



Article Comparative Laboratory Study of the Geochemical Reactivity of the Marcellus Shale: Rock–Fluid Interaction of Drilled Core Samples vs. Outcrop Specimens

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Abstract: The Marcellus shale is an unconventional reservoir of significant economic potential with Total Organic Carbon (TOC) ranging from 1 to 20%. Hydraulic fracturing is used to extract the shale's resources, which requires large amounts of water and can result in mineral-rich flowback waters containing hazardous contaminants. This study focuses on a geochemical analysis of the flowback waters and an evaluation of the potential environmental impacts on water and soil quality. Drilled core samples from different depths were treated with lab-prepared hydraulic fracturing fluids. Rock samples were analyzed using Energy Dispersive Spectroscopy (EDS), while effluents' chemical compositions were obtained using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). A comparison of results from drilled core samples treated with additives for hydraulic fracturing to those treated with deionized (DI) water confirms that, as expected, the major elements present in the effluent were Ca, Ba, and Cl in concentrations greater than 100 μ g/L. The most concerning elements in the effluent samples include As, Ca, Cd, Pb, Se, S, K, Na, B, Mo, and Mn, with Cd and Cr values averaging 380 and 320 μ g/L, respectively, which are above safe limits. Se concentrations and high levels of Ca pose major safety and scaling concerns, respectively. We also compared Marcellus shale drilled core samples' geochemical reactivity to samples collected from an outcrop.

Keywords: flowback water; contaminants; Marcellus shale; geochemical reactivity

1. Introduction

When hydrocarbons are identified in a rock formation that has a permeability lower than 1 millidarcy, it is categorized as an unconventional reservoir [1]. Unconventional reservoirs include coal bed methane, oil sands, tight oil and gas, gas hydrates, and shale oil and gas. Shale gas, in particular, has garnered much attention due to its vast reserves, which account for approximately 50% of all unconventional reserves [2]. The use of hydraulic fracturing enabled the extraction of natural gas from unconventional tight reservoirs such as shale. However, this process consumes large amounts of water, and there is a need for a large volume of infrastructure to collect, recycle, and dispose of the resulting wastewater [3]. Possible methods for managing this wastewater include reverse osmosis, chemical treatments, and distillation, but they can be expensive and require further development [4]. In addition, generated wastewater contains heavy metals and hazardous elements such as Se, Cd, Cr, Zn, and As, which are a cause for concern.

The Marcellus shale formation, located in the northeastern Appalachian Mountains, is of the Middle Devonian age. A stratigraphic study indicates that the Marcellus shale underwent a transition from a stable shallow marine system to a foreland basin [5]. The Marcellus formation, which is dark grey to black in color, contains minerals such as pyrite,



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). dolomite, calcite, and marcasite, and has an estimated thickness of 541 ft (165 m) [6,7]. Horizontal drilling and hydraulic fracturing technologies have been successfully deployed in Marcellus shale plays.

Hydraulic fracturing involves injecting excessive fluids into a wellbore to fracture the formation and connect and activate natural fractures, providing sufficient permeability for oil and gas to be produced. During injection, the resistance of the formation increases, causing the wellbore pressure to rise to the breakdown pressure resulting in fractures. Hydraulic fracturing fluids under high pressure and proppants are then pumped through perforations into the target area until wellbore fractures propagate. Flowback is the term used to describe the flux of hydraulic fluid that returns to the wellbore at the end of the hydraulic fracturing operations [8]. The biggest volume of flowback water occurs shortly after the fracturing is completed and the well is prepared for production [9]. Reactions occur between the formation and the injected fluids, causing mineral dissolution and the precipitation of new minerals, which might have an impact on the reservoir's petrophysical properties [10]. Most of the Marcellus and other northeastern US formations are fractured in horizontal wells. Flowback water can be stored in surface-holding ponds or evaporation ponds or hauled to class II deep injection wells [11]. Reusing flowback water reduces fresh water needs, transport, and storage costs. However, high concentrations of elements such as calcium and barium, as well as arsenic, selenium, and cadmium, can limit reuse without the treatment, and it cannot be accommodated onsite. Scaling due to calcium carbonate buildup in conduits and precipitates that deposit solids on pore walls, blocking pore throats, and decreasing permeability are common issues. Chlorites found in Devonian shales such as the Marcellus shale can vary in composition, and trace element analysis and contamination level are important considerations. Table 1 shows some selected standard metal concentrations for the Marcellus shale.

Table 1. Selected metal concentrations in Marcellus Shale adapted from Bank's mineralogy classification [12].

Metal	Outcrop Average (ppm)	Core Average (ppm)	Cutting Average (ppm)	Sample Average (ppm)
Barium	500–900	100-2000	900-3600	100-3600
Uranium	11–53	10-50	9–34	9–53
Chromium	53-100	70-100	70-120	53-120
Zinc	50-660	50-2290	50-530	50-2290

The objective of this study is to identify the chemical content of flowback waters generated when hydraulic fracturing fluid additives and DI water interact with the Marcellus shale.

2. Materials and Methods

The outcrop was observed and samples were collected for SEM-EDS analysis. To determine the elemental composition of the effluent, ICP-OES analysis was performed. Core samples were extracted from active formations located at depths between 6300 and 6420 ft, with the sample depths and corresponding ID numbers provided in Table 2 and Figure 1, respectively. The outcrop was designated as "0" for reference purposes. To prepare SEM samples for imaging, cores were cut with a diamond tip with a diameter of 10.79 cm (4.25 in) and a thickness of 4.45 cm (1.75 in) to produce samples that conform to the standard SEM stubs of 8 \times 12 mm or 3 \times 25 mm.

Sample ID	TVD Depth [ft]
0	Outcrop
1	6313.4–6313.8
2	6334.1-6334.5
3	6381.5–6381.8
4	6388.55-6388.95
5	6398.05-6398.5
6	6407.5-6407.9
7	6419.25-6419.55

Table 2. Core sample identification and associated true vertical depth.



Figure 1. Experimental coring depths between 1924 and 1956.5 m (6313 and 6419 ft).

2.1. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

Examinations of microstructure and material texture were performed using a scanning electron microscope (SEM) with a nanometer resolution. Energy Dispersive Spectroscopy (EDS) was used with SEM for elemental composition determination. To prepare samples for imaging, a South Bay Technology (Model 900) polishing wheel, silicon carbide sandpaper, and polycrystalline diamond in suspension were used to obtain a final polish of 1 micron. The chemical composition of the effluent resulting from the shale particle reaction was analyzed using the Inductively Coupled Plasma Spectroscopy (ICP-OES) tool. For ICP-OES sample preparations, representative samples of each core and the outcrop were collected. The eight core samples were each crushed using a mechanical hand-crushing tool to a smaller particle size, resulting in an increase in the surface area for reaction. Each crushed sample was thoroughly mixed to obtain particle sizes of 120 μ m. To obtain particles of a desired size range, the sample was initially sieved through a 500 μ m sieve to remove any large particles. The remaining material was then passed through smaller sieves of 250 μ m and 120 μ m, respectively. An amount of 8 g of each sample was used for analysis.

2.2. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

2.2.1. Leaching Tests and Fracturing (Hydraulic Fluid Preparation)

Leaching tests were performed to assess the solubility of clay minerals. The leaching concept is illustrated in Figure 2. Leaching tests are used to assess the potential release of pollutants from solid materials, such as shales, when exposed to variable conditions. During the test, a sample of the shale is placed in contact with a liquid, such as water,

and the resulting solution is analyzed for the presence of contaminants. The presence and concentration of contaminants in the liquid indicate that a leaching test has occurred. The test results can then be compared to regulatory standards or other criteria to determine the potential environmental impact of the effluents' content.



Figure 2. Schematic representation of the leaching test concept, depicting how solids/fluids were investigated independently. The central box represents the testing unit for the solute. The upper arrows entering and exiting the testing unit depict the solvent (DI water or fracturing fluid) that will be introduced into the solute box. The lower arrows entering and exiting the testing unit portray the solid material derived from the core samples and outcrop, which represents the solute.

Next is the preparation of the hydraulic fracking fluid used in this research. The hydraulic fracturing fluid is a solvent that is 99% water and 1% additives (no proppant) and is prepared with the elements shown in Table 3. The initial pH of the prepared solvent is determined and recorded and 10 mL of the unreacted mixture is set aside for baseline ICP-OES analysis.

Table 3. Composition of the hydraulic fluid additives used.

Component	% by Weight Added	Chemical Formula	Use
Acid	0.11	HCl (3–28%)	Acid is used to clean out the perforation intervals of cement and drilling mud before the injection of fracturing fluid. This process also creates an accessible pathway to the formation.
Biocide	0.001	Glutaraldehyde, 2-bromo-2-nitro-1,2- propanediol	Prevent contamination of methane gas and proppant transport reduction by inhibiting organism growth (especially H ₂ S producers).
Breaker	0.01	Peroxy disulfate	Decrease the fluid's viscosity, which enables the release of proppant into fractures and increases the recovery of fracturing fluid.
Clay stabilizer	0.05	Salts (KCl)	Prevent swelling and migration of clays in the formation, which could obstruct pore spaces and lower permeability.

Component	% by Weight Added	Chemical Formula	Use
Corrosion inhibitor	0.001	Methanol	Reduces rust formation on steel tubing, well casings, tools, and tanks (used only in fracturing fluids that contain acid).
Cross-linker	0.01	Potassium hydroxide	This enables the fluid to carry more proppant into fractures during the fracturing process as phosphate esters combined with metals (crosslinking agents) are used to enhance the fluid viscosity.
Friction reducer	0.08	Sodium acrylate-acrylamide copolymer, polyacrylamide (PAM)	Facilitates optimal injection pressures and rates, thereby reducing friction.
Gelling agent	0.05	Guar gum	Improves the viscosity of the fracturing fluid, enabling it to carry more proppant into fractures.
Iron control	0.004	Citric acid, thioglycolic acid	Prevents metal oxides from precipitating and clogging the formation.
Other	0.4	-	
pH adjuster	0.01		Maintain the pH within the functional range.
Proppant	8	Sand	Proppants open fractures, allowing fluids to flow more easily to the wellbore.
Scale inhibitor	0.04	Ammonium chloride, ethylene glycol, polyacrylate	Inhibits the precipitation of sulfates and carbonates (calcium carbonate, calcium sulfate, barium sulfate) that could clog the formation.
Surfactant	0.08	Methanol, isopropanol	Decreases the surface tension of fracturing fluid, thus enhancing fluid recovery.
Water	90		

Table 3. Cont.

2.2.2. The ICP Procedure

Each crushed sample of core 1, core 7, and the outcrop was divided into eight different testing portions (1 per week for 4 weeks treated with additives and 1 per week for 4 weeks treated with DI water (Figure 3). Add 10 g of solvent to each test tube with rock grains. Place test tubes in separate water baths on a heated plate with a magnetic agitator. Both water baths share the hot plate in the center. Magnetic stirrers are placed in each bath: a Thermolyne Cimarec 2 and a Sargent-Welch magnetic stirrer with dial rpm adjustment. To ensure identical stirring rates and influence on test tubes, the same size stirring rod was utilized in both water baths. Over the first week, the temperature was gradually increased to bring the water bath as close to the reservoir temperature as possible without melting plastic containers (140 °F, 60 °C). Daily temperature recordings and pH monitoring were performed, and weekly observations and measurements were recorded. Remove 1 test tube for each sample for DI and hydraulic fracturing water analysis each week. Filter samples through funnels using Whatman circular #2 filter paper, particle size 77 m, and collect filtrate for ICP-OES analysis. ICP-OES analysis of all samples was performed on a Spectro ARCOS FHE 12. For quality control information from the ICP-OES, each sample was run three times.



Figure 3. Schematic representation of the experimental workflow for ICP effluent analysis.

3. Results

The experiments yielded the following results, from structural characterization to effluent elemental analysis.

3.1. Microstructural Characterization

SEM analysis of the core reveals that the samples are clay-rich and contain some fractures, pore fillings, and mineralization. Fracture frequency increases for deeper samples, and porosity is in the same direction (Figure 4). Due to increased pressure and temperature, the frequency of fractures in rock samples tends to increase with depth. This causes the rocks to distort and disintegrate brittlely, resulting in fracture formation. Furthermore, the presence of fluids within the rock can increase pressure and facilitate fracturing, increasing the fracture frequency with depth. Images of cores in Figure 4b,c,d reveal some laminated areas with more metallic materials. Samples generally have a heterogeneous structure consisting of thin layers of metallic components and scattered particles, a typical feature of mudstone.





Figure 4. Cont.

(b)



Figure 4. Optical images of Marcellus shale samples (**a**–**d**) from an outcrop and (**e**–**h**) from drilled cores at depths 6334.5 ft, and 6419.55 ft. Outcrop images show compositional heterogeneity, layered structure, and fractures. Drilled core 2 (6334.5 ft) shows limited networking and connections of non-uniform fractures along bedding planes, with some larger fracture aperture present. Drilled core 7 (6419.55 ft) shows extensive fractures along bedding planes. (**a**) Optical (low magnification, $2\times$) Marcellus shale outcrop sample, shows compositional heterogeneity, layered structure, and fractures. (**b**) Optical image (higher magnification, $7\times$) Marcellus shale outcrop sample reveals fractures/microfractures parallel to layering and different grain sizes within alternate layers. (**c**) Optical image of Marcellus shale outcrop sample. (**e**) Optical image of Marcellus shale drilled core sample 2 (6334.5 ft) (low magnification, $2\times$) shows non-uniform fractures along bedding planes with some larger fracture aperture present. (**f**) Optical image of Marcellus shale drilled core sample 2 (634.5 ft) (low magnification, $2\times$) shows extensive fracture aperture present. (**f**) Optical image of Marcellus shale drilled core sample 2 (6334.5 ft) (low magnification, $2\times$) shows non-uniform fractures along bedding planes [13]. (**g**) Optical image of Marcellus shale drilled core sample 7 (6419.55 ft) (low magnification, $2\times$) shows extensive fractures along bedding planes. (**h**) Optical image of Marcellus shale drilled core sample 7 (6419.55 ft) (high magnification, $7\times$) shows limited networking and connections of non-uniform fractures along bedding planes [13]. (**g**) Optical image of Marcellus shale drilled core sample 7 (6419.55 ft) (high magnification, $7\times$) shows extensive fractures along bedding planes. (**h**) Optical image of Marcellus shale drilled core sample 7 (6419.55 ft) (high magnification, $7\times$) shows networking and connections of extensive fractures along bedding planes.

3.1.1. Marcellus Shale Outcrop Image Analysis

Figures 4 and 5 depict the optical and SEM images of the outcrop and core samples from the zone of interest. The lighter and darker areas in the SEM image (Figure 4b) highlight the differences in the shale's bulk material. These areas were examined at higher magnification as described in Figure 4d, f, h.



Figure 5. SEM micrographs of Marcellus shale samples (**a**,**b**) from an outcrop and (**c**,**d**) from the drilled core, 6334.5 ft. A high magnification image (7×) shows pyrite content among brittle reactive grains, surrounded by clay matrix. Pyrite and bigger nonclay grains are mixed with fine-grained clays. The Marcellus shale core sample 2 (6334.5 ft) shows pyrite framboid encased in clays and the resulting micro-porosity. (**a**) SEM micrograph (low-magnification image, 2×) of the Marcellus shale outcrop sample, presence of larger fractures left to right interconnected by microfractures; aggregations of pyrite and larger nonclay grains embedded in fine-grained clays. (**b**) SEM micrograph (high magnification image, 7×) of the Marcellus shale outcrop sample, pyrite (orange arrow) embedded within brittle reacted grains (blue arrow), surrounded by clay matrix. (**c**) SEM micrograph (low-magnification image, 2×) of the Marcellus shale drilled core 2, presence of fractures occupied with pyrite enveloped in a matrix of fine-grained clay particles. (**d**) SEM micrograph (high magnification image, 7×) of the Marcellus shale drilled core sample 2, depicts pyrite framboid enveloped by clays and the consequent micro-porosity.

Backscatter and Energy Dispersive Spectroscopy (EDS) performed on these areas reveal that the primary chemical composition is iron and sulfide. The small crystalline structure appears to be reacted or slowly dissolved in a drift (Figure 4e). This demonstrates the material's susceptibility to react when exposed to surface alterations. Image 4f shows a fully reacted marcasite crystal that has evolved into a pyrite crystal.

The four images in Figure 5 are all high-magnification SEM images. The grains are mostly marcasite and/or pyrite, with inference on growth and progression.

3.1.2. Marcellus Shale Drilled Core Samples Image Analysis

Core sample 2 (6334 ft, 1931 m) was chosen for observation as one of the shallowest drilled samples (Figure 4e,f) because of a visible feature in the fracture. Initial observations of the sample revealed that there were far fewer metallic particles littering the surface than on the outcrop. It also appears to be more fractured, which is thought to be due to pressure relief when brought to the surface. Core sample 7 (6420 ft, 1957 m) was the deepest core obtained for the experiment and observations. Sample 7 has more fractures than all other samples. The metallic particles are fewer but scattered throughout this sample compared to the outcrop images.

Figure 5 includes four SEM images of Marcellus shale samples. Figure 5a is a lowmagnification (2×) SEM image of an outcrop sample displaying larger fractures connected by microfractures. Pyrite and larger non-clay grains are embedded in fine-grained clays. In Figure 5b, a high magnification (7×) SEM image of the same outcrop sample shows pyrite embedded in brittle reacted grains and surrounded by a clay matrix. Figure 5c displays a low-magnification (2×) SEM image of drilled core 2 of Marcellus Shale, revealing fractures containing pyrite and enveloped in a matrix of fine-grained clay particles. Lastly, Figure 5d depicts a high magnification (7×) SEM image of drilled core sample 2 of Marcellus Shale, presenting a pyrite framboid enveloped by clays and the resulting micro-porosity. EDS revealed that the material forming within the fracture was marcasite and pyrite. Iron and sulfide were the most common elements discovered using backscatter and EDS. This is similar to what was observed in the outcrop.

EDS analysis of samples from core 2 indicates the presence of barite in higher concentrations. This type of particle was discovered embedded in the many clay particles that make up most of the sample rather than within a natural fracture. It was also composed of barite, but the particles surrounding it suggest that it could have formed differently. The clay particles form a swirling pattern around the location of this particle. It also had a pore-like region.

3.2. Microchemical Characterization of Marcellus Shale

Figure 6, below, shows an EDS analysis of core sample 2 (6334 ft, 1931 m). From the EDS analysis of spots 1, 2, 3, and 4, the elements identified are chlorine, magnesium, iron, silicon, sodium, and manganese.

3.3. Effluent Analysis of Fluids Reacted with Marcellus Shale Samples

Element concentrations were determined using ICP-OES analysis. The relative abundances of elements present in the effluent are shown in Figures 7–9. The outcrop is labeled 0, core sample 1 (6313 ft) is labeled 1, and 7 represents core sample 7 (6419 ft). The elements found in considerable amounts are calcium (Ca), sodium (Na), potassium (K), silicon (Si,) and sulfur (S). Equally, lead (Pb), chromium (Cr), arsenic (As), boron (B), cadmium (Cd), cobalt (Co), copper (Cu), iron (Fe), magnesium (Mg), and manganese (Mn) were present.

40.5K 36.0K 31.5K 27.0K 22.5K 18.0K 13.5K 9.0K 4.5K



65.18 55.88 46.58 37.28

27.9 18.6 9.3

Field of

iron, silicon, sodium, and manganese.



Figure 6. EDS of sample 2 showing through the highlighted portions variable chlorine, magnesium,

Figure 7. Cont.

50 um



Figure 7. Average ICP results for treatment with DI water. (**a**) Shows the most abundant samples (~1500 to 9000 ppm). (**b**) Shows the less-abundant samples (~0 to 60 ppm). Dxy (D: deionized water, x: sample ID, y: a period of treatment in weeks); 0: outcrop, 1: core sample 1, 7: core sample 7.



Figure 8. Average ICP results for treatment with fracturing fluid (~1500 to 9000 ppm). (**a**) Shows the most abundant samples (~0 to 60 ppm). (**b**) Shows the less-abundant samples. Fxy (F: fracturing fluid, x: sample ID, y: a period of treatment in weeks); 0: outcrop, 1: core sample 1, 7: core sample.



Figure 9. Relative abundance of the chemical elements detected through ICP. (**a**) The concentrations of major chemical elements measured (5 to 400 ppm). (**b**) Shows the concentrations of minor chemical elements measured (0 to 0.45 ppm).

The Marcellus shale formation is not homogeneous and the mineralogical elements are spatially heterogeneous. Effluents from different core samples showed variable chemical contents; depending on how the solvent reacted, they showed some very interesting trends.

3.3.1. Effluent Analysis: Calcium (Ca) Concentration as a Function of Time When Treated with DI Water and Fracturing Fluid

Samples treated with additives and DI water contained significant amounts of calcium. Figure 10 shows the progression in the concentration of Ca over time for all the samples. Outcrop values went from 5993 ppm in week 1 to 6905.8 ppm in week 4, for a net increase when treated with DI water. While the progression increase was constant, when treated with fracturing fluid, the Ca concentration decreased over time for the outcrop, from 7489 to 6849 ppm. The values increased from 2302 to 2587 ppm for core sample 1 DI water-treated samples and from 3053 to 3536 ppm when treated with the fracturing fluid. When treated with DI water, values for core sample 7 increased from 7438.58 to 8101.59 ppm and from 8649.58 to 9458.15 ppm when treated with the fracturing fluid.





Figure 10. Effluent concentration variations in Ca with time. (**a**) Shows the variation in concentration for the samples treated with DI water. The lowest values recorded are in core 1, and core 7 depicts the highest values, all in a positive trend. (**b**) Shows the variation in concentration when samples are treated with fracturing fluid (FF), with a negative trend for the outcrop at week 4.

3.3.2. Effluent Analysis: Sodium (Na) Concentration as a Function of Time When Treated with DI Water and Fracturing Fluid

Dissolved sodium is relatively constant and lowest for the outcrop, but a net increase is observed for the core samples treated with DI water. The concentrations were higher for core sample 1. When treated with fracturing fluid, the general trend was a positive slope (Figure 11a,b). A sharp increase was observed for the outcrop at week 4. The Na concentration decreased over time for the outcrop, from 34.32 to 24.84 ppm. The values increased from 231.59 to 269.18 ppm for core sample 7 DI water-treated samples and from 224 to 242.99 ppm when treated with the fracturing fluid. When samples were DI water-treated, values for core sample 1 decreased from 343.26 to 340.08 ppm and increased from 316.97 to 330.77 ppm when treated with the fracturing fluid.





Figure 11. ICP results for Na, concentration variations with time. (a) Shows the variation in concentration for the samples treated with DI water. The lowest values recorded are in the outcrop, and core 1 depicts the highest values, all in a positive trend. (b) Shows the variation when samples are treated with fracturing fluid (FF). At week 4, the concentration is highest for the outcrop.

3.3.3. Effluent Analysis: Potassium (K) Concentration as a Function of Time When Treated with DI Water and Fracturing Fluid

The dissolved Potassium (K) showed stable values for the outcrop when treated with DI water. Values ranged from 75.21 to 76.20 ppm for DI water and 3830.94 to 4231.32 ppm for fracturing fluid treatment. Core samples 1 and 7 showed a net positive trend, with higher K values for core 7 (Figure 12a,b). An increase was observed with the additive-treated samples for core 1 (747.96 to 762.61 ppm) and core 7 (846.32 to 943.78 ppm). The trend decreased for the outcrop with a very sharp decline from week 3 to 4, from 4136.11 to 3246.45 ppm. K is a characteristic cation for illite as it provides a balanced non-hydrated layer. The use of a potassium-rich additive in the fracturing fluid could increase K concentration.





Figure 12. Effluent concentration variations in K with time. (**a**) Shows the variation in concentration for the samples treated with DI water. The lowest values recorded are in the outcrop and the highest is in core 7. (**b**) Shows the variation when samples are treated with FF.

3.3.4. Effluent Analysis: Magnesium (Mg), Iron (Fe), and Aluminum (Al) Concentrations as a Function of Time When Treated with DI Water and Fracturing Fluid

Dissolved Mg levels were found in an increasing proportion over time for samples treated with DI water. Outcrop Mg values were the highest for both DI water- and fracturing fluid-treated samples. Values for the outcrop increased from 622.25 to 734.22 ppm for DI water and 600.64 to 640.39 ppm for fracturing fluid treatment (Figure 13a,b). When treated with fracturing fluid, the trend remained positive. Sample 1 values ranged from 166.18 to 265.66 ppm; sample 7 values ranged from 194.83 to 301.79 ppm.





Figure 13. Effluent concentration variations in Mg with time. (**a**) Shows the variation in concentration for the samples treated with DI water. (**b**) Shows variation when samples are treated with FF; the highest values for K concentration are recorded for the outcrop.

Fe²⁺ was another element that was consistently leached out. Values of Fe decreased when the outcrop and core 7 were treated with DI water. The range was 9.45 to 3.95 ppm for the outcrop and 1.05 to 0.51 ppm for core sample 7 (Figure 14a,b). Fe values slightly increased in core 1, ranging from 3.33 to 3.95 ppm. These values decreased when treated with fracturing fluid for core 1, from 1.12 to 1.10 ppm, and considerably increased for the outcrop (0.04 to 0.18 ppm) and core 7 (0.31 to 0.82 ppm).



Figure 14. Effluent concentration variations in Fe with time. (a) Shows the variation in concentration for the samples treated with DI water. (b) Shows the variation when samples were treated with FF. Fe displays the highest values for core 1.

(b)

Al³⁺ concentrations increase for the outcrop and core 1 and decrease for core 7 when DI water-treated. The outcrop values ranged from 0.29 to 5.04 ppm and from 9.03 to 11.09 ppm. Values varied from 3.46 to 1.50 ppm (Figure 15a,b). The reactivity inferences are unique for each sample. When treated with fracturing fluid, the trend remained positive for core 1 (1.64 to 2.13 ppm) but declined for both core 7 (0.36 to 0.080 ppm) and the outcrop (0.46 to 0.12 ppm).



Figure 15. Effluent concentration variations in Al with time. (**a**) Shows the variation in concentration for samples treated with DI water. (**b**) Shows variation in concentration when treated with FF. The highest values for Al are in the outcrop when treated with DI water and the highest in core 1 when FF-treated.

3.3.5. Effluent Analysis: Silicon (Si) Concentration as a Function of Time When Treated with DI Water and Fracturing Fluid

Si levels increased over time with DI water treatment (Figure 16a), with the highest slope being that of the outcrop (20.04 to 55.24 ppm). Core 1 (39.93 to 48.22 ppm) contained more Si than core 7 (28.58 to 30.09 ppm). When treated with fracturing fluid (Figure 16b), the slopes were equally positive. Values for the outcrop ranged from 11.90 to 21.20 ppm; 5.55 to 10.12 ppm for core sample 1 and 0.28 to 7.24 ppm, with a peak value of 34.71 ppm at week 3, for core sample 7.





Figure 16. Effluent concentration variations in Si with time. (**a**) Shows the variation in concentration for samples treated with DI water. (**b**) Shows variation in concentration when treated with FF. The highest values for Si are in the outcrop for DI water and fracturing fluid treatments.

3.3.6. Effluent Analysis: Sulfur (S) Concentration as a Function of Time When Treated with DI Water and Fracturing Fluid

Sulfur exists as the sulfate (SO_4^{2-}) ion. S concentrations increased over time for both DI water (Figure 17a) and fracturing fluid treatments (Figure 17b) for the outcrop and cores 1 and 7. Sulfur values were highest in core 7, lower in the outcrop, and lowest in the core. High concentrations in the outcrop and core 7, for both DI water and fracturing fluid treatments, indicate a possible dissolution of pyrite. The values ranged from 5130.14 to 5897.99 ppm for the outcrop when treated with DI water samples, 6111.79 to 6996.28 ppm for core 7, and 2290.11 to 2675.87 ppm for core sample 1. When treated with fracturing fluid, values ranged from 5192.75 to 4935.78 ppm for the outcrop, 5888.12 to 6595.54 ppm for core sample 7, and 2062.48 to 2621.95 ppm for core sample 1.





Figure 17. Effluent concentration variations in S with time. (a) Shows the variation in concentration for samples treated with DI water. (b) Shows variation in concentration when treated with FF. The highest values for S are recorded in core 7 when DI water-treated and the lowest when treated with fracturing fluid.

3.3.7. Effluent Analysis: Boron (B) and Lead (Pb) Concentration as a Function of Time When Treated with DI Water and Fracturing Fluid

Boron was found in all samples and the levels remained constant in the outcrop but increased for cores 1 and 7 when treated with both fluids (Figure 18a,b). The values for B in DI water-treated effluents for the outcrop ranged from 1.20 to 1.17, from 4.62 to 5.68 ppm for core 1, and 5.29 to 7.44 ppm for core sample 7. The values for B in fracturing fluid-treated effluents for the outcrop decreased from 1.16 to 0.99 ppm, increased from 4.02 to 5.12 ppm for core sample 1, and from 5.02 to 6.78 ppm for core sample 7.





Figure 18. Effluent concentration variations in B with time. (a) Shows the variation in concentration for samples treated with DI water. (b) Shows variation in concentration when treated with FF. The highest values for B were recorded when core 7 was DI water- and fracturing fluid-treated.

Lead is a heavy metal used to protect from radioactive effects. However, improper exposure to lead can pose adverse health risks. Lead content decreased for all samples when treated with DI water, as described in Figure 19a,b. The same was observed for the fracturing fluid treatments. The lowest values were observed for the outcrop and the highest for core 7. The values for Pb in DI water-treated effluents for the outcrop ranged from 0.18 to 0.04 ppm, 0.07 ppm on average for core sample 1, and 0.1 ppm on average for core sample 7. The values for Pb in fracturing fluid-treated effluents for the outcrop decreased from 3.38 to 2.70 ppm, from 4.88 to 4.19 ppm for core sample 1, and from 4.92 to 4.40 ppm for core sample 7.





Figure 19. Effluent concentration variations in Pb with time. (**a**) Shows the variation in concentration for samples treated with DI water. (**b**) Shows variation in concentration when treated with FF.

3.3.8. Effluent Analysis: Case of Trace Elements (Se, Mn, Co, Cu, Mo)

The values for Se in DI water-treated effluents for the outcrop increased from 1.27 to 2.16 ppm, ranging from 0.13 to 0.09 ppm for core sample 1 and from 0.03 to 0.14 ppm for core sample 7 (Figure 20). The values for Se in fracturing fluid-treated effluents for the outcrop decreased from 1.28 to 0.97 ppm, increased from 0.21 to 0.39 ppm for core sample 1, and increased from 0.76 to 0.70 ppm for core sample 7.





Figure 20. Effluent concentration variations in Se with time. (**a**) Variation in concentration for samples treated with DI water. (**b**) Shows variation in concentration when treated with FF.

Figure 21 shows the variations in Mn with time. The values for Mn in DI water-treated effluents for the outcrop ranged from 9.29 to 11.46 ppm, 0.70 to 1.73 ppm for core sample 1, and 0.99 to 0.35 ppm for core sample 7. The values for Mn in fracturing fluid-treated effluents for the outcrop decreased from 13.16 to 11.03 ppm, from 0.12 to 0.01 ppm for core sample 1, and from 1.06 to 1.68 ppm for core sample 7.





Figure 21. Effluent concentration variations in Se with time. (a) Shows the variation in concentration for samples treated with DI water. (b) Shows variation in concentration when treated with FF.

Figure 22 shows the variations in Co with time. The values for Co in DI water-treated effluents for the outcrop decreased from 0.30 to 0.16 ppm, an average of 0.01 ppm for core sample 1, and an average of 0.02 ppm for core sample 7. The values for Co in fracturing fluid-treated effluents for the outcrop decreased from 0.46 to 0.14 ppm, an average of 0.01 ppm for core sample 1, and from 0.02 to 0.03 ppm for core sample 7.





Figure 22. Effluent concentration variations in Co with time. (a) Shows the variation in concentration for samples treated with DI water. (b) Shows variation in concentration when treated with FF.

Figure 23 shows the variations in Cu with time. The values for Cu in DI water-treated effluents for the outcrop increased from 0.27 to 0.35 ppm, from 0.30 to 0.36 ppm for core sample 1, and from 0.26 to 0.31 ppm for core sample 7. The values for Cu in fracturing fluid-treated effluents for the outcrop increased from 0.28 to 0.30 ppm, from 0.00 to 0.30 ppm for core sample 1, and varied between 0.17 and 0.19 ppm for core sample 7.



Figure 23. Effluent concentration variations in Cu with time. (a) Shows the variation in concentration for samples treated with DI water. (b) Shows variation in concentration when treated with FF.

(**b**)

Figure 24 shows the variations in Mo with time. The values for Mo in DI water-treated effluents for the outcrop decreased from 21.26 to 19.38 ppm, an average of 0.15 ppm for core samples 1 and 7. The values for Mo in fracturing fluid-treated effluents for the outcrop decreased from 21.15 to 15.06 ppm, an average of 0.02 ppm for core sample 7, and varied between 0.01 and 0.10 ppm for core sample 1.





Figure 24. Effluent concentration variations in Mo with time. (**a**) Shows the variation in concentration for samples treated with DI water. (**b**) Shows variation in concentration when treated with FF.

3.3.9. Effluent Analysis: Case of Hazardous Elements (As, Cd, and Cr)

Higher concentrations of potentially harmful substances were discovered in the water additive-treated samples. Arsenic values decreased for the DI water-treated outcrop (0.20 to 0.13 ppm) and inversely for core samples 1 (0.14 to 0.16 ppm) and 7 (0.16 to 0.20 ppm), as shown in Figure 25a. With fracturing fluid, the outcrop's arsenic content was the lowest, with values ranging from 0.32 to 0.55 ppm. Values recorded for core sample 1 ranged from 0.49 to 0.68 ppm, and 0.77 to 0.47 ppm for core sample 7 (Figure 25b).





Figure 25. Effluent concentration variations in As with time. (a) Shows the variation in concentration for samples treated with DI water. (b) Shows variation in concentration when treated with FF. The outcrop displays the lowest values in both cases.

Cadmium levels were highest for the outcrop for DI water treatment, varying between 0.38 and 0.39 ppm. Core sample 1 values were 0.386 ppm on average and 0.385 ppm for core sample 7 when treated with DI water. There was a general decreasing trend for the three samples when treated with fracturing fluid; 0.39 to 0.38 ppm for the outcrop, 0.392 to 0.388 ppm for core sample 1, and 0.388 ppm on average for core sample 7 (Figure 26a,b).





Figure 26. Effluent concentration variations in Cd with time. (**a**) Shows the variation in concentration for samples treated with DI water. (**b**) Shows variation in concentration when treated with FF.

Figure 27a,b show the effluent's concentration variations in Cr. Chromium values ranged from 0.37 to 0.34 ppm for the outcrop, 0.34 to 0.35 ppm for core 1, and 0.35 to 0.33 ppm for core 7 when the samples were DI water-treated. Values recorded when the samples were treated with fracturing fluid showed a decline for the outcrop from 0.33 to 0.31 ppm. Values for cores sample 1 went from 0.31 to 0.32 ppm and 0.31 to 0.32 ppm for sample 7.





Figure 27. Effluent concentration variations in Cr. (**a**) Shows the variation in concentration for samples treated with DI water. (**b**) Shows variation in concentration when treated with FF. The highest values for Cr in the outcrop when DI water-treated.

4. Discussion

The discussion section of this study explores the chemical elements found in the effluent and their origins, as well as the potential impacts on rock strength and wellbore integrity.

4.1. Chemical Composition of Marcellus Shale

The composition of Marcellus shales is mainly formed by the neoformation and transformation of clays, including illite, chlorite, kaolinite, and mixed-layer clays. These clays are vulnerable to various chemical reactions, such as swelling, shrinking, hydration, and strength reduction from exposure to water and ions [14]. Clay minerals are classified as (hydr)oxides of silicon, aluminum, or magnesium, and the surface reactions of these

minerals can result in metal leaching [15]. The ability of an ion to readily dissolve to form a material also depends on the degree of crystallinity, the purity of phases formed, pH, and the temperature of the environment [16]. The hydraulic fracturing of Marcellus shales can cause various ions and charged surfaces to form new cations/anions in the environment, which may release potentially harmful materials and form new compounds [17]. The high concentration of dissolved Si in shale samples might be attributed to the presence of more soluble silica polymorphs (possibly biogenic) [18] and Si present in clay minerals, rather than quartz, which is less soluble. DI water treatment resulted in higher Si concentrations than in shale treated with hydraulic fracking additives.

4.2. Chemical Interactions of Shale Minerals with Fluids

Fracturing fluids can cause chemical interactions between clay and non-clay minerals' constituents such as carbonates and quartz present in a geological formation. Shale formations are predominantly formed in marine environments, and their mineral and fluid balance has remained stable over time. However, exposure to water-based engineering fluids can distort the geological equilibrium, leading to chemical reactions [19].

4.2.1. The Major Elements Found

Pyrite oxidation during hydraulic fracturing is a significant source of sulfate ions in fluids, with dissolved oxygen playing a critical role in pyrite breakdown and the formation of Fe^{2+} and sulfate ions, which can potentially block fractures [20]. Recent studies have shown that the salinity of fracturing fluids does not affect pyrite dissolution [21], implying that the concentration of Fe^{2+} is predominantly from the composition of the shale. An increase in sulfur concentration over time for both DI water and fracturing fluid treatments suggests possible pyrite dissolution, with hydraulic fracturing weakening rock strength and affecting wellbore integrity [22]. This dissolution initially leads to the formation of Sulfuric acid (H_2SO_4) and ferrous ions (Fe²⁺); the sulfuric acid can then react with more pyrite, producing ferric ions (Fe³⁺). The values obtained for sulfur with fracturing fluids ranged from 2062.48 to 6995.54 ppm and from 0.31 to 1.12 ppm for Fe^{2+} . Moreover, hydraulic fracturing fluid reactions can lead to the formation of iron sulfide scales, which can accumulate in the wellbore and reduce productivity, influenced by the pH and temperature of the fracturing fluids [23]. Further investigation of the potential environmental impacts of hydraulic fracturing, including the source of pyrite in shale formations and its role in sulfate ion production, is necessary to mitigate negative impacts on the environment and human health. Therefore, monitoring the chemical composition of hydraulic fracturing fluids and their interaction with surrounding rock formations is essential.

Montmorillonites are known to have a strong affinity for exchangeable Na⁺ cations, which is particularly evident in clay minerals such as Californian hectorites that possess high water sorption abilities [24]. Illite typically contains K as its characteristic cation, providing a balanced non-hydrated layer [24,25]. The use of a potassium-rich additive in the hydraulic fracturing fluid could increase K⁺ concentration through cationic substitution between Al³⁺, Fe²⁺, and Mg²⁺ during swelling. When interlayer cations hydrate, they can cause swelling behavior induced by the formation of diffuse double layers through osmosis. Mg²⁺ provides a positive cationic substitution for Montmorillonite. Over time, high concentrations of iron in fluids can lead to rust and the oxidation of production tubes, well casings, and pipelines, resulting in corrosion [24,26]. Boron has been observed to be adsorbed on clays with disequilibrium capable of producing its release. Boron concentrations were relatively the same in all samples (DI water: 4.40 ppm; FF: 4.29 ppm), possibly due to the stabilization process of clays that prevents the re-adsorption of released B, and the precise amount of boron incorporated into the structure of illites may vary depending on paleosalinity [27]. Walker proposed a formula for adjusting salinity that utilized 85% of the estimated potassium content of illite to convert the "adjusted boron content" to pure illite [28]. Illite has the highest capacity to absorb boron, followed by montmorillonite, chlorite, and kaolinite [29].

The concentrations of calcium varied from 2302 to 9456.15 ppm for fracturing fluid treatment. The pyrite oxidation leads to lower pH and solubility of carbonates present, where sulfuric acid (H_2SO_4) reacts with calcium carbonate $(CaCO_3)$, which results in the production of calcium sulfate (CaSO₄) and carbon dioxide (CO₂) [30]. The presence of calcium leads to scaling, as well. Scaling in water containing metal carbonates or bicarbonates occurs when calcium carbonate builds up and forms hardened carbonate scales (CaCO₃) on surfaces. The concentration of calcium required to cause scaling can vary depending on various factors, such as pH, temperature, and the presence of other ions in the water. However, typically water with a calcium concentration of 200 ppm or more is considered hard water and may cause scaling. Nonetheless, the threshold for scaling may differ depending on the specific conditions and the concentration of other ions, such as magnesium, which can also contribute to scaling [31]. The characteristics of the precipitate influence the severity of formation damage. Inorganic scale is made up of carbonate and coarse sand, whereas composite scale is made up of fine particles and inorganic scale mixed with oil. The combined effect is a decrease in permeability [32]. Precipitates reduce permeability by depositing solids (scales) on pore walls, blocking pore throats, and causing bridging across them [33].

4.2.2. The Minor Elements Found

The values for Se showed an increase in the DI water-treated effluents for the outcrop and a decrease in the fracturing fluid-treated effluents, while the values for core sample 1 and core sample 7 varied. These findings are consistent with previous studies that have shown the mobility of Se in shale formations due to its low adsorption capacity [34]. The dissolution of Se could be associated with pyrite due to its affinity with sulfides. The precipitation of Se could also occur in the form of selenite, which is soluble in water [35]. Se could potentially clog pores within the matrix and fractures, leading to a reduction in permeability and thus affecting wellbore integrity. The safe limit for Se in drinking water is 0.01 ppm, which is exceeded in all samples (average DI water: 0.68 ppm, FF: 0.86 ppm) except for core sample 7 [36].

Manganese showed varying values in the DI water-treated effluents for the outcrop and core samples, while the fracturing fluid-treated effluents showed a decrease in all samples. Manganese can occur in shale formations as a component of clay minerals such as illite and smectite. The dissolution of Mn can lead to the formation of amorphous hydrous silica and alumina, which can potentially clog pores within the matrix and fractures, leading to a reduction in permeability [37]. The safe limit for Mn in drinking water is 0.05 ppm, which is exceeded in all samples (average DI water: 4.10 ppm, FF: 4.85 ppm) [36,38]. The presence of high levels of Mn in the effluents could potentially have adverse effects on human health and the environment.

Cobalt showed a decrease in both DI water-treated and fracturing fluid-treated effluents for the outcrop and core samples. Cobalt can occur in shale formations as a component of clay minerals such as illite and smectite. The dissolution of Co could lead to the formation of amorphous hydrous silica and alumina, which could potentially clog pores within the matrix and fractures, leading to a reduction in permeability [38]. Cobalt is not considered to be a major environmental or health concern, and there is no established safe limit for Co in drinking water [39].

Molybdenum showed a decrease in both DI water-treated and fracturing fluid-treated effluents for the outcrop and core samples. Molybdenum can occur in shale formations as a component of sulfides such as molybdenite. The dissolution of Mo could lead to the formation of amorphous hydrous silica and alumina, which could potentially clog pores within the matrix and fractures, leading to a reduction in permeability [40]. The safe limit for Mo in drinking water is 0.07 ppm, which is exceeded in all samples except for the fracturing fluid-treated effluent for core sample 7 (average DI water: 6.69 ppm, FF: 7.12 ppm) [36,40].

Lead is a heavy metal found in trace amounts in shale formations that can pose a threat to the environment and human health if not managed properly. Lead can be mobilized and released into the fracturing fluid and subsequently into the environment through adsorption, desorption, and precipitation reactions [41]. This can occur through the dissolution of lead-containing minerals in the shale, such as galena (PbS), or through the interaction of the fracturing fluid with the cement and metal components of the wellbore. The safe limit for lead in drinking water is $10 \,\mu g/L$ [42]. The values for Pb in DI watertreated effluents for the outcrop ranged from 0.18 to 0.04 ppm, 0.07 ppm on average for core sample 1, and 0.1 ppm on average for core sample 7. The values for Pb in fracturing fluidtreated effluents for the outcrop decreased from 3.38 to 2.70 ppm, from 4.88 to 4.19 ppm for core sample 1, and from 4.92 to 4.40 ppm for core sample 7. These values are above the safe limit for drinking water and indicate a potential risk of contamination if not properly managed. The presence of lead in shale formations can have an impact on rock strength and wellbore integrity. Lead can contribute to the formation of scale and other deposits that can obstruct the flow of oil and gas through the wellbore. Additionally, lead can react with the cement and metal components of the wellbore, leading to corrosion and other forms of degradation [43]. This can result in wellbore failures and the release of contaminants into the environment.

The other elements that were found in high levels, such as cadmium, chromium, and arsenic, suggest the presence of organic sediments because of their propensity to bond to organic matter, with possible infiltration from surface waters. These elements can be released during the decomposition of organic matter in sediments, leading to their accumulation in the sediment. Additionally, the infiltration of surface fluids can introduce dissolved components that can accumulate in the sediment [44]. Besides arsenic, selenium and cadmium can make it unsafe to reuse or recycle water in any way. The average values recorded for As were 0.36 ppm. The standard limits for As in drinking water, soil, and groundwater are 0.01, 0.39, and 0.01 ppm, respectively [42,43,45]. Exposure to arsenic is linked to negative health impacts on the eyes, lymphatic system, kidneys, lungs, and liver, resulting in diseases such as hyperpigmentation, keratosis, cancers, and vascular disorders. Despite being a necessary element, selenium can have adverse consequences on the neurological system and cause brittle hair and misaligned nails. Occupational exposure may cause fatigue, mucous membrane irritation, dizziness, and respiratory effects. The average recorded value for Se is 0.77 ppm compared to the safe limits of 0.05, 20, and 0.05 ppm for drinking, surface, and groundwater, respectively [43,46]. Chronic exposure to cadmium causes several malignancies that affect the urinary, cardiovascular, skeletal, and peripheral nervous systems. Low-level cadmium exposure reduces bone density and alters bone composition [47]. The value recorded for Cr is 0.33 ppm. Chromium acceptable values are 0.1 ppm for total chromium and 0.005 ppm for hexavalent Cr in drinking and groundwater. This range is 34 ppm for total chromium and 0.11 ppm for hexavalent chromium for soil water. Isotopic studies of metallic elements are frequently used to understand the redox history of oceans and sediments. Zinc and cadmium, among other metals, tend to have isotopic compositions that reflect productivity or redox conditions because they tend to be buried in organic-rich sediments [48].

The study revealed low chemical element levels in most samples. Treatment with fracturing fluid resulted in increased concentrations of As, Ca, Cd, Co, K, Mn, Mo, Na, Ni, Pb, S, and Se, while DI water resulted in lower concentrations. Samples treated only with DI water showed increased Al, Cr, Cu, Fe, Mg, P, and Si concentrations. The observed chemical concentrations are significantly impacted by the choice of solvent, DI water or fracturing fluid, and to a lesser degree by drilled core vs. outcrop samples. However, lithium and strontium were not found in any of the effluents.

5. Conclusions

The study aimed to compare the geochemical reaction of Marcellus shale rock, both outcrop and drilled core samples, with laboratory-made fracturing fluids, analyzed through

ICP and EDS. Metal concentrations varied among the shale samples, with outcrop having lower concentrations of some elements than drilled core samples. Simulated flowback water was found to be within the normal range of conventional produced waters, with sulfur, calcium, silicon, sodium, and potassium being dominant elements. Concentrations of metal elements in DI water-treated samples were lower than those in water containing hydraulic fracturing additives. Marcellus shale exposed to fracturing fluids had increased concentrations of As, Ca, Cd, Co, K, Mn, Mo, Na, Ni, Pb, S, and Se.

In addition, the study identified several elements of major environmental concern, namely selenium (Se), cadmium (Cd), and chromium (Cr). Se values exceeded the safe limit of 0.05 ppm at 0.02 ppm, raising safety concerns over accumulation at the surface. The average Cr values of 0.32 ppm (320 μ g/L) were higher than the safe limits for drinking and groundwater (0.1 ppm for total Cr and 0.05 ppm for hexavalent Cr) but were still suitable for soil water. Cd values also exceeded the safe limits for drinking water (3 μ g/L), soil water (0.15 ppm), and groundwater (50 μ g/L) with an average value of 0.38 ppm (380 μ g/L). Moreover, Pb values in both DI water and FF effluents for the outcrop and drilled cores were above the safe limit for drinking water, ranging from 0.04 to 0.18 ppm in DI water-treated effluents, and from 2.70 to 3.38 ppm in FF-treated effluents, indicating a potential risk of contamination if not managed properly.

It is crucial to properly monitor the disposal and reuse of flowback water due to the huge volumes that are utilized in the hydraulic fracturing process.

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