2022

Task 5. Controlling VOC Emissions from Produced Water Recycling

Task proposed and sponsored by NGL Water Solutions

Task developed by NGL Water Solutions and Jade Dragon, LLC

Background

Oil and gas operations often involve large volumes of water, both from fracturing fluids and by-product water that is pumped from the ground during oil recovery.

In conventional oil production, oil is pumped from permeable rock formations, such as sandstone. The permeable layers allow the oil to flow through the formation to the well bore to be recovered. In recent years, oil companies have expanded their efforts to recovering hydrocarbons in geologic formations that have low permeability, such as shale. Known as unconventional plays, these require horizontal drilling and hydraulic fracturing of the shale to create high-surface-area flow paths that will allow the hydrocarbons to flow to the well bore.

Hydraulic fracturing technology requires that large quantities of water be used for the fracturing fluids. Oil recovery also generates huge quantities of byproduct water. Since these waters are often combined in the field, we group them together in the term 'produced water' (PW).

Early in the history of hydraulic fracturing, fracturing fluids were derived from fresh groundwater, but the oil and gas industry has made great strides in preserving groundwater resources by recycling PW from their operations. To facilitate recycling, PW is usually held in large (up to one million bbl) impoundments (often called ponds or lagoons) until ready for reuse in hydrofracturing operations. PW treatment and impoundment adds about $0.25/bbl to the cost of production (as compared with using fresh groundwater), and this effort to recycle PW has improved sustainability substantially in the oil and gas industry.

PW contains small amounts, by volume, of volatile organic compounds (VOCs). VOCs can contribute to low-level ozone, considered a threat to human health and the environment[1]. Ambient ozone is regulated by U.S. national ambient air quality standards and is controlled by reducing VOC emissions.

U.S. states are proposing to limit VOC emissions for PW recycling operations to under two tons per year (2 TPY) for each "produced water management unit" (such as one PW impoundment), based on "potential to emit"[2]. "Potential to emit" describes the presence of VOCs in the water but not the VOCs that are actually released to the atmosphere, making this parameter particularly stringent, since VOCs can remain in the water without being released to the atmosphere.

To add perspective to the proposed 2 TPY limit, VOC levels in raw PW may be >10 ppm to >100 ppm. If VOCs are present at 50 ppm in a 500,000 bbl impoundment, there will be 4 tons of VOCs entrained in the water. The water in the impoundment is replaced with new PW every few days, and each new addition to the impoundment adds additional potential to emit, resulting in significant annual potential to emit, although the actual emissions are significantly lower.

The unintended consequence of such strict limits on VOCs is that produced water recycling could come to a halt, reversing years of effort toward sustainable and responsible reuse of water supplies.

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To mitigate the VOC issue, some states, such as Colorado, have outlawed open-air impoundments in favor of closed-top above-ground storage tanks. This management approach is not feasible in parts of the country, such as the Permian Basin, where high pumping rates require storage of extremely large amounts of water. Tanks of sufficient volume would add a significant capital expense.

The produced water industry urgently needs a solution for reducing the potential to emit by reducing VOCs in PW impoundments without adding operational constraints or significant costs.

SPOT Values

This task involves controlling only VOC emissions from a produced water recycle operation. However, in addition to controlling VOC emissions, it is possible that your team's solution will improve water chemistry in other ways and become a valuable part of a treatment train for producing clean brine.

For that reason, we ask that your team measure and report SPOT values (salinity, pH, ORP, turbidity, etc.– see Table A-1 of Appendix I) of the effluent of your process. The SPOT values are minimum specifications for common clean brine, proposed by the Produced Water Society[3]. Report these values, but do not make efforts to explicitly alter water chemistry to meet the clean brine specifications.

Problem statement

Your team will research, evaluate, and design a solution to limit VOCs (represented by the presence of toluene) from a 50,000 bbl/day produced water recycle operation to under 2 TPY.

The produced water cannot be exposed to the atmosphere prior to treatment, and removal of VOCs can be proposed at any point from the well pad to the central water treatment plant.

Design requirements

Your proposed design should provide specific details and outcomes as follows:

- Base your analysis on a 50,000 bbl/day treatment facility that cannot emit more than 2 tons per year.
- The treatment process must be a closed system.
- Include a Process Flow Diagram (PFD) for the selected treatment process. The PFD must include mass and energy balances (input and output rates, reactants, and reaction rates, etc., as applicable).
- Include VOC and SPOT analyses of the influent and effluent. Do not attempt to manipulate the SPOT parameters.
- All costs must be demonstrated. Cost must be inclusive of all waste stream disposal. Current costs for PW recycling, not including VOC removal, are approximately $0.25/bbl. Your solution should remove VOCs at minimal additional cost.
- Present a Techno-Economic Analysis (a.k.a. Techno-Economic Assessment) to construct a full-scale VOC-removal process to treat 50,000 bbl/day of PW using your selected water-treatment technology.
  This will include your estimate of capital costs (CAPEX) and operational costs (OPEX) for a full-scale solution and appropriate graphical representation of your cost data.
    - Capital expenses typically include, but are not limited to, equipment, pipes, pumps, etc. Do not include costs of buildings and appurtenances to the treatment process.
    - Operating expenses (OPEX) should be calculated as cost/bbl of VOC-free water produced on an annual basis, including, but not limited to, materials needed, including consumables (chemicals, sacrificial components, etc.) In addition to other operating costs that your team identifies, include these operating costs: staff labor rate of $70/hour; solids disposal costs ($50/ton); energy requirements (cost/bbl and Kwh/bbl): research an industrial natural gas rate and state in $/MM BTU; use an electricity rate of $0.09/kWh.
    - Visualization tools: Sensitivity analyses, etc. (Recommended: NMSU TEA Short Course).
- Identify and address the fate of any waste products generated by the PW treatment technology.

- Reflect on alternative designs and situations in which those designs might be more viable than your chosen design, recalling that an optimal solution depends on outside factors–the "best" design may be dependent on region and may change over time.
- Include a public involvement plan, as applicable (see Team Manual).
- Document success in improving energy efficiency, pollution prevention, and/or waste minimization, as it applies to your project to qualify for the P2E2 Award. Place this in a separate section of the report.
- Address any intangible benefits of the selected treatment process.
- Address safety aspects of handling the raw produced water, volatiles, and any final products. Safety issues for both the full-scale design and the bench-scale demonstration should be addressed in both the written report and the Experimental Safety Plan (ESP)

Bench Scale Demonstration

Bench-scale demonstrations will serve to illustrate the design considerations listed above. The bench-scale unit should demonstrate a process that can be scaled up to a plant that treats 50,000 bbls per day of produced water. It will include a synthetic solution of produced water of chemistry given in Table 1. The constituents of the synthetic solution are typical for a sample of produced water from the Delaware Shale play.

At the contest, each team will be provided with 18 liters (5-gallon container) of synthetic solution (chemistry given in Table 1) to work with during the bench-scale demonstration. You are not required to use the entire amount of the solution during the contest bench-scale demonstration.

After treatment, your team shall submit two 40mL VOA (Volatile Organic Analysis) vials with zero headspace for VOC analysis, and two 100 mL samples of treated solution for SPOT analysis. VOA vials are designed to keep volatiles in the aqueous phase. Teams are urged to acquaint themselves with VOA collection methods prior to attending the contest. Sample-collection vials at the contest will be provided by NGL Water Solutions.

Contest Analytical Testing Techniques

At the contest, total VOCs, as represented by toluene, will be analyzed by one of the following (depending on availability of analytical equipment):

- GCMS SW846-8260 or 8021 (or equivalent), with a target of less than 2 ppm for toluene.
- Liquid Chromatography with UV-VIS detection for toluene.

SPOT Parameters will be individually evaluated as indicated below. (See Appendix I, Table A-1)

- ***Salinity*** —refractometer
- ***pH*** — pH meter
- ***ORP***—ORP probe
- ***Turbidity***—light transmittance probe measuring NTU (nephelometric turbidity units).
- ***Oil***—EPA Static Oil sheen test.
- ***Particle size***– visual test for settled solids.
- Samples will not be tested for H_2S (hydrogen sulfide), as it is not expected from the synthetic solution.

Sample Preparation

To prepare samples for preliminary testing at your campus, follow these steps to make 1 liter of synthetic produced water using the chemistry from Table 1, below.

1. Use a wide-mouth, semi-transparent polyethylene or polypropylene container.
2. Mix together water phase.
3. Mix together oil phase.
4. Add solids to oil phase.
5. Add oil phase to water phase and gently mix.
6. Top off with DI water to make 1.0 L.
7. Just before use, use a homogenizer/mixer* to generate small droplets of the oil phase.

*Blend at highest speed for 5 minutes in a 5-gallon bucket. Use a high-speed drill with a paint-mixing paddle.

Note: Although disinfection is usually an essential pre-treatment step, it will be disregarded for the contest.

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Table 1. The bench-scale apparatus shall treat water of the following chemistry[3]
(See Appendix II for more information on the rationale for the chemistry of the synthetic solution.)

Water phase	**Amount per liter of synthetic solution**
DI water	750 mL
Sea Salt*	120 g
Oil phase	**Amount per liter of synthetic solution**
TrueSyn 200 !"*, ****	92 mg
Toluene (Represents VOCs)	50 mg
Solid phase	**Amount per liter of synthetic solution**
Fine-grade Arizona Test Dust (Medium Grade)***, ****	50 mg
Sodium Bentonite Drilling Clay (AquaGel by Baroid Industrial Drilling)****	50 mg

**At the contest, WERC will source the sea salt from a local store (Sprouts store brand). It dissolves fairly easily.*
***Sourcing Option: RB Products will ship to you and* charge for shipping only. Contact micah@rbproductsinc.com
****Sourcing Option: Powder Technologies Inc. offers 4 kg for $80. Contact: levi@powdertechnologyinc.com*
***** Contact WERC–we will gladly ship these items to you. They ordinarily come in industrial quantities.*

Preliminary Report Requirements

The preliminary report describes your proposed approach. It is due February 7, 2022. The report is intended to help your team get early feedback about your plans. This will help you prepare a robust technical report and bench-scale demonstration. Your team will receive guidance from task designers/reviewers within one week of submission.

Be sure to include a process flow diagram showing your mass and energy balances, as applicable.

Technical Report Requirements

The written report should demonstrate your team's insight into the full scope of the issue and include all aspects of the problem and your proposed solution. The report will be evaluated for quality of writing, logic, organization, clarity, reason, and coherence. Standards for publications in technical journals apply.

In addition to the listed requirements, your report must address in detail the items highlighted in the Problem Statement, Design Considerations, Evaluation Criteria, and 2022 Team Manual.

Evaluation Criteria

Each team is advised to read the 2022 Team Manual for a comprehensive understanding of the contest evaluation criteria. As described in this manual, your response to this Task consists of four parts: a written report, a formal oral presentation, a demonstration of your technology using a bench-scale representation, and a poster that conveys the essence of your work in a concise fashion using a mix of text and graphics. General criteria used by the judges in evaluation of these four components are described in the Team Manual.

Judges' evaluation of your entry will include consideration of the following points specific to this task.

- Potential for real-life implementation, including expected reliability and maintainability. The cost of your solution should not exceed $0.25/bbl. Judges will weigh the cost/benefit of your solution against those for other teams.
- Thoroughness and quality of the economic analysis.
- Originality and innovation represented by the proposed technology.
- The quality of your treated sample. The bench-scale processed water will be evaluated for treated water volume and separation efficiency.
- Other specific evaluation criteria that may be provided at a later date (watch the FAQs).

For a copy of the Team Manual, Public Involvement Plan, and other important resources, visit the WERC website: https://iee.nmsu.edu/outreach/events/international-environmental-design-contest/guidelines/.

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FAQs/Dates/Deadlines

- Mid-December, 2021 EH&S Short Course (watch website for dates and registration info).
- Mid-January, 2022: EH&S Short Course; TEA Short Course
- 1 February, 2022: Experimental Safety Plan (ESP) due
- 7 February, 2022: Preliminary Report due
- 7 March, 2022: Send a draft of the technical report to your auditors (approx. date–see Team Manual)
- 28 March, 2022: Technical Report due
- Weekly: Teams are expected to check the FAQs online weekly for any updates in the task requirements. (wercdesigncontest.nmsu.edu)
- On request: WERC will ship to your team materials indicated in Table 1.

Short Courses

WERC is offering two short courses. The optional courses are designed to prepare teams to more effectively complete their technical report and earn digital badges to add to their professional development portfolio. The courses are also available to the general public to gain professional development. Fees will be waived for contest-registered students, faculty, and judges. Watch the WERC website for schedules and registration.

Courses offered:

- Health and Environmental Safety (EH & S) (Mid-December and Mid-January)
- Techno-economic Assessment and Analysis (TEA) (Mid-January)

References

[1] Ground-level Ozone Basics. https://www.epa.gov/ground-level-ozone-pollution/ground-level-ozone-basics. Accessed 7/15/2021.

[2] In the matter of Proposed New Regulation, 20.2.50 NMAC Oil and Gas Sector–Ozone Precursor Pollutants. State of New Mexico Environmental Improvement Board. May 06, 2021.

[3] A Common Clean Brine Specification for Reusing Recycled Produced Water – Draft Guidelines, June 2020. Accessed 8/26/2020: https://www.producedwatersociety.com/

[4] Produced Water, Volumes I and 2, John M. Walsh, Petro Water Technology, 2019.

Awards

Each year, the WERC Environmental Design Contest and its sponsors award more than $25,000 in cash prizes. Successful completion of every stage of the design project qualifies each team for the following awards.

1. Full task awards (First, Second, Third Place; minimum amounts: $2500-$1000-$500, respectively).
2. Virtual Desktop Study Awards (awarded independently of the full bench-scale designs). Amounts TBA.
3. WERC Resources Center Pollution Prevention/Energy Efficiency Award ($1000)
4. Judges' Choice Award ($500)
5. Peer Award ($250)
6. Terry McManus Outstanding Student Award. ($500-$1000, according to funding).
7. Additional awards may be announced later.

Award amounts listed are minimum amounts and may increase with available funding.

Detailed criteria for each award: https://iee.nmsu.edu/outreach/events/international-environmental-design-contest/guidelines/

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Appendix I–Clean Brine (SPOT) Specifications
The table below reflects the minimum specifications for clean brine, proposed by the Produced Water Society. Note that these effluent specifications do not address VOCs.

Your team is asked to report values for all of the parameters below for your treated effluent. You will not be judged by any of the values reported, but it will be helpful for produced water companies to understand the effects of your proposed VOC treatments.

Table A-1. Common Clean Brine Minimum Specification for Reusing Recycled Produced Water[3].

Parameter	**Reference Target for Recycle**
Salinity	Reported after treatment*
pH	6.0-8.0
Oxidation reduction potential (ORP)	>350 mV
Turbidity	<5 mg/L (approx. 25 NTU)
Oil	<30 ppm – no sheen
Hydrogen sulfide (H_2S)	Non-detectable
Particle size	Filter <25 micron

*In the industry, salinity varies by basin and is reported to ensure compatibility with the formation.

Appendix II–FAQs about the produced water synthetic solution in Table 1

Mixing the synthetic solution
It is very important that the oil be mixed quite vigorously before treatment to ensure that the oil phase is homogenously distributed through the mixture. Out in the field, the oil in this produced water is in very small droplets that did not separate in the battery tanks over a few days.

We recommend mixing the solution in a 5-gallon bucket. Since the solution will be measured and mixed in one container and never transferred, this minimizes the amount of oil that would have been lost by adhering to the sides of a container after the solution is transferred. If you use a kitchen blender, you may lose a considerable amount of oil as it sticks to the sides of the blender.

Sea Salt
Some teams have experienced difficulty getting the salt to dissolve. For testing in your home lab, you may need to experiment with different brands of salt. Some off-the-shelf sea salt sold in stores dissolve more easily than others. Teams have had more success using finer-grained salt (crush it, if it is coarse), adding it gradually and mixing with each addition (rather than all at once), and using hot water to initially dissolve the salt.

Questions about the synthetic solution chemistry
Some teams have wondered about the low volumes for TrueSyn 200i and xylene. These values are representative of the produced water when it reaches the impoundment. The water goes through these processes prior to reaching the impoundment: the production lines from shale wells that are producing oil go to battery tanks. Further separation of oil and water occurs in these tanks. The oil is recovered, the water then goes for disposal in UIC Class 2 disposal wells or might be treated for recycle. The water coming off the battery tanks may have 70 – 150 ppm of oil.

Similarly, teams have wondered about the small amount of solids (AZ test dust and sodium bentonite drilling clay) in the synthetic solution. This is representative of the solids in PW when they reach the impoundment. This is why: When the shale formation is fracked, immense quantities of ultra fine solid particles are created and carried to the surface with the PW. The larger particles easily gravity separate. When recycling the PW, companies are interested in removing these very fine particles that remain.