SUPPORTING INFORMATION

Bromate Oxidation of Ammonium Salts: In Situ Acid Formation for Reservoir Stimulation

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MATERIALS AND METHODS

Instrumentation:

- Electrospray Ionization Mass Spectrometry (ESI-MS) Measurements: Flow injection MS analysis was carried out on a Bruker MicroToF MS system. The MS system was interfaced to an Agilent 1200 LC system through an electrospray ionization (ESI) source that was operated in the negative ion mode. The LC was operated at a flow rate of 0.15 mL/min, the isocratic solvent system was 50/50 (v/v) water/acetonitrile (H₂O/CH₃CN), and the sample injection volume was set to 10 uL.

- Titration measurements were performed using a Mettler Toledo EasyPlus Titrator. It is noteworthy to mention that due to chemical incompatibility of the pH probe with HF, the equivalence point for this set of experiments was determined using an acid-base indicator, i.e. phenolphthalein.

- Powder X-ray Diffraction (PXRD) measurements were collected on a Bruker D8 X-ray diffractometer at 45kV, 40mA for Cu Kα (λ = 1.5418 Å) with a scan speed of 1°/min.

- Fourier Transform Infrared (FTIR) analysis of gas was performed on an MKS 2030 with vacuum introduction (base pressure 0.1 atm), filled to 0.9 atm through a 1 m length of 0.010” SST tubing over about 3 minutes. The gas cell was thermostated at 50 °C with the transfer lines at 150 °C. The internal volume of the gas cell was 200-225 mL. Reference spectra were provided by MKS using primary standards (and blends of that standard) or HITRAN (high-resolution transmission molecular absorption database) data.

- The calcium concentration for the acidized core samples was measured on a Perkin Elmer Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Each of the samples were serially diluted and evaluated against a linear calibration curve with calcium concentrations at 0.00, 0.1, 1.0, 10.0, 100 and 1,000 mg/L (correlation coefficient of 0.999 at 315.887nM).

- Thermo Scientific Barnstead Smart2Pure water purification system having a resistivity of 18.2 MΩ.cm was used to generate the de-ionized water (DI-H₂O) for all experimental procedures.

- Haak programmable recirculating silicone oil bath was used to perform the temperature trigger in situ acid generation experiments performed in the Ace Glass Pressure tubes.

- Isotemp Oven (Model 281A) was used to perform the temperature trigger in situ acid generation experiments performed in the Parr acid digestion vessels.
**Experimental Procedures**: All chemicals and solvents used in the preparation of the compounds described herein were of reagent grade and used without further purification.

**Table S1.** Summary of chemical compounds/starting reagents used in this study.

| Chemical Name                          | Formula     | Vendor / Catalog #  |
|----------------------------------------|-------------|---------------------|
| ammonium fluoride                     | NH₄F        | Sigma Aldrich / 338869 |
| ammonium hydrogen difluoride          | NH₄HF₂      | Sigma Aldrich / 455830 |
| ammonium chloride                     | NH₄Cl       | VWR / 0621/500 |
| ammonium bromide                      | NH₄Br       | Alfa Aesar / A16258 |
| ammonium iodide                       | NH₄I        | Sigma Aldrich / 221937 |
| ammonium tetrafluoroborate            | NH₄BF₄      | Sigma Aldrich / 35831 |
| ammonium hexafluorophosphate          | NH₄PF₆      | Sigma Aldrich / B20898 |
| ammonium dihydrogen phosphate         | NH₄H₂PO₄    | Sigma Aldrich / 204005 |
| ammonium hydrogen phosphate           | (NH₄)₂HPO₄  | Fisher Chemical /A686-500 |
| ammonium sulfate                      | (NH₄)₂SO₄   | Fisher Chemical /A702-500 |
| ammonium persulfate                   | (NH₄)₂S₂O₈  | Fritz Industries / OB-1 |
| sodium bromate                        | NaBrO₃      | Fritz Industries / OB-3N |
| potassium bromate                     | KBrO₃       | Alfa Aesar / A18258 |
| sodium chlorate                       | NaClO₃      | Alfa Aesar / 14267 |
| sodium iodate                         | NaIO₃       | Alfa Aesar / 40135 |
| potassium chlorate                    | KClO₃       | Alfa Aesar / A17075 |
| potassium iodate                      | KIO₃        | Acros Organics / 7758-05-6 |

- **Series A: Reaction of NH₄X (X=Cl, Br and H₂PO₄) and NaBrO₃.** In a typical experiment, a solution consisting of NH₄X and NaBrO₃, DI-H₂O (25 mL) was prepared in a 120 mL Ace Glass Pressure Tube. The tube was then capped and heated in a programmable silicone oil bath at temperatures up to 150°C for a timeframe up to 3h to give a transparent solution. The generation of acidic solutions led to the evolution of bromine (Br₂) gas as a side product as clearly evident from the distinct orange color. In the case of each counter ion, a series of independent experiments were performed whereby the ratio of NH₄⁺ to BrO₃⁻ was systematically varied (using 5 mmol BrO₃⁻ as the baseline) in order to determine the optimal stoichiometry required to potentially reach the theoretical acid concentration. The ratios tested range from 1:1, 1.33:1, 1.67:1, 2:1, 5:1 and 10:1 (refer to Figures S1-S2). All solutions were cooled to room temperature, after which an acid-base titration was conducted to determine the acid concentration (mmol).
Figure S1. Amount of acid generated using NH₄Br as a precursor (left) based on NH₄⁺ : BrO₃⁻ at 150°C and (right) at 100°C.

Figure S2. Amount of acid generated based on using NH₄Br as a precursor, i.e. 2 NH₄⁺ : 1 BrO₃⁻ at 100°C with varying degrees of soaking time (i.e. 10 to 180 min).

**Carbonate Dissolution Experiments:** an aqueous solution of 0.754 g NaBrO₃ and 0.535 g of NH₄Cl in 25 mL of water was prepared in a 120 mL glass tube. The pH was measured to be 6.5. The tube was sealed and placed in a heating bath at 150 °C for 2 hours. The tube was then cooled to room temperature, and the pH was determined to be 0.96. Then, 0.5 g of crushed calcite (Indiana limestone rock) was added to the tube. Vigorous dissolution occurred, and the solution was reheated to 150 °C in an oil bath to ensure the reaction went to completion. After cooling the system to room temperature, the liquid was isolated and analyzed via inductively coupled plasma (ICP) to determine the concentration of calcium in solution (7585 ppm) which corresponds to 94.9% of available Ca²⁺ in solution.
• **Series B: Reaction of NH₄X (X=F, HF₂, PF₆, BF₄) and NaBrO₃.** In a typical experiment, a solution consisting of NH₄X and NaBrO₃, DI-H₂O (25 mL) was prepared in a 125 mL Parr (#4748) acid digestion vessel equipped with a PTFE liner. The capped liner containing the solution was then placed into the reaction vessel. One corrosion disc (# 310AC) was then placed on top of the PTFE liner lid followed by the addition of one rupture disc (# 311AC). To complete the assembly, the pressure plate (# 306AC) was added in addition to two spring washers and a compression ring. The cap was then carefully secured with the compression screws. The secured vessel was then heated at temperatures up to 150 °C for a timeframe up to 24h to give a transparent solution. The ratios, i.e. NH₄⁺ to BrO₃⁻, evaluated under these conditions were 1:1 and 2:1 (refer to Figure S3). All solutions were cooled to room temperature, after which an acid-base titration was conducted using an indicator to determine the acid concentration (mmol).

![Figure S3.](image)

**Figure S3.** (left) Amount of acid generated using NH₄X as a precursor (X = F, HF₂, BF₄ or PF₆) and (right) impact of soaking time on acid generation for the NH₄F system.

• **Series C: Reaction of (NH₄)₂X (X=SO₄, HPO₄) and NaBrO₃.** In a typical experiment, a solution consisting of NH₄X and NaBrO₃, DI-H₂O (25 mL) was prepared in a 120 mL Ace Glass Pressure Tube. The same procedure was followed as described for Series A, except the ratios tested were limited to 1:1 and 2:1. In the case of the (NH₄)₂X (X= HPO₄) system, a negligible amount of acid was generated in the case of both ratios after soaking for 3h at 150°C. Conversely, where X = SO₄, the amount of acid generated was measured and found to be 1.607 mmol and 8.674 mmol for the 1:1 and 2:1 ratios under analogous conditions.

• **Series D: Reaction of (NH₄)₂S₂O₈ and NaBrO₃.** In this series of experiments, a solution consisting of two inorganic oxidizers, i.e. (NH₄)₂S₂O₈ and NaBrO₃, in DI-H₂O (25 mL) was prepared in a 120 mL Ace Glass Pressure Tube. The same heating procedure was followed as described for Series A and C. However, the uniqueness of this system, with respect to the unexpectedly high concentration of acid generated under analogous testing conditions, led to a more in-depth evaluation into the impact of reagent ratio on acid yield. Accordingly, the tested ratios included 1:1, 3:1, 5:1, 10:1, 20:1 and 30:1 (Figure S4).
Figure S4. Amount of acid generated based on using \((\text{NH}_4)_2\text{S}_2\text{O}_8\) as a precursor, i.e. \(3 \text{NH}_4^+ : 1 \text{BrO}_3^-\) at 100°C with varying degrees of soaking time (i.e. 10 to 180 min).

- **Series E. Reaction of NH\(_4\)Cl and NaX / KX (X = ClO\(_3\) and IO\(_3\)).** In order to validate that NaBrO\(_3\) is the requisite oxidizer needed to produce acid under these conditions; two independent experiments were performed whereby NaBrO\(_3\) was substituted for alternative inorganic oxidizers having similar properties. Accordingly, solutions consisting of NH\(_4\)Cl and NaX or KX, DI-H\(_2\)O (25 mL) was prepared in a 2:1 ratio in a 120 mL Ace Glass Pressure Tube and heating for 3h at 150°C. As expected, the solutions remained colorless with no evidence of acid generation as the pH values for the heating solutions were measured to be 6.88 and 6.84 for the chlorate and iodate analogs, respectively.
CHARACTERIZATION

ESI-MS Measurements

Table S2. Summary of relevant anions in this study and corresponding abundant ion peaks.

| Anion               | Abundant Ion Peak (m/z) |
|---------------------|-------------------------|
| Br\(^-\)            | 79, 81                  |
| Br\(_2\)\(^-\)       | 158, 160, 162           |
| Br\(_3\)\(^-\)       | 237, 239, 241, 243      |
| BrO\(_4\)\(^-\)      | 143, 145                |
| BrO\(_3\)\(^-\)      | 127, 129                |
| BrO\(_2\)\(^-\)      | 111, 113                |
| BrO\(^-\)           | 95, 97                  |
| Br\(_2\)Cl\(^-\)     | 193, 195, 197, 199      |
| S\(_2\)O\(_8\)\(^2-\) | 96                     |
| HS\(_2\)O\(_8\)\(^-\) | 193                    |
| NaS\(_2\)O\(_8\)\(^-\) | 215                    |
| HSO\(_4\)\(^-\)      | 97                      |
| NaSO\(_4\)\(^-\) (+nH\(_2\)O) | 119 (+18n) |
| H\(_2\)Na(SO\(_4\))\(_2\)\(^-\) | 217                   |
| HNa(SO\(_4\))\(_2\)\(^-\) | 239                |
| NaSO\(_4\)\(^-\) + SO\(_4\)\(^-\) + H\(_2\)O | 116.5        |
| SO\(_4\)\(^2-\) + 2OH\(^-\) | 130                  |
| Impurity from Instrument | 113                |
| NO\(_2\)\(^-\)        | 46                      |
| NO\(_3\)\(^-\)        | 62                      |
**Figure S5.** ESI-MS spectrum collected upon combining (NH₄)₂S₂O₈ and NaBrO₃ (no heating).

**Figure S6.** ESI-MS spectrum collected after mixing (NH₄)₂S₂O₈ and NaBrO₃ for 6 days at room temperature (blue) and 40 °C (orange).
Figure S7. The homogeneity of the Indiana Limestone core sample was confirmed prior to acidizing as evidenced by good agreement between the experimental and calculated PXRD patterns. As expected, the chemical composition of the core was determined to primarily consist of calcite (98.81%), quartz (0.60%), dolomite (0.35%) and ankerite (0.24%). Note that the core sample was ground to a fine powder for the acidizing tests.
Figure S8. Digital images of (a) the acidic fluid produced by reacting NH₄Cl and NaBrO₃ in a 2:1 ratio at 150 °C for 30 min and (b) after reaction with CaCO₃ thereby confirming the fluid is spent, i.e. with respect to pH (>4) and Br₂ disappearance (orange to colorless solution).