleum Association of America (www.ipaa.org)

Fracturing Fluid

- Slurry of water, proppants, and chemical additives
- Various types of proppant include silica sand, resin-coated sand, and man-made ceramics
- Proppants vary depending on the type of permeability or grain strength needed.
- Chemical additives are applied to tailor the injected material to the specific geological formation, to protect the well, and improve its operation
- Chemical additives used in fracturing fluids typically make up less than 1% by weight of the total fluid. Over the life of a typical well, this may amount to 100,000 gallons of chemical additives
- Over its lifetime an average well may require up to an additional 5 million gallons of water for the initial fracturing operation and possible re-stimulation fracturing jobs

Two Case Studies

- Demonstrate how method development and knowledge of sampling and analysis processes enabled natural gas companies to effectively detect and resolve issues related to hydraulic fracturing
- Case Study One
  - Explores the use of method development to analyze for specific chemical additives that are non-routine target analytes in groundwater samples
- Case Study Two
  - Summarizes the investigation conducted into the sampling and laboratory processes to identify the source of a suspected contaminant

Case Study One: Overview

- Major natural gas E&P company
- Sampling program - groundwater samples
- Third-party QA Oversight and Data Management
  - field oversight of sampling activities
  - laboratory data deliverable coordination
  - management of sample data
  - quality assurance (QA) verification and validation of sample data

Case Study One: Overview (Cont.)

- Fracturing fluid containing chemical additives was inadvertently released in flowback water into a shallow aquifer used for potable sources.
- Following emergency response, the Material Safety Data Sheets (MSDS) for the chemical additives were provided to the QA Team.
- Upon review of the information, it was determined that two key organic compounds that are not routinely tested and required method development

Case Study One: Investigation

- QA Team explored options for non-routine compound analysis
- Contracted laboratory already performing the routine analyses and specialty laboratories were contacted
- Laboratories contacted
  - not capable of detecting these chemical additives using current published methods
  - did not have the analytical capacity to handle the sample volume/turn-around-times (TATs)
- Cost and time required to develop a new analytical method was not favorable to the laboratories or the project stakeholders

Case Study One: Method Development

- QA Team collaborated with an alternate contract laboratory to develop methods
- Based on the chemistry of the non-routine compounds, analysis by GC/MS, HPLVC, HPLC, HPLC/MS, IC were considered by the QA Team and laboratory
- Method development
  - instrument and analysis techniques, including extraction techniques, surrogates, analytical conditions, development of standard operating procedures (SOPs), method detection limit (MDL) studies, precision and accuracy were evaluated by the QA Team and laboratory
  - At the conclusion of the evaluation, it was determined that GC/MS and HPLC/MS instruments and analysis techniques would be used for the analysis of the two non-routine compounds

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Case Study One: Conclusions

- Routine analytical methods may not exist for the groundwater characterization data needs of natural gas fracturing activities
- Robust method development process is needed
- Time, cost, capacity, and TAT will need to be considered for the project and the contracted laboratory
- QA Oversight chemistry support can help ensure data quality objectives are met

Case Study Two: Overview

- Major natural gas E&P company
- Sampling program of 45 residential water wells
- Third-party QA Oversight and Data Management
  - field oversight of sampling activities
  - laboratory data deliverable coordination
  - quality assurance (QA) verification and validation of sample data

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Case Study Two: Overview (Cont.)

- QA Team observed large number of detections for a diol compound
- QA Team suspected that the similarity in concentrations suggested that these results may be artifacts of contamination and probably not native to the project samples
- Over a three-week period, the QA Team investigated possible scenarios and sources of the suspected compound contamination

Case Study Two: Investigation

- The diol compound was detected at trace levels in laboratory method blanks at sufficient concentrations that placed doubt on 64% of the compound results.
- QA Team was authorized to perform audit of the sampling teams
  - QA Team discovered that field blanks had not been collected to date.
- QA Team examined the historical data
  - QA Team examined historical data and observed low-level method blank contamination that placed doubt on 60% of the compound results.
- QA Team tightened the DQOs
  - QA Team directed laboratory management to tighten the data quality specifications in two areas - blank contamination and instrument carryover.
- Adding Blind Field Blanks
  - sampling team collected the first set of blind field blanks, each at a different residence.
  - Results of the three DI water blanks revealed concentrations (0.8 - 5.9 mg/L) of the compound similar to the levels detected in project samples.

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Case Study Two: Investigation (Cont.)

- The laboratory was questioned about the hydrochloric acid-preserved VOA vials that were issued to the sampling team
- QA Team discovered that laboratory personnel were using unpreserved VOA vials for method blanks
- Laboratory did **not** certify the hydrochloric acid-preserved VOA vials that were issued to the sampling team for diol analysis
- QA Team recommended the laboratory immediately analyze:
  - specific lot number of hydrochloric acid-preserved VOA vials that were issued to the sampling team
  - analyze the deionized water used for decontamination and field blanks,
  - unpreserved VOA vials used for laboratory method blank, and
  - isopropyl alcohol used in field as a decontamination rinse.

Case Study Two: Observations & Findings

- Based on the information gathered during this investigation, the following findings can be reasonably made regarding the detection of the diol compound
  - The diol compound was detected in many samples collected in HCl preserved VOA vials at concentrations between 0.5 mg/L and 5 mg/L
  - The inconsistent method blank contamination resulted in only partial qualification of the large number of the compound detections. It was determined that the laboratory was analyzing method blanks from *unpreserved* vials and that the investigative samples were in HCl preserved vials
  - Based on the results of analysis for the compound in the HCl-preserved vials that were provided to the sampling team, the weight of evidence supports the conclusion that the diol compound reported in the project samples was the direct result of the contamination from the laboratory-supplied HCl-preserved VOA vials

Case Study Two: Compound Results

Summary of the Diol Compound Results

Time Period	Total Number of Samples	Number of Non-detect Values	Number of Reported Detected Values	Percent Detects
Using HCl preserved VOA vials	240	27	213	89%
Using unpreserved VOA vials	69	66	3	4%

Case Study Two: Recommendations & Corrective Actions

- Based on the findings of this forensic investigation by the QA Team as to the reporting of the diol compound, the following recommendations and corrective actions are offered:
  - Laboratories should certify bottleware lots supplied to the sampling teams for analytes being requested down to the project reporting limits.
  - The same lot of bottles/vials should be used for project samples and method blanks, where applicable.
  - Field samplers should always be instructed to collect field blanks. Contamination issues can be discovered sooner if sampling personnel collect field blanks and equipment blanks from the beginning of sampling programs.
  - Sampling teams should undergo periodic field audits.

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