NM STATE WERC ENVIRONMENTAL DESIGN CONTEST
NMSU College of Engineering

NGL Water Solutions 2023

Task 5. Request for Proposals:
Recovering Ammonia from Produced Water for Beneficial Reuse

Task proposed and sponsored by NGL Water Solutions
Task developed by staff from Chevron, Hydrozonix, NGL Water Solutions, Oxy, Select Energy

Background

Your team is tasked with the job of serving as a sustainability professional to design a system that creates economic value from processing byproducts. In this instance, ammonia needs to be removed to facilitate the beneficial reuse of treated produced water. As is required in any sustainable system, the cost of recovering the ammonia should be offset by converting it to a useable resource. Of important consideration is the current value of anhydrous ammonia. As a commodity, it is worth $1170 per metric ton.

<u>Produced Water from Oil and Gas Operations</u>

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).

<u>Uses of Ammonia: From Fertilizers to Hydrogen Production</u>

Ammonia is a key component in a variety of useful compounds. Approximately 90% of worldwide ammonia production is used in the form of ammonium nitrate for fertilizer, as it helps replenish nitrogen into the soil and aids in increasing other vital nutrients. Other forms of ammonia are used for household cleaning products, refrigerants, diesel exhaust fluids (DEF), and water purification at water- and wastewater-treatment plants. [1]

The most promising new use for ammonia is for producing hydrogen gas. Hydrogen gas shows promise as a carbon-neutral fuel that could be used to replace petroleum-based fuels in the manufacturing and transportation industries. Hydrogen produces large amounts of energy when burned in the presence of oxygen and has the advantage of burning without producing CO_2.

The current limitations of using hydrogen as fuel are that 1) Natural gas is a primary source of H_2 (having the potential to raise the carbon footprint). Alternatively, 2) H_2 can be produced by electrolysis of water, but to date, the process is too energy intensive to be economically feasible.

Ammonia (NH_3) is an obvious source of hydrogen, but until recently was not feasible because hydrogen production from ammonia has typically been a high-temperature, energy-intensive process with slow reaction times. In the past two years, researchers at Northwestern University and in Japan have discovered methods of speeding reaction times at low operating temperatures, now making ammonia an attractive source of hydrogen [2], [3].

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Ammonia Production

Ammonia has typically been produced from fossil fuels. When thus derived, the substance is non-carbon-neutral. Although researchers are currently developing processes for producing "Green Ammonia" using nitrogen from air, we propose the attractive alternative of recovering already-existing ammonia from PW. This approach could serve three mutually advantageous purposes: 1) develop a beneficial, economically feasible means of recovering ammonia, 2) provide an additional income stream for produced water companies that may offset their costs of 3) treating PW for beneficial reuse. Thus, finding a feasible means of recovering ammonia from PW will promote reuse of the water and help preserve the nation's fresh water supply.

As the price of natural gas increases, industrial plants producing ammonia have shut down or dramatically slowed production. Finding a means of feasibly recovering ammonia from PW would broaden the world's access to this chemical.

Teams should be aware that some treatments may alter the chemical structure of the ammonia. For example, altering the oxidative state may change the structure of ammonia (NH_3) to nitrate (NO_3).

Recycling Produced Water

While an ever-growing percentage of PW is being recycled for reuse within the oil and gas industry, the vast majority of PW volumes are still managed by disposal-well injection. Concurrently, the large volumes of PW being injected can induce seismic activity. Oil and gas regions such as the Permian basin in west Texas and southeast New Mexico are some of the most arid regions in the country, and the industry is at a point where large-scale desalination of PW is being contemplated. Doing so would drastically decrease injected volumes which would alleviate seismic events. It would also introduce large volumes of fresh water back into the environment creating potential for use in agriculture, industry, habitat, and recreation.

To do this, processes must be designed to successfully remove all constituents of concern in PW. Dissolved solids such as sodium, calcium and chloride are by volume the largest constituents of concern in produced water and will require desalination. Other constituents such as ammonia and certain organics are not removed via desal technology. Therefore, they must be removed prior to desal or from the resulting desal distillate.

Ammonia in Produced Water

PW contains on average 430 mg/L ammonia by mass. Ammonia and ammonium are nutrients, but can be toxic to freshwater eco systems. Discharged volumes of treated PW need ammonia to be under certain thresholds. As a guideline, the EPA recommendation for protecting freshwater organisms under chronic conditions (30 days) is 1.9 ppm (or 1.9 mg/L total ammonia nitrogen) [4].

SPOT Values

While the primary focus of this task is the recovery of ammonia nitrogen in a useful or marketable form from produced water recycle operations, other characteristics of your post-treatment PW are important because they bear on the overall reusability of this water. Specifically, the so-called "SPOT" values (salinity, pH, oxidation-reduction potential, turbidity, etc.) are of interest. Table 2 provides desired value ranges of these parameters for common clean brine as proposed by the Produce Water Society [6].

Measure and report the values of the SPOT parameters for both your pre- and post-treatment PW. While not required in this task, additional project value and consideration will be given to teams who include the steps necessary to bring the parameter(s) within the desired range for clean brine as outlined below in Table 2.

Should you elect to adjust your post-treatment PW to fall within the necessary range for the SPOT parameters, then, just as you will do for the ammonia-removal process itself, include in your report the cost, equipment required, etc. of bringing these parameters to within the desired ranges. Note that there is no desired range for salinity. Simply report this value for your post-treatment water. Note also that you are not expected to measure hydrogen sulfide concentration other than to simply note any H_2S odor.

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Problem Statement

Your team will research, evaluate, and design a solution to remove and recover ammonia from a 50,000 bbl/day produced water recycle operation.

Your solution should be logistically and economically feasible. The recovered ammonia shall be in a form that can be sold on the market. The effluent water quality should be useful for commercial applications.

Design Requirements

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

- Ammonia should be recovered in a usable state from the synthetic sample of produced water.
- The process should remove and recover ammonia at minimal additional cost, and hopefully return a profit.
- Base your analysis on a 50,000 bbl/day treatment facility.
- The bench-scale treatment and recovery processes must be contained in a closed system. Due to safety issues with ammonia, all plans must be submitted in the ESP and approved prior to operation at the contest.
- Include a Process Flow Diagram (PFD) for the selected treatment process. The PFD must include mass and energy balances (input and output rates, waste streams, reactants, reaction rates, etc.).
- Include ammonia analysis and SPOT analyses of the influent and effluent.
- If you elect to treat the PW after ammonia removal to meet the SPOT value ranges listed, address this treatment in your report and demonstrate that your PW meets the SPOT parameters in your bench-scale demonstration, once ammonia is removed.
- All costs must be demonstrated. Cost must be inclusive of all waste-stream disposal.
    - Consider the current costs for desal pretreatment or PW recycle, not including ammonia removal, to be approximately $0.25/bbl.
    - As of this printing, ammonia has a value of approximately $0.08/bbl of PW. Teams may use this value for TEA computations or provide updated values.
- Present a Techno-Economic Assessment and Analysis (TEA) to construct a full-scale ammonia-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 treated 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 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 $0.10/kWh.
    - Visualization tools: Sensitivity analyses, etc.
    - Teams are advised to create a multi-disciplinary team by inviting a business major to help draw up economic plans for full-scale implementation of your designs.
- Identify and address the fate of any waste products generated by the PW treatment technology.
- Include a public involvement plan, as applicable (see Team Manual).
- To be considered for the WERC P2 Award, in a separate section of the report (titled "Pollution Prevention"), document success in improving energy efficiency, pollution prevention, and/or waste minimization, as it applies to your project.
- Address any intangible benefits of the selected treatment process.
- Address safety aspects of handling the raw produced water, ammonia, and any final products. Safety issues for the full-scale design should be addressed in the written report. Safety issues for the bench-scale demonstration should be addressed in both the written report and the Experimental Safety Plan (ESP).

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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 a Delaware Basin shale play.

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

After treatment, your team shall submit four 100-mL samples of effluent, two for ammonia analysis and two for SPOT analyses.

Contest Analytical Testing Techniques

At the contest, two analyses will be conducted for ammonia:

1. Ammonia remaining in the processed synthetic water will be analyzed through ion chromatography.
2. Ammonia captured by your process will be weighed, or other appropriate analysis technique, according to your bench-scale design.

SPOT Parameters will be individually evaluated as indicated below.

- *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. Add solids to oil phase.
4. Add oil phase to water phase and gently mix.
5. Top off with DI water to make 1.0 L.
6. Just before use, use a homogenizer/mixer* to generate small droplets of the oil phase.
   *Use a high-speed drill connected to a paint-mixing paddle; blend on highest speed for 5 minutes.

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

Table 1. The bench-scale apparatus shall treat water of the following chemistry [5]

Water phase	**Amount per liter of synthetic solution**
DI water	750 mL
Sea Salt	120 g
Ammonium chloride	1575 mg
Oil phase	**Amount per liter of synthetic solution**
TrueSyn 200 I*, ***	92 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

**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.*

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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 ammonia.

Your team is asked to report and discuss values for all of the parameters below for your treated effluent. It will be helpful for your team, and for produced water companies, to understand the effects of your proposed ammonia-recovery treatments on these values. If you elect, you may increase the value of your project by including steps, costs, etc. to ensure that the treated effluent meets these SPOT values after ammonia extraction.

Table 2. Common Clean Brine Minimum Specification for Reusing Recycled Produced Water [6].

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 a specific formation.

30% Project Review

Suggested submission date: Feb. 6, 2023

Final submission date: February 24, 2023

An engineering "30% Project Review" reviews the engineering firm's preliminary design and aspects of a project with a client. It provides the client an opportunity to suggest modifications for inclusion in the final design. The goal is to define the scope of the project, present a project schedule, report progress to date to meet the final deadline, and determine fatal flaws, if any.

For the design contest, the review should not exceed four pages. Submit the project review as soon as possible. You are allowed to change your plans after submitting it. Although the review is not scored, your team will receive feedback from the judges for improving your project. (The higher the quality of your review, the more help you will get from the judges.)

At a minimum, the review must include:

- **A brief description of your project:** One bulleted list outlining: goals, planned solution to the problem, and any anticipated drawbacks.
- **A project schedule** (schedule for completion of the contest solution, including progress to date)
- **Process flow diagram** with all mass and energy balances, as needed.
- **Table of Contents** planned for the technical report (place topics in order, one line per topic)

Experimental Safety Plan (ESP)

The ESP outlines your team's plans for safely operating your bench-scale demonstration at the contest. This document is submitted in February (see dates below). Instructions are provided in the team manual. The Team Leader, or a designated team member, shall attend a mandatory short course that outlines the ESP process. Teams will not be able to run a bench-scale demonstration if the ESP is not received by the deadline. Your team should follow your school's safety procedures while conducting tests prior to attending the contest.

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Evaluation Criteria

Each team is advised to read the 2023 Team Manual for a comprehensive understanding of the contest evaluation criteria. As described in the manual, there are five events: a written report, a formal oral presentation, a demonstration of your technology using a bench-scale representation, a poster presentation, and a Flash Talk. Criteria used by the judges in evaluation of these five components are described in the Team Manual.

For a copy of the Team Manual, Public Involvement Plan, and other important resources, visit the WERC website: Guidelines | werc.nmsu.edu

Your response to the problem statement will include consideration of the following points specific to this task.

- Potential for real-life implementation, including expected reliability and maintainability.
- Thoroughness and quality of the process-flow diagram.
- Thoroughness and quality of the economic analysis.
- Originality and innovation represented by the proposed technology.
- The results of your bench-scale demonstration: How effective is the treatment technology?
- Other specific evaluation criteria that may be provided at a later date (watch the FAQs online).

Short Courses

WERC is offering two short courses:

- ***Mandatory:*** Preparing the Experimental Safety Plan. The Team Leader, or a person assigned by them, must attend the course prior to submitting the ESP (and before February 20, 2023).
- ***Optional:*** Environmental Health and Safety (EH&S). The course is designed to prepare teams to complete the EH&S portion of their technical report. Individuals can earn a digital badge to add to their professional development portfolio. Course fees will be waived for contest-registered students, faculty, and judges. Watch the WERC website for schedules and registration information.

Dates, Deadlines, FAQs (***dates subject to change— watch website FAQs***)

- Today: Email us to let us know you are interested in this task. We will contact you with breaking news.
- Opening mid-December, 2022: Optional Course: WERC Safety and Environmental Topics. Live—See website for dates and times. See Team Manual for more information.
- Opening mid-December, 2022: Mandatory Course: Preparing the Experimental Safety Plan. February 20, 2023: deadline for attending. On-demand—See website & Team Manual for information.
- February 6 - 24, 2023: 30% Project Review Due
- February 6 - 24, 2023: Experimental Safety Plan (ESP) due.
- April 7, 2023: Technical Report due
- Weekly: Check FAQs weekly for updates:
  - Task-specific FAQs: 2023 Tasks/Task FAQs
  - General FAQs: 2023 General FAQs
- All dates or task requirements are subject to change. Check FAQs for updates online.

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References

[1] Chemical Safety Facts. https://www.chemicalsafetyfacts.org/ammonia/ (accessed 7/8/22)

[2] Dae-Kwang Lim, Austin B. Plymill, Haemin Paik, Xin Qian, Strahinja Zecevic, Calum R.I. Chisholm, Sossina M. Haile. Solid Acid Electrochemical Cell for the Production of Hydrogen from Ammonia. *Joule*, 2020; 4 (11): 2338
DOI: 10.1016/j.joule.2020.10.006

[3] Ogasawara, K., et al. (2021) Ammonia Decomposition over CaNH-Supported Ni Catalysts via an NH2−-Vacancy-Mediated Mars–van Krevelen Mechanism. ACS Catalysis. doi.org/10.1021/acscatal.1c01934.

[4] Environmental Protection Agency Notice. 2013. Final Aquatic Life Ambient Water Quality Criteria for Ammonia—Freshwater 2013. Federal Register.gov (Accessed 7/13/2022)

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

[6] A Common Clean Brine Specification for Reusing Recycled Produced Water – Draft Guidelines, June 2020. Accessed 8/26/2021: https://www.producedwatersociety.com/

Appendix–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 do not separate in the battery tanks over a few days.

We recommend mixing the solution in a 5-gallon bucket, mixed with a paint-stirring paddle. 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. 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 separate by gravity. When recycling the PW, companies are interested in removing these very fine particles that remain.