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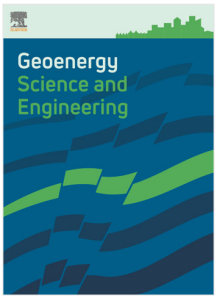

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Water-rock interactions and self-remediation: lessons from a hydraulic fracturing operation in the Vaca Muerta formation, Argentina

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1 Abstract

In order to analyze the effect of a new gelling agent for hydraulic fracturing, fluid samples from different stages of the operation (hydraulic fracturing fluid, coil tubing, flowback and produced waters) were collected from a well in the the Vaca Muerta formation in Argentina. Collected samples were analyzed for major and trace elements, first within a few days after sampling, then reanalyzed 6 months later and again 2 years after sampling. Results show that the salinity of samples increased quickly with time, from 2000 mg/L up to 43,000 mg/l a month later, due to the mixing of hydraulic fracturing fluids with formation

water. No evidence of water-rock reactions was observed. Results from the later analyses showed that the composition of the samples evolved with time with a sensible decrease of concentration for most trace elements over the course of these two years (e.g. Ba from 137 mg/L to 55 mg/L, Mn from 8mg/L to 5mg/L) and heavy metals (e.g. As 100μg/L to 1μf/L, Co 160 μg/L to 1.4 μg/L, Cr from 160 μg/L to 26μg/L). Interpretation of the results shows that delayed, post-sampling, precipitation of barite in the preserved samples is the reason for such a decrease. This opens a very interesting option for mitigation and remediation of wastewaters from hydraulic fracturing as natural or even triggered precipitation of barite could involve most of the dissolved heavy metals and decrease strongly their concentrations.

2 Introduction

The exploitation of hydrocarbons trapped in tight formations is continuing its worldwide expansion with countries like USA or Canada producing a large percentage of their hydrocarbon resources through shale gas plays like the Marcellus, Eagle Ford, Permian Basin formations in the United-States (, EIA), the Montney, Duvernay and Horn River formations in Canada (Board, 2017; of Canada, 2018; of Canadian Academies, 2014). Numerous other countries are joining the movement, with recent hydraulic fracturing operations in Argentina where the giant reservoir of Vaca Muerta was discovered in 2010 (Administration, 2013) is exploited.

Hydraulic fracturing and the exploitation of shale gas can appear as a controversial technology and its global expansion is met with criticism from ecological organizations (Brittingham et al., 2014). Indeed, concerns remain about the potential contamination of freshwater resources by fugitive methane emanations (Osborn et al., 2011; Humez et al., 2019) or by hydraulic fracturing fluids migration (Darrah et al., 2014; Warner et al., 2012; Bondu et al., 2021). Other environmental risks are linked to the very high water consumption (Gallegos and Varela, 2015; Gregory et al., 2011a; Vengosh et al., 2014; Kondash et al., 2018), as well as the treatment and recycling of thousands of cubic meters of potentially toxic wastewaters produced per well (Thiel et al., 2015; Gregory et al., 2011b). Indeed, after hydraulic fracturing of the reservoir, when the well is opened to production, a large quantity of water (called flowback water) is produced (Kondash et al., 2017). These fluids are a mixture of hydraulic fracturing fluids with formation brine as well as products of water-rock interactions, the latter being frequently enhanced by the additives used for the optimization of the hydraulic fracturing operation itself (Osselin et al., 2018, 2019; Birkle, 2016; Birkle and Makechnie, 2022; Li et al., 2017; Lu et al., 2017; Phan et al., 2020). These flowback fluids are characterized

by a very high TDS (total dissolved solids), usually several times the salinity of seawater and contain usually non-negligible quantities of trace elements and heavy metals (e.g. As, Ni, Co, Cr) with a potentially high toxicity (Haluszczak et al., 2013; Blauch et al., 2009; Abualfaraj et al., 2014; Phan et al., 2015; Johnson and Graney, 2015; Ni et al., 2018; Bern et al., 2021). The disposal and remediation of these high salinity fluids is complicated and operators usually choose to reinject these fluids underground in nearby porous formations, usually into stratigraphically deep reservoirs, well below aquifers utilized for water supplies. However, considering the very high consumption of freshwater by hydraulic fracturing operations (several thousand cubic meters per stage), and especially in areas where the freshwater resource is already under strain, there is a strong incentive to recycle and reuse these flowback fluids for the next hydraulic fracturing operation (Liu et al., 2020). One way to simplify the processing of flowback fluids for reuse in hydraulic fracturing operations is to control the downhole water-rock interactions and the release of heavy metal and traces by the formation (Osselin et al., 2019; Lerat et al., 2018). An extensive understanding of the downhole geochemical behavior during hydraulic fracturing and subsequent flowback is then required in order to optimize and tailor the geochemistry of flowback fluids. In particular, it was shown that the use of oxidative breakers was not optimal because of its very aggressive behavior towards minerals like pyrite and organic matter releasing heavy metals in the flowback fluids (Renock et al., 2016; Yang et al., 2021).

This study presents the analysis of flowback samples from a well operated in Argentina. This well presents the particularity of having been treated with a novel fracturing fluid mixture, not involving the classic couple guar gum and oxidant breaker. Instead, the gelling agent (i.e. the additive modifying viscosity for a better proppant transport into the fractures) was composed of fragile polymers. Upon opening the well to production, when a lower viscosity is desirable for smooth flowback (i.e., once the proppant has been transported deep into the hydraulic fractures), the decrease in viscosity is not achieved by an aggressive oxidative attack on the polymer but by a simple mechanical shearing and breaking of the polymer due to the rough and intersected nature of the hydraulic fractures network. If the polymer is forced into a steep angle because of the geometry of the hydraulic fractures, it will break into smaller pieces. Thus the downhole geochemistry is strongly different from other classic hydraulically fractured wells such as from the Marcellus or the Montney shales, because of the absence of oxidative action on the sulfide minerals and on organic matter.

Several water samples were collected during the different stages of the procedure, the hydraulic fracturing itself, the coil tubing operation which opens the different stages to the main wellbore, and finally the flowback once the well is opened to production. All samples were analyzed for major elements and traces

as well as several stable isotopes in order to elucidate the downhole behavior and see if the absence of oxidative breaker was impacting beneficially the overall composition of returned waters in view of recycling and reuse of such waters for further hydraulic fracturing operations or simply for disposal.

3 Material and Methods

Study site and well completion The considered well is located in the province of Neuquen, North-West Patagonia, Argentina (Figure 1). The target formation is the Vaca Muerta formation, a carbonate marl with black shale and lime mudstone. The targeted interval (between 2600 mbs (meters below surface) and 2800 mbs) presents an average composition of 15% albite feldspar($NaAlSi_3O_8$), 30% quartz (SiO_2), 25% calcite ($CaCO_3$), 22% illite (clay mineral), with a bit (3%) of pyrite (FeS_2) and traces of dolomite and apatite.

In this zone, several pads were constructed, with each pad being the starting point of three horizontal wells in a two pronged fork shape. The horizontal portion of the studied well was divided into 15 stages. After the drilling of the well and the perforations, but before any hydraulic fracturing, the well was spearheaded with HCl to cleanse debris and prepare the formation for the hydraulic fracturing operation. Hydraulic fracturing was proceeded with a slickwater mixture with freshwater obtained from the overlying sandstone aquifer. The water used came from two different wells labeled WW3 and WW4.

The 15 stages were proceeded from toe (the far end of the horizontal wellbore) to heel, and stages were separated from each other by small aluminum plugs. After all stages were fractured, the well was subjected to a coil-tubing operation to open the stages to production. This operation consists of inserting a flexible drill into the horizontal wellbore and drilling the plugs which opens the stages. During this operation, no water is produced and the whole system supposedly works as a closed loop. However, due to some overheating of the water and the equipment, it was necessary to add four trucks of freshwater during the operation with each truck containing $25m^3$ of water. Before the addition, the same amount was bled from the closed loop and replaced with the freshwater from the trucks. One truck was added between the 7th and the 8th stage, another between the 13th and 14th stage and 2 trucks between 14th and the last plug for a total of $100m^3$ of freshwater (Figure 2).

Finally, the well was left to rest one week between the end of the coil-tubing operation and the beginning of flowback (i.e. opening of the well to production).

Analytical Methods Samples were obtained on site during the coil-tubing procedure and the flowback (Oct-Nov 2015). Samples from the water wells used for the hydraulic fracturing fluids (WW3 and WW4)

Figure 1: Location of the Neuquen reqion

were also obtained as well as one produced water sample from another hydraulically fractured well on another pad, which was put to production four months before the operation on the considered well. This sample, named PW, was considered to be representative of the formation brine. In total, three samples were taken during coil-tubing (CT1, CT2 and CT3), one after the first plug was drilled, one between plugs 7 and 8, and one after the last plug was drilled. Unfortunately, the first CT sample was not kept. A total of 6 flowback (FB1 to FB6) samples were obtained during the first 2 days of flowback at regular intervals.

After filtration (0.1μm), the pH of the samples was measured before being preserved on site (acidification pH < 2 for cation analysis) and shipped a few days later to INDUSER (Induser Group SRL, Laboratory of Chemical and Microbiological Analysis, Buenos Aires, Argentina) for analysis. Samples were analyzed for all major and trace elements by the laboratory as well as numerous organic species. Cations were quantified by ICP-OES (inductively coupled plasma optical emission spectrophotometer) and anion concentrations were measured by ion chromatography. Bicarbonate alkalinity was measured by titration. Total dissolved solids (TDS) content was calculated by adding all measured concentrations of dissolved species and the consistency of the results (QA/QC) was verified by checking that the ionic balance was below 5% for all samples.

Stable isotope analysis were made at BRGM (French Geological Survey, Orléans, France). Water isotopes ratios (δ^2H and δ^{18}O) were determined by CF-IRMS (continuous flow isotope ratio mass spectrometry) and results are reported in the δ notation $\delta = (R_{spl}/R_{std} - 1) \times 1000$, with R_{spl} the isotope ratio in the sample and R_{std} the isotope ratio of a standard reference. For water isotopes, the standard reference is V-SMOW.

The exploitation of the results from INDUSER showed that the detection limits from this laboratory were too high for the samples and very little could be read from these analyses (see Supplementary Information Tables 1-4). Additional analyses were then requested for the trace elements with some done at TOTALEnergies (Laboratory of Inorganic Chemistry, CSTJF, Pau, France) and some at BRGM (French Geological Survey). The TOTALEnergies analyses where proceeded in July 2016 (i.e. 8 to 9 months after sampling due to delays on the exportation of the samples). Concentrations of trace elements were measured at BRGM on Thermo Scientific XSERIES 2 ICP-MS with a precision generally better than 5%. Analyses were performed on April 2018 i.e. more than 2 years after sampling. Finally, radium quantification was made by ALGADE by gamma-spectrometry, using Pb214 and Bi214 for Ra226 and Ac228 for Ra228 according to the norm NF EN ISO 550 1070. Analyses were proceeded on 3 samples (PW, FB1 and FB6) in August 2016 i.e. 9 months after sampling.

QA/QC The quality of trace element analyses is highly dependent on the quality of sample preparation on site. Samples were routinely filtered with a 0.1 μm pore size syringe filter, following the recommendation of Claret et al. (2011) to avoid conventional filters with larger pore sizes 0.2 μm or 0.45 μm. Filtration was performed immediately after fluid sampling on the borehole fluid circulation loop.

A QC check of the analyses was performed by checking with PHREEQC (Appelo and Postma, 2005; Parkhurst and Appelo, 2013), the charge balances and the equilibrium of the fluids with calcite. As this equilibrium is usually quickly reached in sedimentary systems and as calcite belongs to the mineralogy of the considered formation, it demonstrates that pH, alkalinity and calcium concentration are correctly analyzed and by extension major elements, based on the charge balance. For metals, redundancy of analyses in different laboratories was planned as a means of quality control, but the results of this cross-check are part of the discussion of the article.

4 Results

The behavior of the well can be divided into 2 phases: (i) the hydraulic fracturing and coil-tubing until October 8th 2015 and (ii) flowback and production from Oct. 8th 2015 as represented on Figure 2. During the first phase, the TDS increases by an order of magnitude, going from ≈1500 mg/L in the hydraulic fracturing fluid (average between WW3 and WW4), to 13,978 mg/L for sample CT1 in the midst of coil-tubing operations, and nearly doubling to 23,824 mg/L for CT2 at the end of coil-tubing. After the well is opened to flowback, the first sample presents a TDS value almost identical to the end of CT (22,999 mg/L). TDS increases quickly up to 41,996 mg/L after a few hours of flowback maintain stable for the remaining flowback period (i.e. 48 hours).

Evolution of other major elements is represented on Figure 3 as a function of Cl, as chloride is usually considered conservative during the whole duration of the process (Li et al., 2017; Engelder et al., 2014). The goal of such a plot is to allow the identification of conservative and non-conservative species. Conservative species will correlate linearly to Cl concentrations, while the absence of correlation indicates the presence of mineral precipitation/dissolution and cation exchange.

All major elements are evolving similarly to the TDS content with an increase between hydraulic fracturing fluids and CT1 (e.g. Na from 650 mg/L to 5030 mg/L), a minor increase during CT (Na from 5030 mg/L to 7910 mg/L), followed by a small drop between CT and FB1 (from 7910 to 7820 mg/L). A fast increase upon flowback (from 7820 to 13,550 mg/L) is followed by a period of almost no variation until the

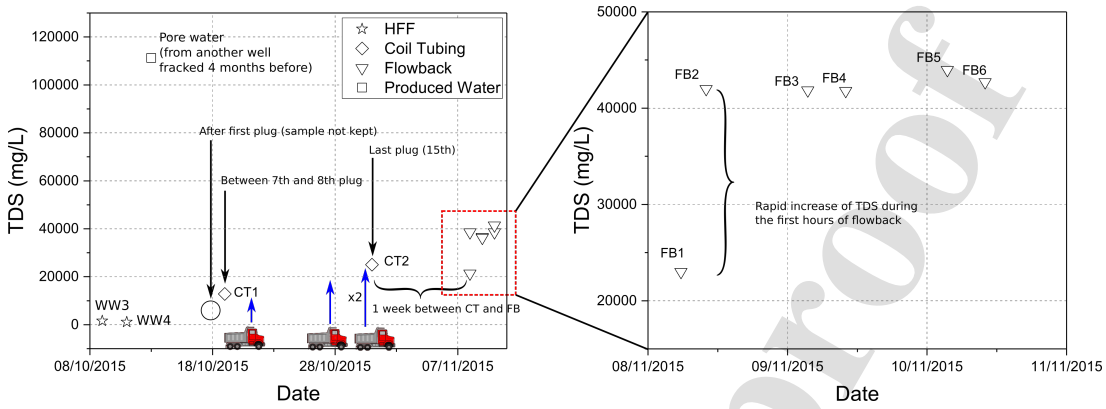

Figure 2: Evolution of TDS as a function of time during coil-tubing and flowback (INDUSER). The right figure shows a zoom of the flowback period

end of the sampling period. Interestingly, Na, Ca and Mg concentrations plot linearly with Cl for HWW, coil tubing and flowback samples, except sample PW which plots either higher for Ca, Mg, and lower for Na and K. Finally, the drop between CT2 and FB1 is proportionally more pronounced for K (from 87 mg/L down to 56.2 mg/L) than for the other major species respectively to Cl.

Alkalinity also shows an increase from 450 mg/L for the hydraulic fracturing fluid to 895 mg/L for CT1 and up to 1480 mg/L for FB3. The PW value for the alkalinity is actually smaller than for the hydraulic fracturing fluid with a value of 136 mg/L.

Barium presents an increase in concentration similar to the major elements but does not seem to plot linearly with Cl (Fig. 4). The first coil-tubing sample shows a value almost at zero, when CT2 plots at 23.9 mg/L and the flowback concentrations are around 135 mg/L. On the opposite, sulfate concentration is high for hydraulic fracturing fluids (300 mg/L) and drops quickly during coil-tubing (CT1 at 200 mg/L and CT2 at 106 mg/L) before reaching around 35 mg/L during flowback (Fig. 4). There is no value for sulfate concentration for FB1. Radium is measured at 1.58 Bq/L in the initial flowback sample and increased to 13.65 Bq/L in the last flowback sample. The produced water sample presents a Ra activity of 137.3 Bq/L.

Water isotopes present a behavior similar to the major dissolved species, with a steady evolution from -88.8 and -95.3‰ for δ^2H values of respectively WW3 and WW4 to -66.5‰ at the end of coil-tubing, then -65.0‰ for FB1 and a plateau ratio around -53.5‰ for flowback samples after the first (Fig. 5). Oxygen isotope values increase from -11.0 and -12.3‰ in WW3 and WW4 samples up to -5.9‰ for CT2 and -6.0‰ at the beginning of flowback. The flowback plateau is around -4‰. Finally the produced water sample PW is measured at δ^2H = -33.0‰ and $\delta^{18}O$ = -1.5‰. A cross-plot $\delta^{18}O$ versus δ^2H shows that WW3 and WW4

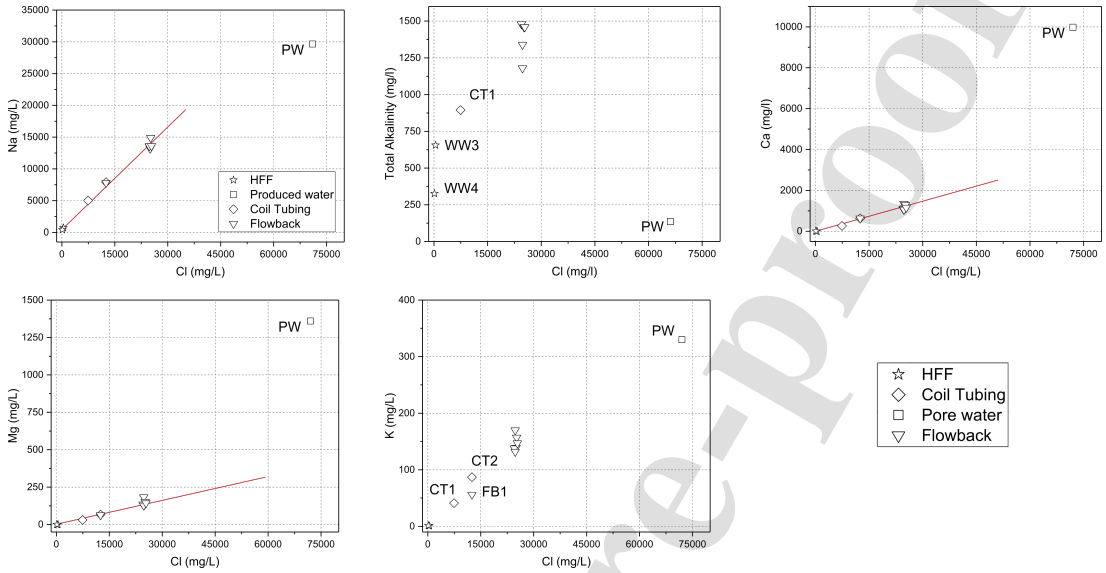

Figure 3: Plots of major species against Cl during coil-tubing and flowback (INDUSER)

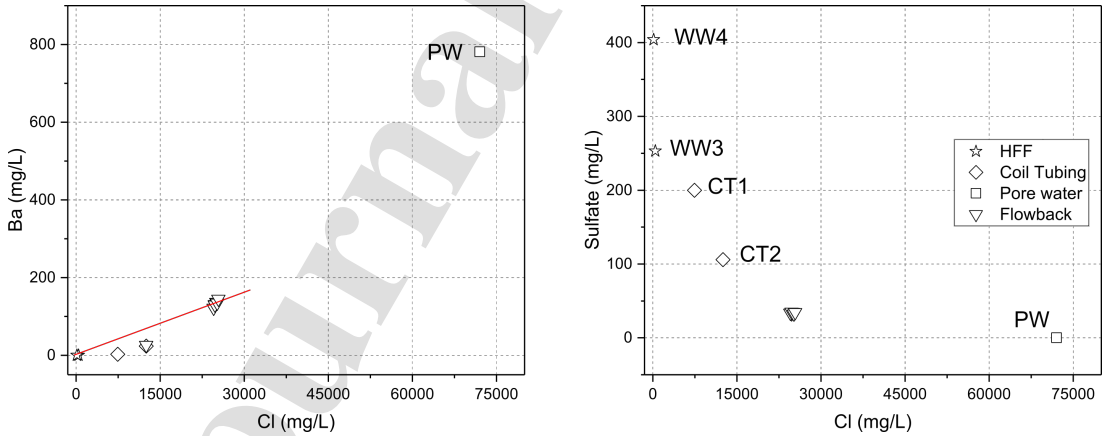

Figure 4: Plot of Ba and sulfate against Cl during coil-tubing and flowback (INDUSER)

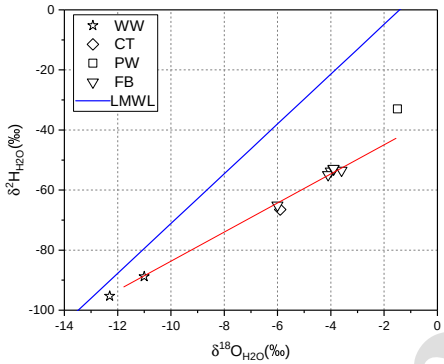

Figure 5: Cross plot of δ^2H vs δ^{18}O and the LMWL (BRGM)

plot close to the Local Meteoric Water Line (LMWL) (Hoke et al., 2013) while subsequent samples depart from this line.

Few samples with heavy metals concentrations beyond the INDUSER detection limit (Nov. 2015) present values between 100 and 200 μg/L. The highest values measured for heavy metals are 210 μg/L for As in PW, 190 μg/L for Co in FB1, 240 μg/L for Cu in FB1, 200 μg/L for Cr in CT2. Mn presents values between 5 and 15 mg/L, B up to 85 mg/L for FB4 and Fe up to 200 mg/L for FB5. However, values measured from BRGM (April 2018) differ strongly. For example 0.67 μg/L of As in PW, 1.4 μg/L of Co in FB2, 1.7 μg/L of Cu in FB2 and 22.9 μg/L of Cr in CT2. For boron, FB samples drop from around 80 mg/L to 50 mg/L, while CT2 increases from 31.1 mg/L to 65.2 mg/L between INDUSER and BRGM results. Mn decreases from 7.5-8 mg/L in flowback to 5.5 mg/L and from 5.1 mg/L to 1.668 mg/L in sample CT2 (Figure 6). Only three samples were quantified for Fe in BRGM, with sample CT2 presenting the largest drop between 97.1 mg/L for INDUSER down to 12 mg/L for BRGM, while PW concentrations decrease from 173 mg/L to 155 mg/L. The concentrations of Fe in FB3 does not change with 122 and 125 mg/L in INDUSER and BRGM analysis respectively.

Similarly Ba shows a decrease in concentration from INDUSER to TOTAL (July 2016) to BRGM for each sample, with drops between 15% of the initial value (PW) and around 60% for FB values (Figure 6). Strontium presents a similar behavior, to the exception of PW with an increase from 1750 mg/L for INDUSER results up to 3002 mg/L in TOTAL analysis towards 2863.2 mg/L.

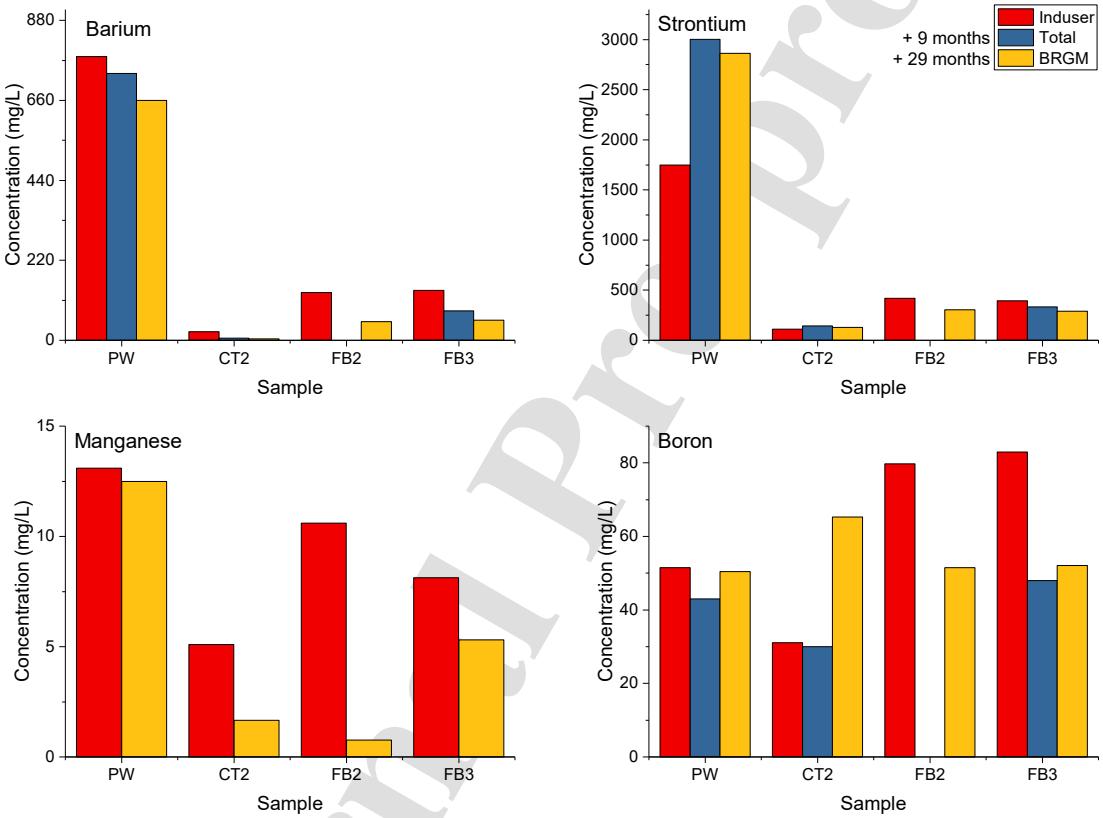

Figure 6: Evolution of Ba, Sr, Mn and B with time (i.e. according to the different laboratories). Error bars are significantly smaller than the variation (e.g. 1mg/L Induser and 0.5μg/L BRGM for Ba)

5 Discussion

TDS and water-rock interactions The evolution of salinity in flowback water has been extensively described in numerous publications and is the result of mixing of the hydraulic fracturing fluids with formation brine as well as caused by chemical interactions between hydraulic fracturing fluid/formation water and reservoir rock (Osselin et al., 2018; Rowan et al., 2015; Hakala et al., 2021; Huang et al., 2020). These reactions usually involve salt dissolution if present in the mineralogy (halite, gypsum, anhydrite, calcite, dolomite) and potential oxidation of sulfide minerals (pyrite FeS_2) and organic matter from fracturing water containing strong oxidants (O_2, oxidant breaker) (Osselin et al., 2019; Xu et al., 2018).

In the studied case, it is necessary to differentiate the behavior during coil-tubing from flowback. After hydraulic fracturing, the injected fluid stays in the fractures during the whole coil-tubing operation as there is no fluid production. The only exception is the addition of freshwater to cool down the fluid, which was preceded by bleeding of the same volume of water from the well. As a result, since the bleeding decreased the quantity of water in the fractures, a small proportion of formation water was allowed into the hydraulic fractures and mixed with the hydraulic fracturing fluid. This explains the increase of TDS for samples CT1 and CT2 compared to WW3 and WW4. At the end of CT, the system was left to rest for a week with little change in water composition. As no fluid was produced, no formation water was allowed in the system and no change of TDS is detectable. This is another confirmation that the source of high TDS in flowback water is not only the dissolution of autochthonous salts but mostly the mixing with high TDS formation brine. The only remarkable feature between CT2 and FB1 is the small drop of K which is likely due to some cation exchange with the clay minerals of the reservoir, e.g. replacement of Ca by K in the exchangeable sites of the illite fraction (Essington, 2005).

Then, as the well is opened and flowback begins, a very fast increase of TDS is observed as the formation brine starts mixing with the hydraulic fracturing fluid. This increase is followed by a plateau where flowback water salinity stays roughly the same. One of the reasons of this plateau is that almost all the easily mobilized formation brine (i.e. mobile formation water close to the hydraulic fractures, probably in natural fractures) already mixed with the fracturing fluids between FB1 and FB2. After that point, the mixing slows down as the flow rate of formation water into the hydraulic fractures is smaller since the system is tapping into tighter permeability rocks and less mobile sources of formation brine (Osselin et al., 2018).

Interestingly, pore water sample PW does not seem to correspond to the end-member for conservative mixing. Indeed, water isotopes are considered conservative in this context (Rowan et al., 2015) and PW

does not fall (e.g. excess of +10‰ of δ^2H) on a line joining the hydraulic fracturing fluids, coil tubing fluids and flowback (Fig. 5). Since PW is a sample from another well fractured four months before, it is possible that it does not correspond to the formation water of the considered well, either because four months is potentially not long enough to reach the final composition of the formation water; because of some interactions between wells shifting the global conservative mixing; or simply because the formation water changes composition with the location of the well. Disregarding PW, it appears that Na, Ca, Mg and K are likely to be conservative (to the exception of some cation exchange with the clay minerals), while Ba and sulfate are probably not. Water isotopes further support this interpretation as they show a mostly conservative mixing behavior during the whole coil-tubing and flowback duration (Fig. 5). The very similar values in the water isotope ratios between CT2 and FB1 confirms the absence of mixing and water exchange during the whole week between the end of coil-tubing and the beginning of flowback.

Saturation indexes of minerals have been modeled with PHREEQC v3 with the Pitzer database (Appelo, 2015) and results are represented in Figure 7. Calcite is at equilibrium for PW and or CT, but shows a slight oversaturation for FB samples. This is perfectly consistent with the presence of calcite in the mineralogy of the formation. A slight precipitation of calcite may then be expected but the simulation results confirm that Na, Ca, Mg and K should be mostly conservative. The non-conservative behavior of Ba and sulfate can, on the other hand, be explained by the oversaturation of barite during the whole duration of the operation. PW – which can be considered as more or less representative of the formation brine despite not being the actual end-member of the mixing in the considered well – is quite Ba-rich (781 mg/L), while the freshwater used for the hydraulic fracturing operation is rather sulfate-rich (300 mg/L). Precipitation of barite is then likely, especially with the addition of the four 25m^3 trucks of sulfate-rich freshwater. The behavior of radium, even in the absence of the first end-member can be linked to barium behavior: in the first flowback sample, Ra and Ba are both very low due to barite precipitation incorporating Ra in the crystal structure (Scheiber et al., 2014). Then the Ra concentration increases due to mixing with formation water.

Once the samples are preserved and acidified, calcite becomes strongly undersaturated and is not expected to precipitate. On the other hand, barite ($BaSO_4$) is not impacted by acidification and stays supersaturated in all samples.

Evolution of trace concentrations with time in preserved samples As described in the result section, the concentrations of heavy metals and trace elements vary widely between the three laboratories. Rejecting the hypothesis that the analyses were erroneous, the reason for this discrepancy is that between the sampling

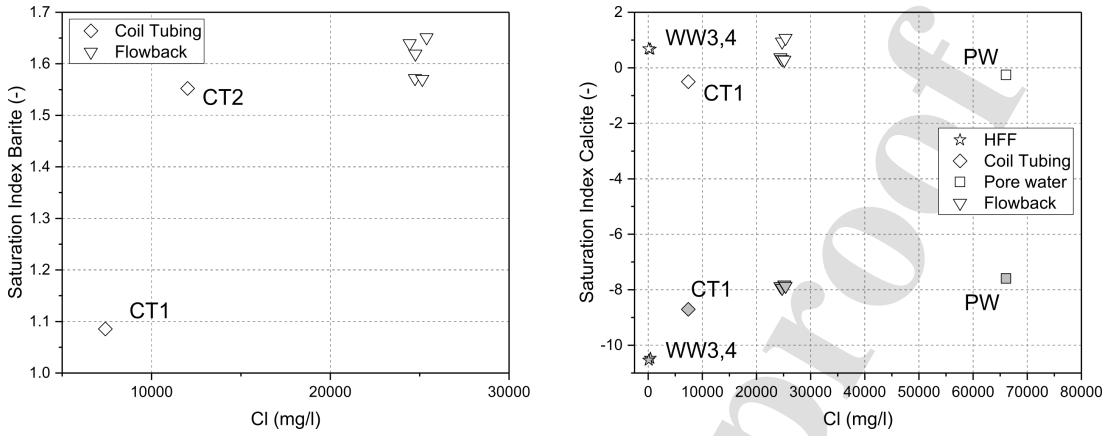

Figure 7: Evolution of barite and calcite saturation indices in the samples and the effect of acidification (Calculated from INDUSER data)

and the analyses, the samples were not really quenched by the acidification and evolved. Acidification is mainly used for preventing the precipitation of oxi-hydroxide iron complexes ($Fe(OH)_3$) which are known to co-precipitate with other metallic cations (Appelo and Postma, 2005). However, as can be seen from the Ba evolution (Fig. 6 and from the SI from Figure 7, barite is very likely to have precipitated during the delayed analyses as its saturation index is not impacted by acidification. This precipitation plays a similar role as the iron oxi-hydroxides as barite co-precipitates with several traces such as Ra, As, Cu, Zn, Ag, Ni, Hg, Co, V, Pb, Mn and Cr and other rare-earth elements (Gupta, 1991; Crecelius et al., 2007). Most of the elements precipitate as a substitution to the Ba in the barite structure while some (Mn as permanganate MnO_4^- or Cr as chromate CrO_4^{2-}) substitute to sulfate (Tokunaga et al., 2016). This is consistent with the analytical results showing an overall decrease in all the mentioned cations as well as decrease of Ba with time. Strontium usually forms a solid solution with barite upon precipitation and presents indeed a decrease with time for all FB samples. The large increase between INDUSER and BRGM value for PW and CT2 is on the other hand not clear. As radium was only measured 9 months after sampling (similar time as TOTALEnergies analyses), it is likely that the actual values are higher than the ones measured.

Boron shows a similar increase with a large increase between INDUSER and BRGM results for CT2. One possible explanation is the slow decomposition of some colloidal complexes with time releasing Sr and B into solution (Appelo and Postma, 2005) during the 2 years between INDUSER and BRGM analyses. However the filtration on 0.10μm filters should not let some colloidal particles through. A damaged filter, a mishandling of the samples or simply the difficulty associated with Boron analyses may explain the

discrepancy

The behavior or trace elements over these two years leads to two important conclusions:

- Acidification of samples is not enough to stabilize a sample with high sulfate and barium concentrations. Analyses have to be made as soon as possible on flowback waters (or any high salinity brine containing these two elements) in order to avoid any experimental error showing lower trace elements concentration than in reality. Similarly, if the behavior of B and Sr is linked to the decomposition of colloidal particles, then the filtration has also to be carefully controlled. The current case is quite extreme since most of the analyses have been made more than two years after sampling, but not completely uncommon.

- Barium sulfate precipitation is a potential mitigation and remediation process to lower the concentration of heavy metals and potentially toxic species. Indeed, the concentrations of most trace elements have decreased by several orders of magnitude during the two years period, reaching eventually concentrations below the detection limit. This can provide an mitigation approach to recycle hydraulic fracturing waters by adding either Ba ions for sulfate rich wastewaters or sulfate in barium rich wastewaters (e.g. Marcellus). The precipitation of barium sulfate (barite) could scavenge a large amount of trace elements and heavy metals from the returned waters decreasing their concentrations below detection limits. Since hydraulic fracturing is using thousands of m^3 of freshwater and producing large amounts of highly saline wastewater, the recycling of such returned waters is a necessity to lower the pressure on water resources and a quick way to reduce the trace elements and heavy metals concentration could help alleviate this issue. This however means that the potential solids would have to be treated with proper care as they would be incorporating radioactive species (Ra) and heavy metals that were scavenged during precipitation of barite.

It is important that values for the heavy metals before barite precipitation in our case were still at low levels. The highest concentrations were between 100 and 200 μg/L. These values, while being higher than the drinking water guidelines (Organisation, 2017), are still orders of magnitude lower than other industrial pollution such as mine tailing (for example As average concentrations of 22.53 mg/L in the polluted groundwater linked to Chéni mine in France Bodénan et al. (2004)). Finally, the combination of barite precipitation with the absence of oxidative breaker and the low initial trace and heavy metals concentrations in formation water leads to high TDS, Na-Cl type, returned waters presenting low to very low concentrations for all minor species and thus low to very low toxicity except for the hypersalinity.

6 Conclusion

The presented study was initially designed to analyze the effect of a new gelling agent for hydraulic fracturing operations. This new gelling agent does not require an strong oxidative breaker (such as persulfate), which limits the potential water/rock interaction during the hydraulic fracturing and the flowback period. Water samples were taken during the different periods of the process (coil tubing and flowback) and were analyzed for major and trace elements. Results showed that, as expected, little water/rock interaction occurred except the precipitation of barite.

However, due to the high detection limits of the first Argentinian laboratory which analyzed the results, it was decided to duplicate the analyses both at TotalEnergies and at BRGM. Because of custom delays, these additional analyses were performed only 9 months later for some (TotalEnergies) and more than 2 years after sampling (BRGM). These extra results show a systematic decrease in the heavy metal content from the initial analyses. This decrease is interpreted in terms of post-sampling barite precipitation which scavenges heavy metals. This opens an potential mitigation technique for flowback and produced waters to improve their quality and go towards their recycling.

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8 Supplementary Information

Analytical results for the different samples described in this study. When applicable, results from the 3 laboratories (INDUSER, TOTAL and BRGM) are mentionned.

Sample	Date DD/MM/YYYY	Time HH:mm	pH -	TDS mg/L	Cl mg/L	Alkalinity mg/L	Na mg/L	Ca mg/L	Mg mg/L
WW3	09/10/2014	-	9.1	1998	444	656	730	4	0.4
WW4	11/10/2015	-	9.1	1264	125	326	415	6.8	0.11
PW	13/10/2015	15:00	6	115795	71000	136	29657	9980	1360
CT1	19/10/2015	10:00	6.3	13978	7410	895	5030	264	30.7
CT2	31/10/2015	07:30	6.7	23824	12500	-	7910	630	66.4
FB1	08/11/2015	11:40	6.5	22999	12482	-	7820	633	62.9
FB2	08/11/2015	16:00	6.9	41996	24740	1180	13550	1350	183
FB3	09/11/2015	09:30	6.4	41858	25000	1480	13210	1130	134
FB4	09/11/2015	16:00	6.4	41790	24760	1340	13590	1060	127
FB5	10/11/2015	09:30	6.3	43982	25150	1460	14910	1290	153
FB6	10/11/2015	16:00	7	42716	25390	1460	13620	1160	143

Table 1: Selected results from the flowback water samples (Induser) - Major elements (<LQ = below quantification limit)

Sample	Date DD/MM/YYYY	Time HH:mm	K mg/L	SO_4 mg/L	δ^2H ‰	$\delta^{18}O$ ‰
WW3	09/10/2014	-	0.9	253	-88.8	-11.0
WW4	11/10/2015	-	1.3	404	-95.3	-12.3
PW	13/10/2015	15:00	330	<LQ	-33.0	-1.5
CT1	19/10/2015	10:00	41	200	-	-
CT2	31/10/2015	07:30	87	106	-66.5	-5.9
FB1	08/11/2015	11:40	56.2	-	-65.0	-6.0
FB2	08/11/2015	16:00	170	32.8	-53.4	-3.6
FB3	09/11/2015	09:30	139	34.9	-53.7	-4.0
FB4	09/11/2015	16:00	132	35.1	-54.9	-4.1
FB5	10/11/2015	09:30	157	32.5	-	-
FB6	10/11/2015	16:00	147	34.5	-52.8	-3.9

Table 2: Selected results from the flowback water samples (Induser) - Major elements (<LQ = below quantification limit) - Continued

Sample	Date	Time	Ba			Sr			Mn		B			Fe	
	DD/MM/YYYY	HH:mm	Induser	Total mg/L	BRGM	Induser	Total mg/L	BRGM	Induser	BRGM mg/L	Induser	Total mg/L	BRGM	Induser	BRGM mg/L
WW3	09/10/2014	-	<LQ	-	0.1	<LQ	-	0.174	< LQ	4.42 (μg/L)	0.7	-	0.646	0.64	-
WW4	11/10/2015	-	<LQ	0.18	0.075	<LQ	0.27	0.213	< LQ	9.29 (μg/L)	0.4	0.2	0.189	0.53	-
PW	13/10/2015	15:00	781	734	660	1750	3002	2863.41	13.1	12.489	51.5	43	50.434	173	155
CT1	19/10/2015	10:00	2.9	-	-	63.5	-	-	4.21	-	23.3	-	-	24.2	-
CT2	31/10/2015	07:30	23.9	5.5	4.043	111	145	129.021	5.1	1.668	31.1	30	65.229	97.1	12
FB1	08/11/2015	11:40	26.4	-	-	219	-	-	10.3	-	<LQ	-	-	307	-
FB2	08/11/2015	16:00	131	-	51.804	421	-	306.326	10.6	0.761	79.7	-	51.467	198	-
FB3	09/11/2015	09:30	137	81	55.237	394	335	287.217	8.12	5.313	83	48	52.038	122	125
FB4	09/11/2015	16:00	130	-	59.898	389	-	305.807	7.51	5.490	84.7	-	55.176	121	-
FB5	10/11/2015	09:30	135	-	69.464	382	-	306.514	7.61	5.439	81.2	-	53.577	199	-
FB6	10/11/2015	16:00	145	-	70.472	366	-	316.825	8.08	5.539	-	-	55.589	130	-
Quantification limit			1	0.0005	0.0005	1	0.001	0.001	0.05	0.001	0.2	0.005	0.005	0.2	0.001

Table 3: Selected results from the flowback water samples and evolution between INDUSER and BRGM - Traces elements (<LQ = below quantification limit; - not measured)

Sample	Date	Time	As		Co		Cu		Cr		Ra
	DD/MM/YYYY	HH:mm	Induser μg/L	BRGM	Induser μg/L	BRGM	Induser μg/L	BRGM	Induser μg/L	BRGM	Algade Bq/L
WW3	09/10/2014	-	<LQ	1.61	<LQ	<LQ	<LQ	1.64	<LQ	1.64	-
WW4	11/10/2015	-	120	12.28	<LQ	<LQ	<LQ	-	<LQ	<LQ	-
PW	13/10/2015	15:00	210	0.67	<LQ	0.51	<LQ	1.81	<LQ	30.3	137.3
CT1	19/10/2015	10:00	<LQ	-	<LQ	-	<LQ	-	<LQ	-	-
CT2	31/10/2015	07:30	<LQ	0.83	<LQ	1.13	180	<LQ	200	22.9	-
FB1	08/11/2015	11:40	<LQ	-	190	-	240	-	190	-	1.58
FB2	08/11/2015	16:00	<LQ	<LQ	160	1.4	<LQ	1.7	160	25.7	-
FB3	09/11/2015	09:30	100	1.03	<LQ	0.6	<LQ	2.37	<LQ	73.3	-
FB4	09/11/2015	16:00	<LQ	0.96	<LQ	0.51	<LQ	2.49	<LQ	75.5	-
FB5	10/11/2015	09:30	<LQ	4.43	<LQ	<LQ	<LQ	2.59	<LQ	85.8	-
FB6	10/11/2015	16:00	<LQ	1.02	<LQ	<LQ	<LQ	2.57	<LQ	86.0	13.65
Quantification limit			0.10		0.10		0.10		0.10		

Table 4: Selected results from the flowback water samples and evolution between INDUSER and BRGM - Traces elements (<LQ = below quantification limit; - not measured) - Continued

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Highlights

- New gelling agent presents no water-rock interactions during hydraulic fracturing
- Decrease of trace and heavy metals with time in flowback samples
- Barite precipitation is responsible for this self-remediation

Credit Author Statement :

F. Osselin: Formal analysis, writing – original draft

E.C. Gaucher : Conceptualization, funding acquisition, formal analysis, writing – review & editing

P. Baldony-Andrey: Conceptualization, funding aquisition

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Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

P. Baldony-Andrey is an employee and E. C. Gaucher is a former employee of TotalEnergies.