D5.2
A report, along with laboratory scale samples, on the additives to be used in hydraulic fracturing formulations to reduce the amount of NORM extracted in flow-back and produced water.

WP 5 – Formulation of Hydraulic Fracturing Fluids

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Key word list

European shale gas basins, Hydraulic fracturing fluids, Green formulations, Polysaccharides, Magnetic water treatment, Antiscaling agents, Naturally occurring radioactive materials, Alkali earth metals salts, Magnetic field, Salts precipitation

Definitions and acronyms

<table>
<thead>
<tr>
<th>MF</th>
<th>Magnetic Field</th>
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<tr>
<td>MW</td>
<td>Molecular Weight</td>
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<tr>
<td>MWT</td>
<td>Magnetic Water Treatment</td>
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<tr>
<td>NORM</td>
<td>Naturally Occurring Radioactive Material</td>
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<tr>
<td>PAC</td>
<td>Polyacrylate sodium salt</td>
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<td>PAS</td>
<td>Polyaspartate sodium salt</td>
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<tr>
<td>PG</td>
<td>Polyglutamate sodium salt</td>
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<tr>
<td>SH</td>
<td>Sodium Hyaluronate</td>
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<tr>
<td>VES</td>
<td>Viscoelastic Surfactant</td>
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<td>XRD</td>
<td>X-ray Diffraction</td>
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1. Introduction

The main task of WP 5 is the formulation of hydraulic fracturing fluids specific for the shale formations found in Europe. Since every shale formation is unique, fracturing fluids effective in North American shale formations might not be effective in European ones. In this framework the study of formulations with physical-chemical properties that are appropriate with the pressure-temperature conditions and the composition of shale gas formations is fundamental for the potential exploitation of European shale basins.

At the same time, the environmental concerns about shale gas extraction cast doubts on the toxicity of the chemical additives, which are present in fracturing fluids. Thus, in order to minimize the environmental impact of hydraulic fracturing and reduce the amount of pollutants in the flowback and produced water, all the substances which are potentially dangerous are excluded and replaced by greener alternatives.

On this basis, the four primary objectives of WP5 are:

1) To formulate effective hydraulic fracturing fluids that contain no hazardous substances;
2) To formulate hydraulic fracturing fluids that are effective at high salt concentrations;
3) To generate a scientific method for the formulation of fluids based on the geochemical properties of a shale formation;
4) To design additives that limit the extraction of salt and NORM from shale formations.

1.1 General context

Deliverable 5.2 summarizes the results obtained in the period M24-M36, which includes Task 5.1 (Preparation of formulations specific for EU formations), Task 5.2 (Laboratory testing of formulations), Task 5.3 (Develop formulations effective at high salt content) and Task 5.4 (Design additives that limit the extraction of NORM from a formation).

This deliverable provides a report on the possible strategies for the limitation of NORM extraction: in particular, two green and environmental friendly methods are proposed, along with laboratory scale samples of the best formulations containing NORM-reducing additives.

1.2 Deliverable objectives

The aim of Deliverable 5.2 is to provide an extensive overview of the possible approaches that can be used to limit the amount of NORM extracted in the flowback water during shale gas operation or that can be employed for the treatment of wastewaters after gas extraction. We take into account the current state of the art on the water treatment techniques and the most commonly used additives together with the geochemical data.
found in the literature for the currently exploited formations in US and Europe, as well as advanced in water management strategies proposed by WP 8. Thus, we propose two green strategies for NORM reduction: the first takes advantage of a physical method that is the magnetic water treatment, while the second one is based on the use of NORM-reducing chemical additives. In the latter case, different chemicals which are completely safe in terms of composition are proposed and their performances are evaluated also by adding these additives to the green formulations developed in the last years in order to mimic their behavior in complex formulations, thus simulating real operative conditions.

2. Methodological approach

2.1 Physical method: magnetic water treatment

The first investigated approach is the magnetic water treatment (MWT), which is one of the most commonly used techniques for water and wastewater purification [1]: it is a physical treatment that avoids the use of expensive and potentially harmful chemicals, such as polyphosphates or corrosive substances. MWT was discovered in the first decades of the 20th century observing that the placement of an external magnet on steel pipelines causes a reduction of scale deposition [2]. Starting from this observation, commercial magnetic water treatment devices were produced and are still used. Several theories were developed to explain this curious phenomenon: the most accepted states that magnetic field affects the structure of water molecules surrounding ions in solution, thus changing their hydration and so the precipitation mechanism [3].

In the first stage of our work, we accomplished an accurate analysis of the current state of the art on MWT and the theory developed to explain this phenomenon, based on scientific publications from the literature. Then, we started studying the effect of a weak static magnetic field (MF) on the precipitation of insoluble calcium carbonate in water to assess if MWT can be a feasible way to reduce the likelihood of pipeline obstruction, normally occurring when water used during hydraulic fracturing comes in contact with naturally occurring water in the geological formation. Some experiments on magnetically treated and untreated solutions of calcium sulfate were also performed, since CaSO₄ is another component of mineral scales; in addition, experiments on different calcium salts allow us to clarify if the chemical nature of the anion exposed to the magnetic field (MF) affects the efficacy of the magnetic treatment.

Finally, the study was extended to the effect of MF on the precipitation of Sr(II) and Ba(II) carbonates since they possess very low solubility in water so are responsible for scales formation: however, no literature works report on the use of MF for the reduction of their precipitation. In addition, barium and strontium salts possess chemical properties similar to those of radium, which is the main component of NORM. Considering that radioactive
materials cannot be handled in our lab, Ba(II) and Sr(II) compounds were chosen to mimic the behavior of radium. The idea was to assess if MWT is effective in the control of other alkali earth metals salts in order to understand if it can be efficiently used as a “green strategy” to reduce the drawback of NORM extraction and/or to treat flowback waters containing NORM ions.

All the experiments were carried out at 25 and 60 °C in order to explore the role played by temperature: indeed, in real operating conditions during shale gas extraction, the temperature reached in the pipelines is above 100 °C [4].

2.1.1. Magnetic treatment

Carbonate crystals were precipitated by mixing equal volumes (2 mL) of 8 mM Na$_2$CO$_3$ with 8 mM CaCl$_2$, BaCl$_2$ or SrCl$_2$ either at 25 or 60 °C. In the case of calcium sulfate, the crystals were precipitated by mixing Na$_2$SO$_4$ and CaCl$_2$ 0.5 M at 25 °C. The effect of magnetic field on salt precipitation was investigated by exposing 2 mL of each ion solution to a static magnetic field of 0.4 Tesla for 15 min at room temperature before the mixing. After the magnetic treatment, the magnetized solutions were removed from the magnet and mixed at 25 and 60 °C.

2.2 Chemical method: NORM-reducing additives

Simultaneously, we investigated a chemical approach based on the use of scale inhibitors as additives for the limitation of scales formation. Water used during the hydraulic fracture stimulation can promote the formation of mineral scales when coming in contact with naturally occurring water in the geological formation. Additionally, changes in temperature and pressure can cause mineral solids to precipitate from the fluid. To prevent this, a scale inhibitor is usually injected throughout the hydraulic fracturing fluid at relatively low dosages throughout the frac fluid (75 to 120 ppm) and make up 0.0075% - 0.012% of the total fluid volume [5]. Owing to their compatibility with other fracturing additives and their resistance to chemical and biological breakdown, the most commonly used chemicals are carboxylic acid and acrylic acid polymers.

In our work, we investigated polyacrilate (PAC), polyglutammate (PG) and polyaspartate (PAS) sodium salts. PACs are used commercially as scale inhibitors, but they are not environmentally friendly; in this study they were tested as reference to compare the performance obtained with green innovative chemicals, such as PG and PAS. Figure 1 shows the chemical structures of the investigated NORM-reducing additives, while Table 1 lists their molecular weights.
Table 1: Molecular weights of the used antiscalcing agents.

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</tr>
<tr>
<td>PG-low M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>3-15</td>
</tr>
<tr>
<td>PG-high M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>15-50</td>
</tr>
<tr>
<td>PAC-low M&lt;sub&gt;w&lt;/sub&gt;</td>
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</tr>
<tr>
<td>PAC-medium M&lt;sub&gt;w&lt;/sub&gt;</td>
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</tr>
<tr>
<td>PAC-high M&lt;sub&gt;w&lt;/sub&gt;</td>
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Figure 1: Chemical structures of the investigated scale inhibitors.

All the additives were used at a concentration of 10 mg/L (i.e., 0.001 wt% of the total formulation), in line with the data found in the literature [6,7].

First of all, we qualitatively evaluated the efficacy of the chemicals in Figure 1 against calcium sulfate formation in pure water; tests were performed both at 25 and 60 °C to assess the performances of the scale inhibitors also at high temperatures, such as in real operative conditions. Then, the behaviour of these additives was studied in the final polysaccharide dispersions developed during this project: sodium hyaluronate-based formulation containing 0.5 wt% of polysaccharide, 0.05 wt% of sodium citrate as physical cross-linker and 0.001 wt% of antiscalant agent was chosen as model system.

Finally, the effect of antiscalants on the precipitation of other insoluble salts, such as strontium sulfate, was investigated as well in order to gain information on their
effectiveness against the precipitation of other sparingly soluble salts of alkali earth metals. Again, the idea was to understand if the use of very small amounts of green antiscalants could be a feasible method to limit the formation of mineral scales, also in the presence of radioactive materials, such as radium salts.

2.3 Experimental techniques

For the study of magnetic water treatment, the size and the morphology of CaCO$_3$, BaCO$_3$ and SrCO$_3$ crystals were assessed by means of optical microscopy at the two studied temperatures. From the comparison of optical micrographs acquired at different conditions (temperature, magnetic treatment, chemical nature of the magnetically treated ions), we qualitatively predicted the efficacy of the magnetic treatment in the presence of different salts and we gained information on the effect of both temperature and chemical nature of the treated ions on the MWT. Regarding calcium carbonate, fluorescence (for the first time) and XRD experiments were also performed to monitor the conversion between the two main polymorphs of CaCO$_3$ upon magnetic treatment.

In the case of scale inhibitors, the performances of the studied chemicals were evaluated by simply comparing the amount of precipitate formed in the presence of the different antiscalants with respect to the same solution without additives. Also in this case, optical images were acquired in order to understand how crystal growth is affected by the addition of these additives. All the experiments were performed both at 25 and 60 °C to mimic the operating conditions in the field.

3. Summary of activities and research findings

3.1 Magnetic water treatment

3.1.1 Effect of temperature

Our study started from the investigation of the effect of temperature on the precipitation of calcium, barium and strontium carbonates. Figure 2 compares the optical micrographs obtained after 60 min from the mixing of the starting solutions at 25 and 60 °C.
Figure 2: Optical micrographs of calcium, strontium and barium carbonates precipitated after 60 min from the mixing of non magnetized solutions at 25 and 60 °C. Scale bar: 100 μm.

The optical micrographs recorded at room temperature on calcium carbonate reveal the formation of calcite (rhombohedral crystals) and vaterite (spherical crystals). This result is in line with previous studies on CaCO₃ polymorphs formed from highly super-saturated solutions: it was found that vaterite and calcite are formed at low temperature (14−30 °C), while the conversion into aragonite (orthorombic structure, often in form of needle-like crystals) is favoured at higher temperatures (60−80 °C) and becomes the predominant form at about 70 °C [8]. Accordingly, optical microscopy at 60 °C shows the presence of aragonite together with calcite and hexagonal plate vaterite crystals. Similar results were obtained by means of fluorescence (Figure 3).
Figure 3: Fluorescence excitation spectra of CaCO₃ crystals in solution at 25 (empty circles) and 60 °C (filled circles) in the absence of magnetic field. Red: λ<sub>exc</sub> = 220 nm, black: λ<sub>exc</sub> = 238 nm, green: λ<sub>exc</sub> = 254 nm, blue: λ<sub>exc</sub> = 272 nm.

The sample investigated at 25 °C shows strong emission signals centred at about 300 (λ<sub>exc</sub> = 272 nm) and 600 nm (λ<sub>exc</sub> = 238 and 254 nm), while the sample at 60 °C shows a significant broad peak at about 350 nm (λ<sub>exc</sub> = 272 nm) and an emission peak centred at 555 nm (λ<sub>exc</sub> = 254 nm). Since the signals at 300 and 600 nm are particularly intense only for the sample obtained at 25 °C, we can infer that they are related to calcite, and that this is the most abundant polymorph at such temperature. This interpretation agrees with the observations obtained from the optical images. Instead, the signals centred at 350 and 555 nm are mainly visible in the sample at 60 °C, so they are probably due to aragonite crystals. This observation, together with a reduction in the intensity of calcite emission bands (300 and 600 nm), indicates a partial conversion of calcite into aragonite at higher temperature, in agreement with previous literature works and with our optical microscopy experiments. The temperature-induced formation of aragonite is also confirmed by XRD measurements reported in Figure 4, where the peaks at 26.3, 27.3, 41 and 46° associated with aragonite appear in the pattern of the sample precipitated at 60 °C.
Regarding strontium and barium carbonates, no different allotropic forms exist in the temperature range investigated: optical micrographs show that the morphology of crystals remains the same for both samples at 25 and 60 °C. In particular, strontianite (SrCO$_3$) crystals possess a dendritic structure, while witherite (BaCO$_3$) precipitates forming floc crystals. However, the size of the crystals increases as temperature is raised up to 60 °C.

In conclusion, our results reveal that temperature strongly affects crystal dimension, causing an increase in their size, especially in the case of strontium and barium carbonates. This is in agreement with previous studies on the precipitation of carbonate-scaling minerals as a function of T and P, where it is reported that the alkali earth carbonates are less soluble at temperatures above 25 °C [9]. We consider this to be a good result for applicative purposes, because we expect a similar behaviour also for NORM ions: the formation of larger scales within the formation is expected to hamper the extraction of NORM during field operations. On the other hand, the formation of larger scales at high T could be a problem in the case of calcium carbonate, since this is the most abundant scaling mineral and consequently its enhanced precipitation is responsible for pipelines obstruction: however, we have demonstrated that aragonite formation is favoured at 60 °C. Since aragonite is less densely packed with respect to calcite, aragonite scales are softer and more soluble with respect to calcite deposits.

### 3.1.2 Effect of magnetic field

We quantified the effect of magnetic field on salts precipitation. Figure 5 shows the optical images obtained at 25 °C on precipitates from solutions exposed to the static magnetic field and compared to those obtained from untreated solutions.
In the case of calcium carbonate, according to literature results [10], the magnetic exposure of the starting solutions leads to a suppression of the nucleation and an acceleration of the growth that results in the decrease of the number of crystals and an increase of their size. Our fluorescence spectra, reported in Figure 6, show a strong decrease in the intensity of the magnetized sample in agreement with a lower amount of crystals in solution.
Figure 6: Fluorescence excitation spectra of CaCO₃ crystals in solution at 25 °C starting from non-magnetized (empty circles) and magnetized (inset) solutions. Red: λ_{exc} = 220 nm, black: λ_{exc} = 238 nm, green: λ_{exc} = 254 nm, blue: λ_{exc} = 272 nm.

Regarding Sr(II) and Ba(II) carbonates, our results did not detect an effect of the magnetic field on the crystal morphology. However, the suppression of nuclei and the formation of few larger crystals occur for witherite. Instead, in the case of strontianite, the exposure to the static MF has the opposite effect, inducing the precipitation of smaller crystals.

Our experimental results suggest that the application of an external MF is an effective method to reduce the amount of precipitate not only in the case of CaCO₃, as already extensively reported in previous works, but also in the case of other insoluble salts.

The effect of MWT on calcium sulfate scales was investigated as well, since gypsum (CaSO₄·2H₂O) is another of the main components of mineral scales. Based on optical micrographs (Figure 7), our results suggest that there are no significant changes in the crystalline structure of the precipitate after magnetic treatment of the reactants: needle-like crystals are visible in the case of both magnetized and non-magnetized solutions. Regarding the size of the precipitated crystals, we can observe the opposite effect of MF with respect to calcium carbonate: CaSO₄ crystals obtained from magnetized solutions are smaller than those precipitated from untreated solutions. However, it seems that the magnetic treatment reduces the amount of precipitate, as observed for calcium carbonate. The different behavior observed for carbonate and sulfate can be ascribed to the different chemical properties of the two ions, in particular their diamagnetic/paramagnetic nature.
However, we believe that this issue needs to be further considered and more experiments have to be acquired, for example using an alternating magnetic field.

![Micrographs of calcium sulfate precipitated at 25 °C immediately after the mixing of non magnetized (left) and magnetized (right) solutions. Scale bar: 100 μm](image)

**Figure 7:** Optical micrographs of calcium sulfate precipitated at 25 °C immediately after the mixing of non magnetized (left) and magnetized (right) solutions. Scale bar: 100 μm

### 3.1.3 Combined effect of temperature and magnetic field

Considering the strong effect of both high T and static MF on insoluble salts precipitation, we assessed what happens when both high temperature and magnetic treatment are combined simultaneously. The goal was to understand if scale formation during shale gas operations can be limited by pumping down hole formulations previously exposed to the magnetic field. Considering that temperature in field operations is around 100 °C, tests on magnetically treated solutions were performed at 60 °C to assess if they retain their behaviour against salts precipitation in real conditions.

**Figure 8** compares the optical micrographs of Ca(II), Sr(II) and Ba(II) carbonates precipitated from magnetized solutions at 25 and 60 °C.

![Micrographs of Ca(II), Sr(II) and Ba(II) carbonates](image)

**Figure 8:** Optical micrographs of calcium, strontium and barium carbonates precipitated at 25 (top) and 60 (bottom) °C after 60 minutes from the mixing of magnetized solutions. Scale bar: 100 μm.
In the case of CaCO$_3$, the optical images reveal that the combination of high T and MF leads to: i) a good conversion of calcite into aragonite and ii) a strong suppression of the number of crystals in solution. XRD measurements in Figure 9 show a strong decrease in the signals associated with calcite compared to those obtained after the treatment with the magnetic field at 25 °C where a significant contribution of aragonite peaks appears.

![XRD patterns of CaCO$_3$ crystals precipitated after the magnetic treatment at 25 (black) and 60 (red) °C. Spectra are offset along y-axes.](image)

Figure 9: XRD patterns of CaCO$_3$ crystals precipitated after the magnetic treatment at 25 (black) and 60 (red) °C. Spectra are offset along y-axes.

The fluorescence spectra shown in Figure 10 indicate an enhancement in the emission peaks of aragonite when CaCO$_3$ is precipitated at high T from magnetized solutions. The sample obtained at 60 °C in the presence of MF produces emission signals roughly twice as intense as those obtained at 25 °C after magnetization of the solutions, indicating the presence of larger amounts of small crystals. The comparison of these results with those obtained from the sample precipitated at 60 °C without any magnetic treatment suggest that the kind of polymorph in solution depends mainly on the temperature. There is an increase in the aragonite content at higher temperatures, while the magnetization prior to mixing the reactants can reduce the amount of precipitate.
Similar results were obtained for witherite and strontianite from optical images. As in the previous cases the crystal morphology remains unchanged, while the formation of fewer larger crystals is favoured.

The experimental results suggest that the crystal growth is favoured with respect to the nucleation step when high T and MF are combined together during the precipitation of the alkaline earth insoluble salts, thus leading to the formation of a smaller amount of larger crystals. In addition, regarding CaCO₃, the combination of these two parameters promotes the formation of aragonite. With this in mind, we can conclude that the combined application of high T and external magnetic fields can be an easy and feasible way to control scale formation and limit the problem of pipes obstruction. Furthermore, the formation of fewer scales of larger dimensions limits the likelihood of NORM extraction in the flowback water at the end of operation.

### 3.2 Use of antiscaling agents

In this section, we discuss the qualitative results obtained on the precipitation of calcium and strontium sulfates in the presence of different scale inhibitors. It is worth noting that,
differently from what we have done in the study of magnetic water treatment, the role of antiscalants was assessed on the precipitation of sulfates instead of carbonates: the choice was done on the basis of crystals morphology. In fact, sulfates precipitate forming larger crystals with respect to carbonates so it is easier to observe possible morphological variations induced by the addition of antiscalants by means of optical microscopy. For the same reason, we do not report results on barium salts in the presence of antiscalants since it precipitates immediately due to its very low solubility in water forming very small crystals that are difficult to observe with a good resolution using our optical microscope.

3.2.1. Effect in pure water

First of all, the performance of the studied antiscalants was assessed in pure water. Figure 11 shows CaSO$_4$ precipitates without and with the different studied antiscalants and the corresponding optical micrographs. In particular, we can observe a strong reduction of the amount of precipitated salt especially in the case of PAS, PG-low M$_w$ and PAC-medium and high M$_w$.

Optical images reveal that, differently from the big fluffy crystals obtained when calcium sulfate is precipitated in neat water, the addition of the additives leads to the formation of less compact crystals for all the investigated molecules; however, the most remarkable effect on gypsum morphology is obtained for PAS and PAC-medium and high M$_w$. 
Figure 11: Effect of different antiscalants on the precipitation of calcium sulfate in water at 25 °C. Top: picture of the precipitates; bottom: corresponding optical micrographs. Scale bar: 100 μm. (0) no antiscalant; (1) PAS; (2) PG-low M<sub>w</sub>; (3) PG-high M<sub>w</sub>; (4) PAC-low M<sub>w</sub>; (5) PAC-medium M<sub>w</sub>; (6) PAC-high M<sub>w</sub>.

Similar results were found in the case of SrSO<sub>4</sub> (see Figure 12).
Figure 12: Effect of different antiscalants on the precipitation of strontium sulfate in water at 25 °C. Top: picture of the precipitates; bottom: corresponding optical micrographs. Scale bar: 100 μm. (0) no antiscalant; (1) PAS; (2) PG-low $M_w$; (3) PG-high $M_w$; (4) PAC-low $M_w$; (5) PAC-medium $M_w$; (6) PAC-high $M_w$.

Considering that scale inhibitors are added in very small amount, far from the stoichiometric concentration of the scaling species, scale suppression can be ascribed to physical mechanisms: the adsorption of antiscalant molecules on active growth sites of crystals leads to reduced crystal growth rates and to the formation of distorted crystal structures. The crystal distortion weakens the tenacity of the scale and the highly irregular stressed crystals tend to slough off as crystal growth occurs [11]. In addition, all the tested scale inhibitors possess negative charges in their chemical structure: the electrostatic repulsion between approaching crystals is another possible mechanism to prevent the crystal growth.
Considering that PAS possesses two negative charges while the other additives are monovalent salts, it is not surprising that it is one of the most performing agents.

Regarding the use of antiscalants with different molecular weights, the choice was done on the basis of previous literature reports. Indeed, it was proved that a minimum number of monomer units is required to have effective binding to the crystal surface that differs from mineral to mineral: for example, in the case of calcium sulfate in the presence of polyacrylates, it was found the optimum effectiveness with molecular weight of ~2000 Da [12]. In another study on polyaspartate scale inhibitors, Ross et al. proved that polyaspartates in the range of 3000-4000 Da are the most effective for inhibition of calcium carbonate and barium sulfate, while, for calcium sulfate inhibition, the optimum molecular weight was found to be in the range of 1000-2000 Da [13].

In general, as the molecular weight increases, there might not be a proportional increase in binding effectiveness for a polymer. Additionally, the number of molecules in a given weight of polymer decreases, resulting in decreased activity. Finally, it has to be considered that larger molecules move in solution slower than smaller ones at the same temperature, as the adsorption on the surface of growing crystals is dependent on their diffusion coefficient in solution. Accordingly, the precipitation of larger crystals both in the case of CaSO₄ and SrSO₄ is observed in the case of the formulations containing high Mₚ PG and PAC.

The effect of high temperature (60 °C as in the case of MWT) on the performances of antiscalcing agents was also investigated. Tests were carried out just on calcium sulfate in water as an example and the obtained optical micrographs are shown in Figure 13.

![Figure 13: Optical micrographs showing the effect of different antiscalants on the precipitation of calcium sulfate in water at 60 °C. Scale bar: 100 μm. (0) no antiscalant; (1) PAS; (2) PG-low Mₚ; (3) PG-high Mₚ; (4) PAC-low Mₚ; (5) PAC-medium Mₚ; (6) PAC-high Mₚ.](image-url)
Increasing temperature, the formation of bigger crystals is favored also in the presence of scale inhibitors because calcium sulfate solubility in water decreases with respect to room temperature. The worst performances of all the studied additives at 60 °C with respect to those observed at room temperature can be explained considering that, due to a decrease of salt solubility at high T, the scale layer forms more rapidly and becomes thicker, thus reducing the scale inhibition efficiency. Similar behaviour is reported in the literature on calcium carbonate scales precipitated at high temperature in high salinity wastewater [14]. Another possible factor that reduces the efficacy of antiscalants at high T could be an enhancement of the thermal motion of antiscalant molecules, which probably reduces the rate of their adsorption on the forming crystalline nuclei. However, PG-low M_w and PAC-high M_w show very good performances in the reduction of precipitate amount.

### 3.2.2. Effect in polysaccharide-based formulations

In the final part of the work, the effectiveness of antiscaling agents was evaluated in the polysaccharides-based formulations developed during this project. It is worth noting that antiscalants performances were evaluated only in polysaccharidic formulations and VES formulations were not considered for these tests since in the presence of a viscoelastic surfactant salts interact with the surfactant rather than with the scale inhibitor. Figure 14 shows calcium sulfate precipitates and the corresponding optical micrographs in the presence of scale inhibitors added to sodium hyaluronate-based formulation.
Figure 14: Effect of different antiscalants on the precipitation of calcium sulfate in SH-based formulation at 25 °C. Top: picture of the precipitates; bottom: corresponding optical micrographs. Scale bar: 100 μm. (0) no antiscalant; (1) PAS; (2) PG-low M_w; (3) PG-high M_w; (4) PAC-low M_w; (5) PAC-medium M_w; (6) PAC-high M_w.

We can observe that crystal morphology is completely different from that observed in pure water, also without additives. The formation of more ordered crystals with shorter needles suggests that probably the polysaccharide matrix acts as “templating agent”: considering the high viscosity of polysaccharides-based systems, we can argue that crystalline nuclei move slower with respect to neat water. In addition, we observe that the differences among the studied antiscalants are less remarkable with respect to what was observed in pure water: the amount of precipitate and the crystals morphology are more or less the same for all samples. However, all antiscalants show very good performances, even better than those
observed in water. We might explain this unexpected result considering that sodium hyaluronate is negatively charged so the polysaccharide itself acts as a scale inhibitor. This, combined with the presence of antiscalant additives, ensures the stop of crystallites growth, thus significantly decreasing the amount of precipitate.

The obtained results are expected to be of great interest for practical applications since we have demonstrated that scaling minerals precipitation can be inhibited by adding very small concentrations of green additives whose effectiveness is enhanced in the final polysaccharidic formulations developed for the extraction of the shale gas. In addition, it is possible to tune the effectiveness of these completely safe and degradable additives against scales of different chemical composition simply varying the kind and molecular weight of the additives.

4. Conclusions and future steps

We developed two completely safe and environmental friendly approaches that can be successfully used to limit the amount of NORM in the flowback water and/or for the treatment of wastewaters after the extraction of the shale gas from European formations.

The first method is a physical treatment consisting in the exposure of the frac fluid to a weak static magnetic field of 0.4 Tesla before being pumped in the pipelines. We have demonstrated that magnetic water treatment leads to a suppression of the nucleation and an acceleration of the growth that results in the decrease of the number of crystals and an increase of their size. This result was already known for calcium carbonate but our experiments demonstrate the same behavior for other scaling minerals, such as strontium and barium carbonates and calcium sulfate. The formation of a smaller amount of larger crystals is enhanced by the combination between the exposure of the frac fluid to an external MF and the high temperature that can be found in the wells during extraction operations. In addition, in the case of CaCO₃, the combination of MF and high T promotes the formation of aragonite, which is less densely packed and thus more soluble with respect to the other polymorph of calcium carbonate usually formed at room temperature and in the absence of magnetic treatments.

The results are expected to be valuable for applications: MWT can be an easy and feasible method to reduce insoluble alkali earth metals scales and thus the likelihood of pipelines obstruction. In addition, the method can be also applied to reduce the problem of NORM extraction since the formation of fewer scales of larger dimensions makes more difficult the extraction of NORM ions in the flowback water at the end of operation.
The second method studied in this work is based on the use of green innovative chemical additives, *i.e.*, scale inhibitors. We assessed their effectiveness against the precipitation of both calcium and strontium sulfate evaluating their performances in terms of reduction of precipitate and/or control of crystals size. Tests were carried out both in pure water and in the final polysaccharide dispersions, in particular in sodium hyaluronate-based formulation. We demonstrated that these additives are effective at very low concentrations, *i.e.*, at 0.001 wt% of the final formulation and that their performances are even enhanced when added to the polysaccharidic matrix. This unexpected result can be ascribed to the fact that also hyaluronate chains act as inhibitor of the crystal growth thanks to their negative charge thus enhancing the effectiveness of the final formulation against salts precipitation.

All the experiments were conducted both at 25 and 60 °C to assess if the studied molecules retain their effectiveness against scales formation at high temperatures, thus simulating real operative conditions in the extraction wells. The obtained results show that some scale inhibitors exhibit a remarkable tolerance towards high temperature, so they can be effectively used in real applications.

Furthermore, we have seen that, depending on the chemical composition of mineral scales, the effectiveness of scale inhibitors can be tuned simply varying the kind and molecular weight of the additive. Good results were obtained also in the case of strontium salts: the use of very small amounts of green antiscalants could be a simple way to limit the formation of mineral scales, also in the presence of radioactive materials, such as radium salts.

5. Publications resulting from the work described


6. Bibliographical references


