Utilizing Acid Mine Drainage for Marcellus Shale Activities in Pennsylvania

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DE-FE0000975 - Sustainable Management of Flowback Water during Hydraulic Fracturing of Marcellus Shale for Natural Gas Production
Marcellus Shale Activities in Pennsylvania

- Hydraulic fracturing is utilized to recover natural gas from the Marcellus shale.

- A single well can require one to five million gallons of water.

- Water needed for frac jobs - 40% from public water supplies, 60% comes from surface waters (rivers).

- 15% to 40% of injected water recovered during flowback.
Marcellus Shale Activities in Pennsylvania

• Marcellus flowback water typically contains high levels of total dissolved solids (TDS) (ranging from 70,000 to 250,000 mg/L), hydrocarbons, and metals.

• Flowback water must be treated before being reused or discharged to streams.

• Flowback can be reinjected into the well but high levels of metals (Ba, Sr, Ca) can result in precipitation in the well.

• PA has only 7 water disposal wells where flowback can be pumped. Thus the majority of flowback and produced is hauled by truck to OH.

• Increased truck traffic is a large problem for congestion, road safety and road wear.
Treating Marcellus Shale Flowback

- Reverse osmosis and distillation can be used to treat flowback but these methods have high capital and energy costs.

- After high TDS levels were measured in the Monongahela River in the fall of 2008, the Pennsylvania Department of Environmental Protection ordered a restriction on the amount of flowback water can be received at POTWs in the basin.

- This restriction can limit or halt gas drilling operations in some locations in western Pennsylvania.

- Technologies are being developed to clean flowback and produced water for reuse in the frac process.
Project Overview and Goals

• Consider AMD for use as make-up water at well sites in order to reduce the amount of freshwater needed and lower the associated transportation costs.

• Remove barium, strontium and calcium from flowback water with sulfate and carbonate ions that are often found in AMD in order to prevent precipitation in the wells.

• Outline better water management practices resulting in lower freshwater use and decreased costs for the gas industry.

• Develop a treatment in which flowback water is economically treated on site and reused to frac adjacent wells
AMD in Pennsylvania

- AMD flows from many PA coal mines
- Pyrite associated with coal oxidizes to form Fe + $\text{SO}_4$
- Low pH
- Affects aquatic and plant life
- AMD remains untreated if mines are abandoned
Marcellus + AMD = ?????

What questions need to be answered?

• Can AMD be used as makeup water?

• What happens when flowback mixes with AMD?

• What precipitates might form when the two streams are mixed and how are they removed?

• Is there enough AMD in PA?

• Is it close enough to the wells?
Using AMD as Makeup Water

• There is no consensus yet among the Marcellus operators about the use of impaired water for frac jobs.

• Some operators are willing to utilize acid mine drainage (AMD) for fracing while others will not.

• Most companies devising their own guidelines about water quality and blends.

• Researchers are working with the University of Pittsburgh Law School to investigate the PA regulations regarding AMD usage and liabilities.
Defining PA Flowback Reuse Guidelines

Barnett Shale study (2007)
Ba, Ca, Mg, sulfate, and carbonate need to be present at low concentrations in order to avoid any scaling in the well
Bacteria can lead to the formation of sour gas and corrosion
Fe < 20 mg/L to minimize precipitates
Cl < 10,000 mg/L to minimize precipitation and the amount of friction reducers added

Marcellus – University of Pittsburgh study (2010)
Cl needs to be < 50,000 mg/L
Fe and sulfate < 50 mg/L
Use of biocides
Flowback water database has been created containing analyses and locations of 160 water samples from 63 sites in PA

- Average TDS – 106,000 mg/L (range 680 to 345,000 mg/L)

- Major ions - Cl, Na, and Ca; Ba, Sr and Mg

- Cl represents on average 57% of the TDS in PA samples

- Oil, grease and radioactivity have been recorded at only a few of the sites

- Ba levels in flowback water in NE PA as high as 14,000 mg/L
PA Flowback Regional Trends

- Ca levels were higher in samples from southwestern PA
- Sr levels were higher in the northeastern part of the state
- Ba highest in northeast PA - very low in the southwest PA
PA Flowback GIS Database
PA AMD Database

- An AMD database has been created and includes flow rates and chemical analyses for 242 sites over time.

- For the reclaimed sites, water analyses before and after treatment are included in the database.

- Users can search for AMD sites based on desired flow rates, chemical analyses and location with search results being displayed on a map.

- Database not yet public – researchers willing to make public.
AMD and Marcellus Well Locations

Marcellus shale wells permitted

Acid mine drainage sites in PA
Flowback Treatability Studies

• Preliminary lab tests have shown that barium, strontium and calcium can be removed from flowback water when it is mixed with sulfate and carbonate ions that are often found in AMD.

• MINEQL+ and Phreeqci chemical equilibrium models are being tested to see which one has best applicability to solve the chemistry problems related to Marcellus.

• Mixing experiments were conducted to investigate the precipitation kinetics.
Mixing AMD and Flowback

Removal of constituents after mixing flowback water and AMD at different ratios.
Mixing AMD and Flowback

![Bar chart showing removal percentage of major ions (Ba, Ca, Fe, Mg, Sr, SO4[2-]) at different sulfate concentrations (1000 mg/L, 2000 mg/L, 4000 mg/L, 6000 mg/L, 8000 mg/L)]
Flowback Treatability Studies

- Sulfate was shown to be an excellent removal reagent for barium but very high concentrations of sulfate are needed in order to remove strontium.

- Two equilibrium models show good agreement with the experimental results in predicting barium and strontium sulfate precipitation.

- The presence of calcium ions was found to limit the removal of strontium.

- The addition of sodium bicarbonate improves the strontium removal and allows calcium to precipitate. However, an increase of pH seems to have a negative impact on barium and particularly strontium precipitation.
Current Status

• Currently identifying precipitates with SEM

• Testing filtrations systems

• Minimize membrane fouling – may be due to organics in the flowback
Research Implications

• Develop water reuse guidelines and chemical use for Marcellus frac jobs in PA.

• Increase the use of AMD and define successful parameters of AMD and flowback treatment.

• Devise approaches to reduce the amount of freshwater needed for Marcellus Shale development and minimize the disposal liability and costs associated with new well drilling.
Marcellus + AMD = ??????

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Other NETL Water Treatment R&D Projects

- WVU - Zero Discharge Water Management for Horizontal Shale Gas Well Development
- GE Global Research - Cost Effective Recovery of Low-TDS Frac Flowback Water for Re-use
- Altela, Inc. - An Integrated Water Treatment Technology Solution for Sustainable
- TEES - Pilot Testing: Pretreatment Options to Allow Re-Use of Frac Flowback and Produced Brine for Gas Shale Resource Development
- NETL ORD - Quantify Environmental Impacts of Shale Gas Development
More Information

Project summary and updates at [www.netl.doe.gov](http://www.netl.doe.gov)

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