

# **Report as of FY2011 for 2011PA159B: "Development of a Subsurface Reactive Transport Model for Predicting Potential Water Quality Problems in Marcellus Shale"**

## **Publications**

Project 2011PA159B has resulted in no reported publications as of FY2011.

## **Report Follows**

**PROJECT TITLE AND PRINCIPAL INVESTIGATORS**

**Development of a Subsurface Reactive Transport Model for Predicting Potential Water Quality Problems at Marcellus Shale**

Li Li, Dept. Energy and Mineral Engineering, Penn State University; and Susan L. Brantley; Dept. of Geosciences, Penn State University

**KEYWORDS:**

Marcellus Shale, reactive transport model, geochemistry, water quality, contamination

**STATEMENT OF REGIONAL OR STATE WATER PROBLEM:**

Understanding the potential water quality problems during the development of Marcellus Shale is important to the general public who has been very concerned about the potential environmental impacts. The general public will be interested in how, at what level, at what time frame, and under what conditions water quality will be deteriorated by natural gas production from tight shale. A fast and cost-effective way of such estimation is a model that is capable of helping us understand and predict the coupled flow, transport, and reaction processes that could potentially lead to water quality problems. As such, it is very important to develop such a model to help understand, predict and potentially manage water quality problems.

**STATEMENT OF RESULTS OR BENEFITS.**

The outcome of this proposal will be a reactive transport model and a database of reactions important for water quality issues in Marcellus Shale. The model and the database that can be used as a tool to understand the coupled flow, transport, and reaction processes involved in groundwater contamination problem at Marcellus Shale. They can also be used to predict and potentially manage conditions that could minimize or even avoid water contamination during the development of Marcellus Shale.

**NATURE, SCOPE, and OBJECTIVES** of the project, including a timeline of activities.

The goal of this work is to develop a model that can be used to understand, quantify, and predict reactive transport processes that could potentially lead to water quality deterioration during the development of Marcellus Shale formation.

## **METHODS, PROCEDURES, and FACILITIES.**

Li will be responsible for developing the reactive transport model based on the generic code CrunchFlow. Li has used CrunchFlow for more than 5 years and has published more than 5 high impact papers using CrunchFlow code. Li and Brantley will work together to understand the chemical weathering and water chemistry data of Marcellus Shale to identify important geochemical reactions associated with water quality and to use the existing data to validate the model. Li maintains a suite of computers adequate for the task of reactive transport modeling in this proposal. In addition, for computationally expensive tasks, high-performance computing resources are available through EMS Earth and Environmental Systems Institute (EESI) and Institute for Cyber Science (ICS) at Penn State. Brantley's group maintains excellent experimental facilities for water and solid geochemistry analysis. If more data are needed these can easily be obtained.

## **PRINCIPAL FINDINGS AND SIGNIFICANCE**

The development of Marcellus Shale can lead to potential environmental problems. In particular, the interaction between Marcellus Shale rocks and water, including hydraulic fracturing and flow back water, is a big concern. The ultimate goal of this work is to establish a reaction network and a reactive transport model to predict the potential impact of Marcellus Shale development on water quality.

We are currently in our first step in establishing the reaction network involved in water rock interactions in Marcellus Shale and in developing thermodynamic and kinetic database for the reactions. We use the soil and aqueous geochemistry data collected by Dr. Ryan Mathur's students in Juniata College at Huntingdon, PA, as part of research within the Shale Hills Critical Zones Observatory (CZO). Based on their data, the primary parent rock mineral composition is listed in Table 1. With this mineral composition, the reaction network involved is listed in Table 2. The reactions include the dissolution of primary minerals, including pyrite, albite, quartz, and clays (illite, chlorite, smectite). The precipitation of secondary minerals occurs as a result of the primary mineral dissolution. These include the precipitation of kaolinite, iron hydroxide, and carbonate. The general form of reaction rate laws for the mineral dissolution and precipitation reactions are listed in Table 3.

With the above established reaction network and thermodynamic and kinetic database, we are in the process of matching the weathering data listed in Table 4 to validate the model. We use existing generic reactive transport code CrunchFlow (Steeffel and Maher, 2009). Reactive surface areas of different minerals were used as matching parameters. The following is among the major findings:

- With the presence of dissolved oxygen, pyrite oxidative dissolution plays a pivotal role in determining the water chemistry of the system. The pore water maintains a pH range of 4-6, which is consistent with the pore water data collected.
- The dissolution of primary minerals leads to the precipitation of kaolinite. The low pH maintained by pyrite dissolution increase the dissolution rates by several orders of magnitude.
- The oxidative dissolution of pyrite leads to the precipitation of iron hydroxide.

These findings are significant in terms of implications for the predicting impacts of water rock interactions on water quality. This is because a similar set of reactions exist when hydraulic fracturing or flow back fluid interacts with Marcellus shale rocks. After fully matching the weathering data, we will obtain a more quantitative understanding on the water rock interactions and will have the predicting capability for Marcellus shale water rock interactions.

Table 1. Initial minerals in the parent rock

Mineral	Volume Fraction (%)
Quartz	34.4
Illite	39.2
Pyrite	1.0
Smectite	9.7
Albite	2.1
Chlorite	12.2
TiO <sub>2</sub>	0.8

Table 2. Mineral dissolution reactions and their corresponding equilibrium constants at 25°C.

Mineral Dissolution Reaction	Log(k <sub>eq</sub> )
Quartz = SiO <sub>2</sub> (aq)	-3.999
Illite + 8 H <sup>+</sup> = 0.25 Mg <sup>2+</sup> + 0.6 K <sup>+</sup> + 2.3 Al <sup>3+</sup> + 3.5 SiO <sub>2</sub> (aq) + 5 H <sub>2</sub> O	9.026
Albite + 4 H <sup>+</sup> = Na <sup>+</sup> + Al <sup>3+</sup> + 3 SiO <sub>2</sub> (aq) + 2 H <sub>2</sub> O	2.76
Kaolinite+ 6 H <sup>+</sup> = 2 Al <sup>3+</sup> + 2 SiO <sub>2</sub> (aq) + 5 H <sub>2</sub> O	6.81
Smectite + 6 H <sup>+</sup> = 0.33 Mg <sup>2+</sup> + 0.165 Ca <sup>2+</sup> + 1.67 Al <sup>3+</sup> + 4 SiO <sub>2</sub> (aq) + 4 H <sub>2</sub> O	2.49
Siderite + H <sup>+</sup> = Fe <sup>2+</sup> + HCO <sub>3</sub> <sup>-</sup>	-0.19
Pyrite + H <sub>2</sub> O + 3.5 O <sub>2</sub> = 2 H <sup>+</sup> + 2 SO <sub>4</sub> <sup>2-</sup> + Fe <sup>2+</sup>	107.67
Chlorite+ 16 H <sup>+</sup> = 0.55 Mg <sup>2+</sup> + 3.45 Fe <sup>2+</sup> + 2 Al <sup>3+</sup> + 3 SiO <sub>2</sub> (aq) + 12 H <sub>2</sub> O	14.996
Fe(OH) <sub>3</sub> + 2H <sup>+</sup> = 0.25 O <sub>2</sub> (aq) + Fe <sup>2+</sup> + 2.5 H <sub>2</sub> O	-27.235

Table 3. TST rate laws of the minerals

Mineral	Rate Law	Reference
Quartz	$R = 10^{-11.5} [H^+]^{0.35} + 10^{-13.39} + 10^{-10.5} [OH^-]^{0.5}$	(Brantley et al. 2008)
Illite	$R = 10^{-11.72} [H^+]^{0.6} + 10^{-15.06} + 10^{-12.31} [OH^-]^{0.6}$	(Kohler, Dufaud et al. 2003)

<b>Kaolinite</b>	$R = 10^{-12.19} [H^+]^{0.55} + 10^{-14.36} + 10^{-10.71} [OH^-]^{0.75}$	(Huertas, Chou et al. 1999)
<b>Albite</b>	$R = 10^{-8.7} [H^+] + 10^{-11.5} + 10^{-14.6} [H^+]^{-0.4}$	(Chou and Wollast 1985)
<b>Smectite</b>	$R = 10^{-12.66} [H^+]^{0.21} + 10^{-16} + 10^{-12.22} [OH^-]^{0.33}$	(Golubev, Bauer et al. 2006)
<b>Siderite</b>	$R = 10^{-4.6} [H^+]^{0.75} + 10^{-8.65}$	(Duckworth and Martin 2004)
<b>Pyrite</b>	$R = 10^{-8.19} [H^+]^{-0.11} [O_2]^{0.5}$	(Williamson and Rimstidt 1994)
<b>Chlorite</b>	$R = 10^{-9.79} [H^+]^{0.49} + 10^{-13} + 10^{-10.76} [OH^-]^{0.43}$	(Alekseyev 2007)

Table 4. Elemental chemistry and corresponding t values for soils collected on Marcellus shale in central Pennsylvania

Sample	Depth range cm	Depth cm	Al <sub>2</sub> O <sub>3</sub> (%)	BaO (%)	CaO (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	K <sub>2</sub> O (%)	MgO (%)	Na <sub>2</sub> O (%)	P <sub>2</sub> O <sub>5</sub> (%)	SiO <sub>2</sub> (%)	TiO <sub>2</sub> (%)	Σ(oxides) (%)	Total N (%)	Total C (%)	Total H (%)	LOI* (%)
CEA 1	0-10	5	11.6	0.07	0.29	5.00	2.34	0.56	0.22	0.12	66.3	1.11	87.6	0.32	3.37	0.94	12.4
CEA 2	10-20	15	14.8	0.07	0.23	6.98	3.07	0.73	0.23	0.12	65.8	1.11	93.1	0.13	0.72	0.64	6.9
CEA 3	20-26	23	15.6	0.07	0.24	5.87	3.29	0.74	0.21	0.07	66.2	1.12	93.4	0.13	0.57	0.69	6.6
CEA 4	26-34	30	16.9	0.06	0.25	7.67	3.44	0.80	0.22	0.09	61.8	1.03	92.3	0.12	0.40	0.72	7.7
CEA 5	34-44	39	17.0	0.06	0.22	7.93	3.49	0.79	0.22	0.09	62.1	1.04	92.9	0.12	0.40	0.71	7.1
CEA 6	44-52	48	16.9	0.06	0.20	6.73	3.50	0.85	0.23	0.09	63.3	1.06	92.9	0.11	0.30	0.73	7.1
CEA 7	52-60	56	16.5	0.06	0.15	9.99	3.35	0.82	0.23	0.13	60.5	1.01	92.7	0.12	0.34	0.79	7.3
CEA 8	60-65	62	17.9	0.06	0.12	5.34	3.68	0.80	0.26	0.06	64.7	1.09	94.0	0.12	0.26	0.69	6.0
CEA 9	65-71	68	17.0	0.06	0.09	6.89	3.49	0.85	0.24	0.07	63.6	1.06	93.4	0.11	0.29	0.62	6.6
CEA 10	71-82	76	17.1	0.06	0.07	6.72	3.58	0.82	0.24	0.07	63.3	1.06	93.0	0.12	0.26	0.69	7.0
CEA 11	82-89	85	18.1	0.06	0.05	4.14	3.85	0.81	0.25	0.05	65.0	1.09	93.4	0.13	0.26	0.69	6.6
CEA 12	89-98	93	18.0	0.06	0.06	5.74	3.78	0.85	0.24	0.06	63.6	1.08	93.5	0.12	0.42	0.75	6.5
CEA 13	98-109	104	17.6	0.07	0.05	5.13	3.75	0.86	0.24	0.07	64.4	1.08	93.3	0.12	0.29	0.67	6.8
CEA 14	109-115	112	17.1	0.06	0.04	5.80	3.58	0.87	0.23	0.05	63.8	1.06	92.6	0.12	0.33	0.74	7.4
CEA 15	115	115	17.8	0.07	0.04	5.70	3.73	0.89	0.24	0.06	63.7	1.07	93.3	0.12	0.33	0.69	6.7

## References

- Alekseyev, V. A. (2007). "Equations for the dissolution reaction rates of montmorillonite, illite, and chlorite." *Geochemistry International* **45**(8): 770-780.
- Chou, L. and R. Wollast (1985). "STEADY-STATE KINETICS AND DISSOLUTION MECHANISMS OF ALBITE." *American Journal of Science* **285**(10): 963-993.
- Duckworth, O. W. and S. T. Martin (2004). "Role of molecular oxygen in the dissolution of siderite and rhodochrosite." *Geochimica Et Cosmochimica Acta* **68**(3): 607-621.
- Golubev, S. V., A. Bauer, et al. (2006). "Effect of pH and organic ligands on the kinetics of smectite dissolution at 25 degrees C." *Geochimica Et Cosmochimica Acta* **70**(17): 4436-4451.
- Huertas, F. J., L. Chou, et al. (1999). "Mechanism of kaolinite dissolution at room temperature and pressure Part II: Kinetic study." *Geochimica Et Cosmochimica Acta* **63**(19-20): 3261-3275.
- Kohler, S. J., F. Dufaud, et al. (2003). "An experimental study of illite dissolution kinetics as a function of pH from 1.4 to 12.4 and temperature from 5 to 50 degrees C." *Geochimica Et Cosmochimica Acta* **67**(19): 3583-3594.
- Williamson, M. A. and J. D. Rimstidt (1994). "THE KINETICS AND ELECTROCHEMICAL RATE-DETERMINING STEP OF AQUEOUS PYRITE OXIDATION." *Geochimica Et Cosmochimica Acta* **58**(24): 5443-5454.

## STUDENTS & POSTDOCS SUPPORTED

Peyman Heidari, Petroleum and Natural Gas Engineering, PhD student.

## PUBLICATIONS

This is our first year on this project; no publication from this project yet.

## ADDITIONAL FUNDING ACQUIRED USING USGS GRANT AS SEED MONEY

(source, amount, starting and ending dates, title)

PI Li Li is developing a CAREER proposal titled “Energy and Sustainability: Water rock interactions at Marcellus Shale.”

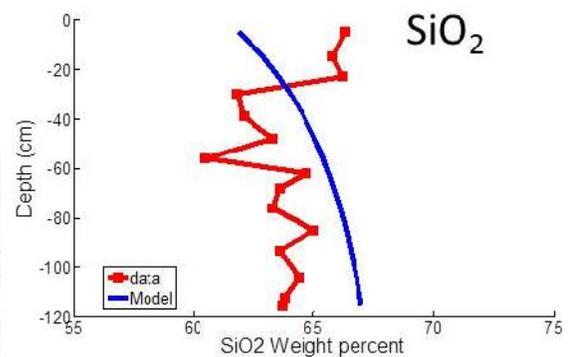
## PHOTOS OF PROJECT

A. Marcellus shale weathering to soil near Huntingdon, PA



by Peyman Heidari, Li Li, Susan Brantley (PSU)

B. Model output and data comparison ( $\text{SiO}_2$ )



C. Model output and data comparison (Fe)

