TITRATION ANALYSIS
FOR
GOLD KING MINE
SILVERTON, SAN JUAN COUNTY, COLORADO

Prepared for
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Region 8

Prepared by
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Region 8 Superfund Technical Assessment and Response Team

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Project Dates of Sampling:	August, 2015
Contract Name:	START IV
Contract No.:	EP-S8-13-01
Technical Direction Document No.:	0001/1508-04

Purpose: To determine the concentration of sodium hydroxide or calcium hydroxide necessary to treat a volume of mine waste water from the Gold King Mine.

Method

The mine waste leachate was cooled to a temperature of 40-45°F (4.4-7.2°C) by placing 1-liter aliquots of the leachate in a refrigerator and freezer.

A titration setup was created using the following equipment:

- Burette connected to ring stand with a burette clamp
- 500 mL beaker for leachate
- Stir plate with magnetic stir bar
- YSI connected to ring stand with a clamp for pH measurements

Sodium hydroxide solutions were made by diluting 50% (w/w) NaOH to concentrations of 3%, 9%, 12% and 15% (Appendix A). Calcium hydroxide solutions were made by diluting solid $Ca(OH)_2$ to concentrations of 3% and 6% (Appendix A). Titrations were run in order of increasing concentration beginning with NaOH titrations then moving to $Ca(OH)_2$ titrations. Each titration was considered complete at a pH of 7-7.5.

Results

Photographs of the titration process are available in Appendix B. Graphs of titrant volume vs. pH are available in Appendix C.

3% Sodium Hydroxide

Volume of Titrant (mL)	pH
0	2.94
1.0	3.45
2.0	4.01
3.0	4.85
4.0	5.61
5.0	6.19
5.5	6.91
6.0	7.63

Observations

Temperature of the leachate prior to adding titrant: 4.6°C
Temperature of the leachate at pH endpoint: 8.4°C

No change in color was initially observed. After continued reaction and settling, an orange precipitate formed and settled on the bottom of the beaker. The type of precipitate (floc) was fluffy.

9% Sodium Hydroxide

Volume of Titrant (mL)	pH
0	2.94
0.5	3.29
1.0	4.17
1.5	5.25
1.7	5.79
1.9	6.54
2.0	7.11

Observations
Temperature of the leachate prior to adding titrant: 5.3°C
Temperature of the leachate at pH endpoint: 8.3°C

An orange precipitate formed immediately at the endpoint and settled on the bottom of the beaker. The type of precipitate (floc) was fluffy. Water above the precipitate was clear.

12% Sodium Hydroxide

Volume of Titrant (mL)	pH
0	2.97
0.2	3.24
0.5	3.41
0.7	3.96
1.0	4.73
1.1	5.23
1.2	5.62
1.3	5.94
1.4	6.37
1.5	7.15

Observations
Temperature of the leachate prior to adding titrant: 8.8°C
Temperature of the leachate at pH endpoint: 10.6°C

The pH did not immediately respond to titrant aliquots. Instead, the pH was observed to continuously increase slowly with each aliquot added. This could be a result of the slow stir rate used to simulate river mixing. An orange precipitate formed immediately at the endpoint and settled on the bottom of the beaker. The type of precipitate (floc) was fluffy. Water above the precipitate was clear.

15% Sodium Hydroxide

Volume of Titrant (mL)	pH
0	2.90
0.1	3.32
0.2	3.76
0.3	4.33
0.4	4.74
0.5	5.05
0.7	5.74
0.9	6.52
1.0	7.97

Observations
Temperature of the leachate prior to adding titrant: 5.4°C
Temperature of the leachate at pH endpoint: 8.8°C

The pH did not immediately respond to titrant aliquots. Instead, the pH was observed to continuously increase slowly with each aliquot added. This could be a result of the slow stir rate used to simulate river mixing. An orange precipitate formed immediately at the endpoint and settled on the bottom of the beaker. The type of precipitate (floc) was fluffy. Water above the precipitate was clear.

3% Calcium Hydroxide

Volume of Titrant (mL)	pH
0	2.93
1.0	4.92
1.5	6.28
1.6	7.87

Observations
Temperature of the leachate prior to adding titrant: 5.2°C
Temperature of the leachate at pH endpoint: 14.5°C

3% $Ca(OH)_2$ was not completely soluble and a gradient of $Ca(OH)_2$ was observed in the burette. Therefore, the results of the titration may not be indicative of the target titrant concentration. An orange precipitate formed immediately at the endpoint and settled on the bottom of the beaker. The type of precipitate (floc) was pin. Water above the precipitate was clear.

6% Calcium Hydroxide

Volume of Titrant (mL)	pH
0	2.91
0.1	3.21
0.2	3.53
0.4	3.82
0.5	4.50
0.6	4.79
0.7	5.1
0.8	5.5
0.9	5.82
1.0	6.13
1.1	Initial: 6.67 After 5 minutes: 7.64

Observations

Temperature of the leachate prior to adding titrant: 5.2°C
Temperature of the leachate at pH endpoint: 14.5°C

6% $Ca(OH)_2$ was not completely soluble and a gradient of $Ca(OH)_2$ was observed in the burette. Therefore, the results of the titration may not be indicative of the target titrant concentration. An orange precipitate formed immediately at the endpoint and settled on the bottom of the beaker. The type of precipitate (floc) was pin. Water above the precipitate was clear.

Sodium Hydroxide Calculations

50% NaOH

$M_1V_1 = M_2V_2$

FINAL VOL.

3% $(50\%)(V_1) = (3\%)(100\ mL)$

$V_1 = 6\ mL$

6% $V_1 = 12\ mL$

9% $V_1 = 18\ mL$

12% $V_1 = 24\ mL$

15% $V_1 = 30\ mL$

18% $V_1 = 36\ mL$

21% $V_1 = 42\ mL$

24% $V_1 = 48\ mL$

Calcium Hydroxide Calculations

$Ca(OH)_2 = 74.093$ g/mol

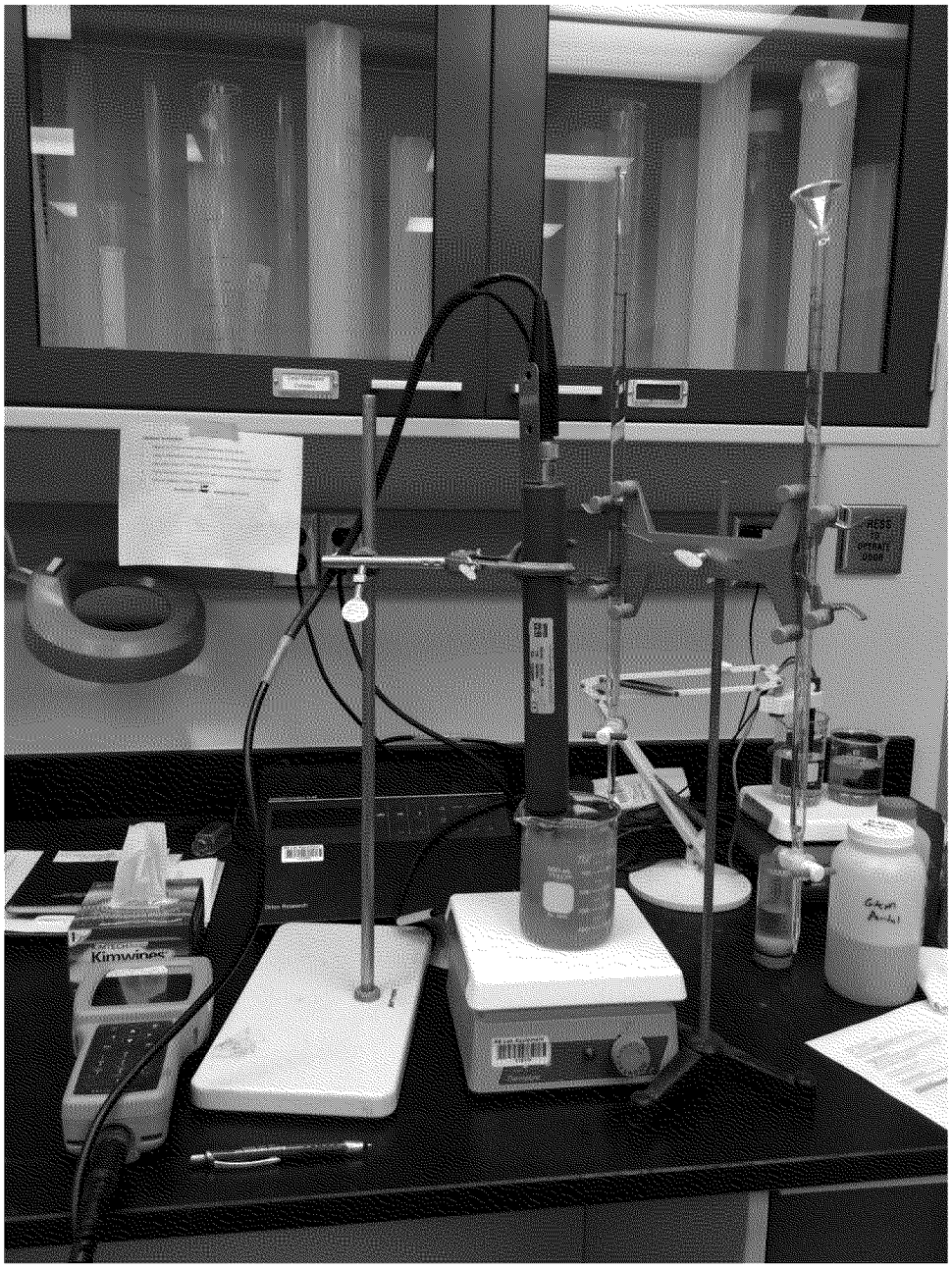
~~$C_1V_1 = C_2V_2$~~

Calculations by weight.

3% making 50 mL
1.5 g $Ca(OH)_2$
48.5 mL H_2O (DI)

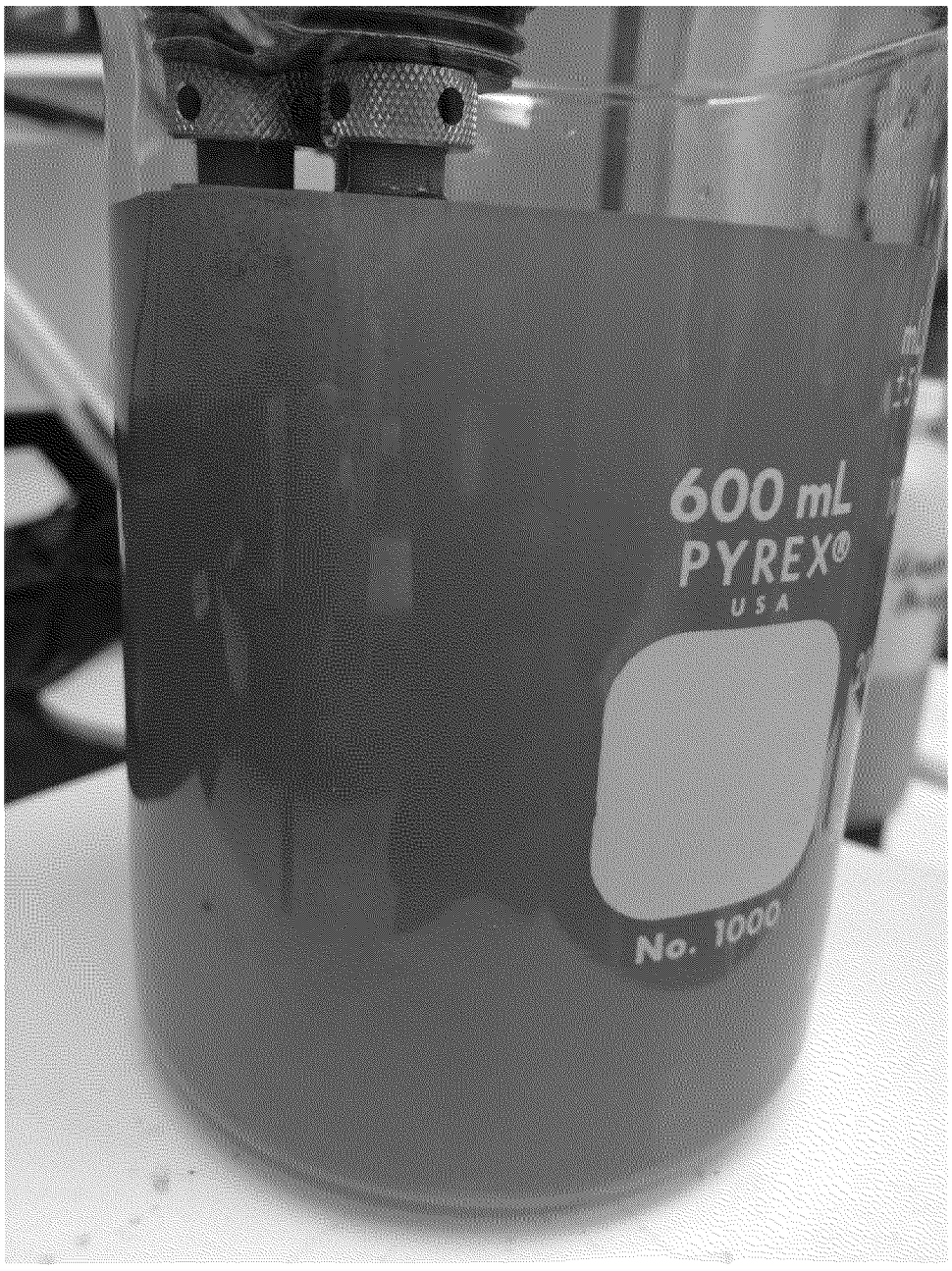
6% making 50 mL
3 g $Ca(OH)_2$
47 mL H_2O (DI)

Appendix B: Photograph Log for NaOH and $Ca(OH)_2$ Titrations Performed 8/19/2015

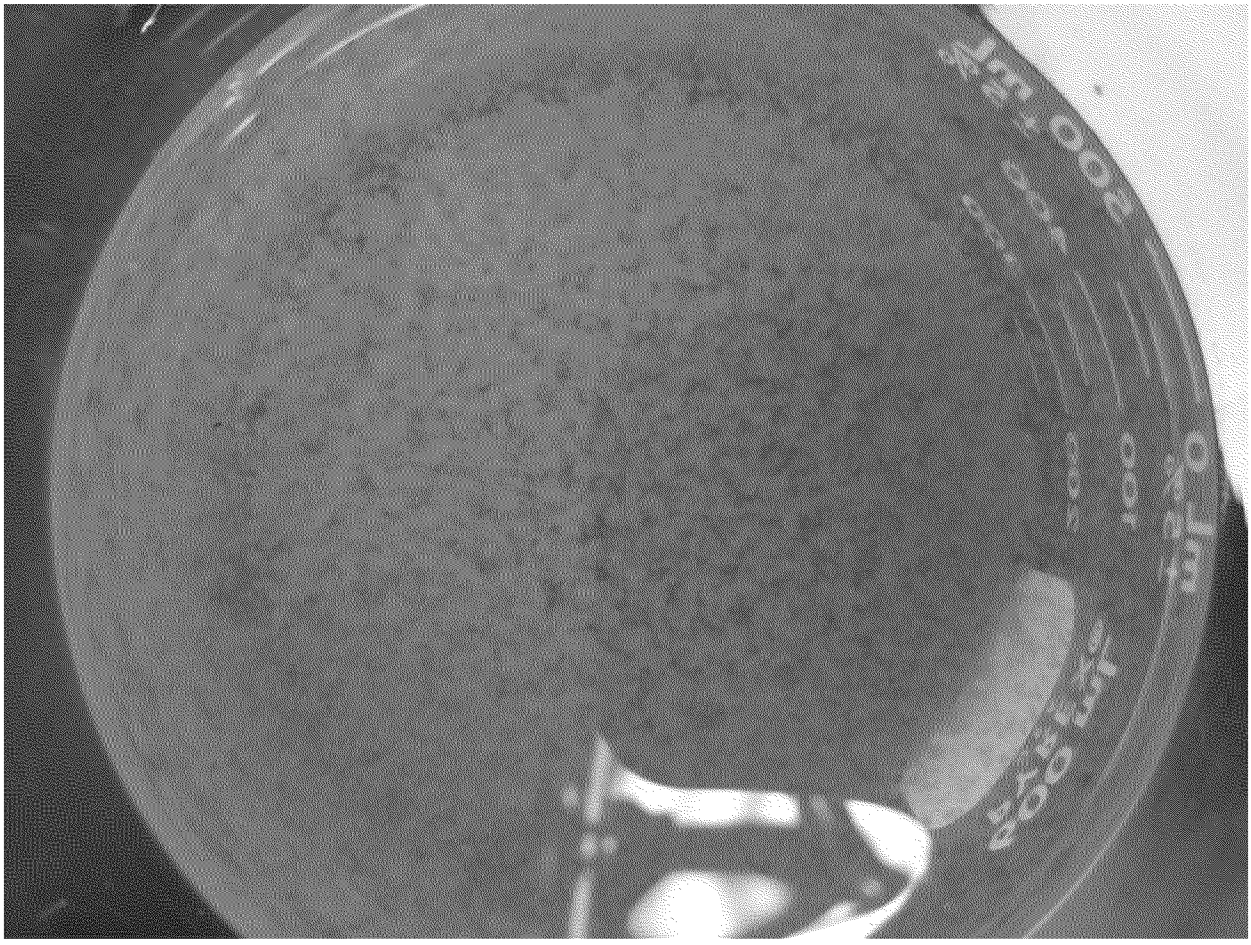


The titration setup including the YSI on the left ring stand and the burette on the right ring stand. A magnetic stir bar is inside the beaker. The leachate in the beaker is a representation of the leachate color and consistency before adding titrant.

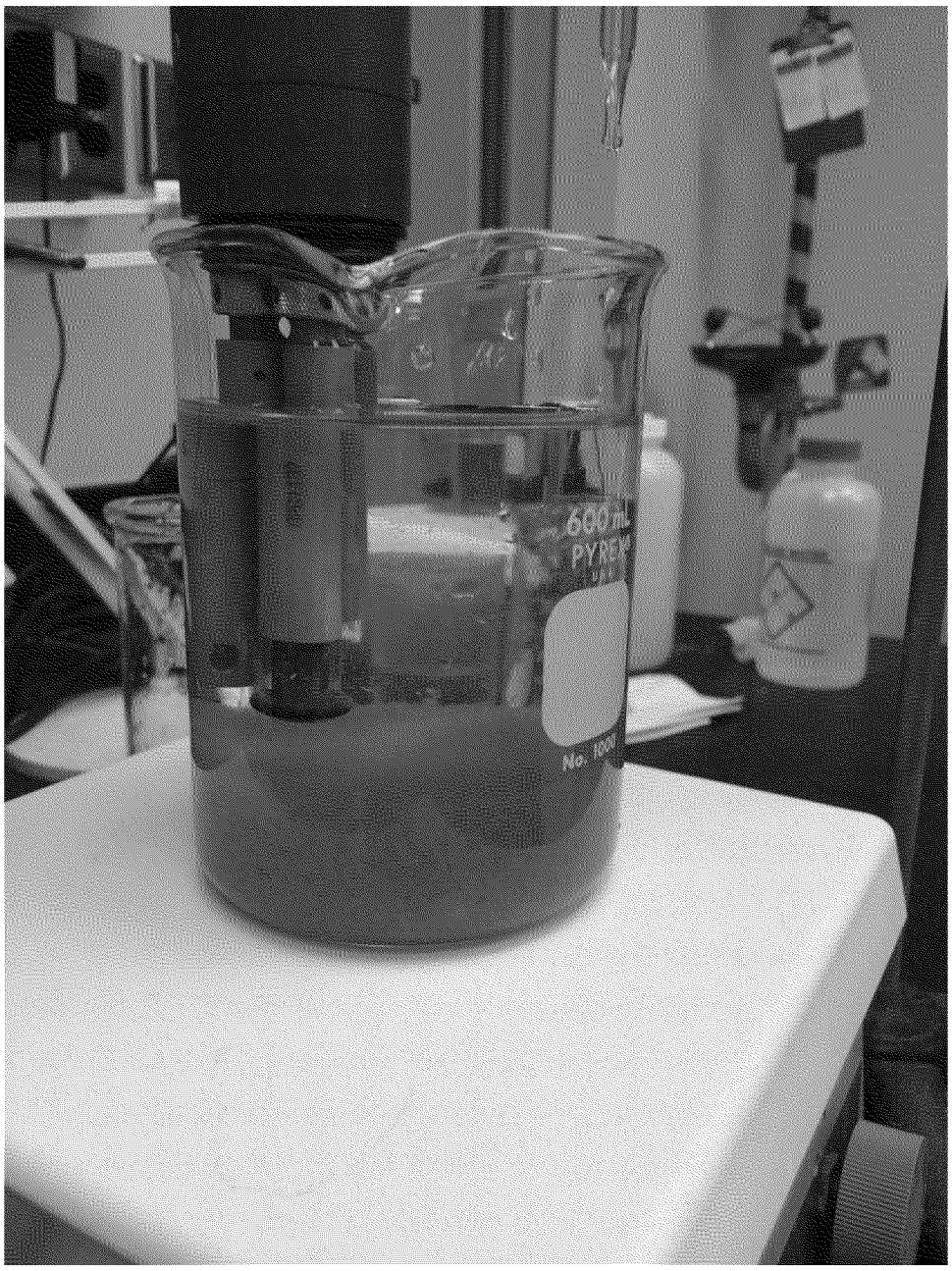
A close-up view of the YSI and burette above the beaker while the magnetic stir rod is on.



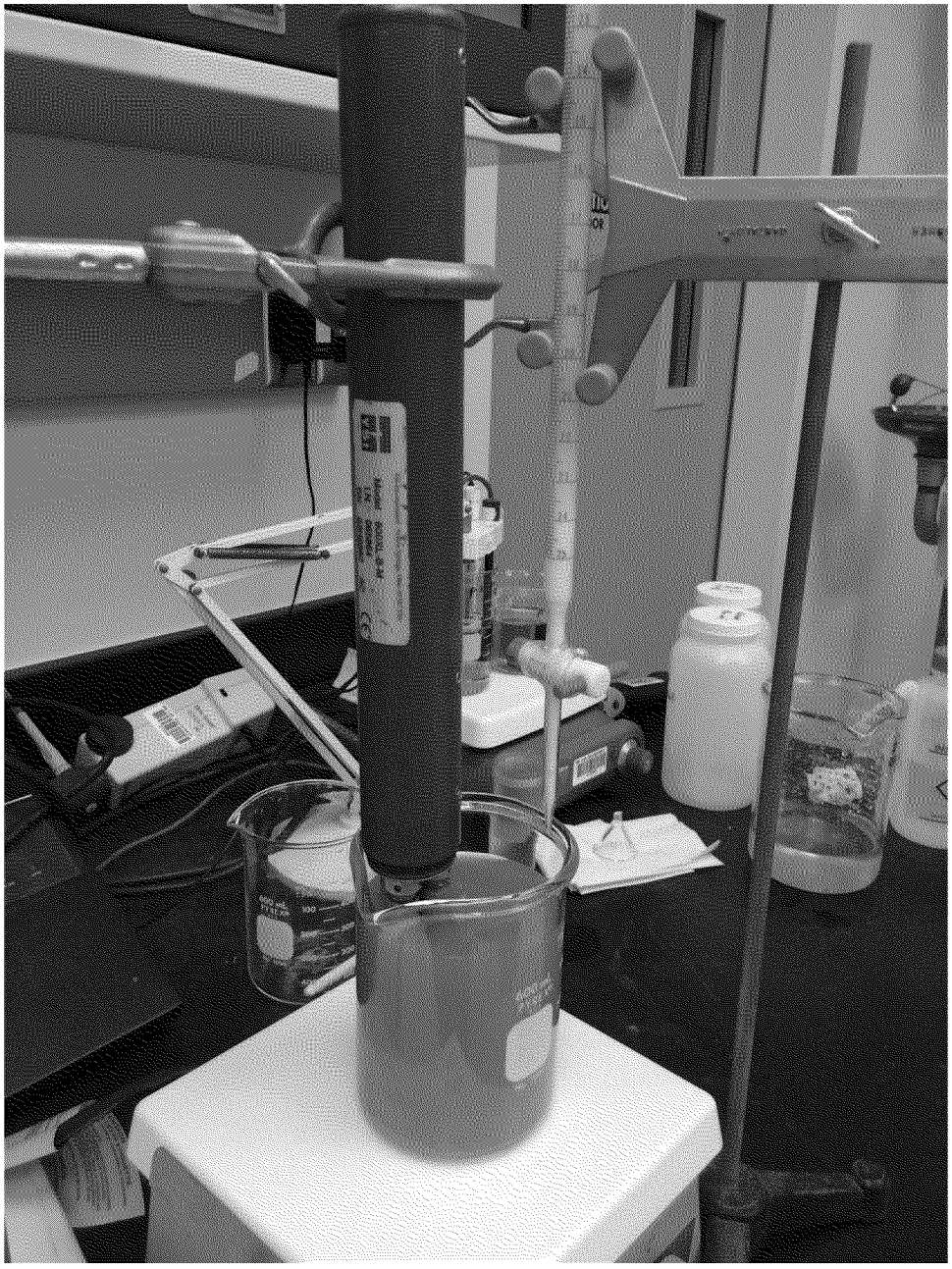
An example of the floc at the pH endpoint during the 9% NaOH titration while the stir bar is operating.



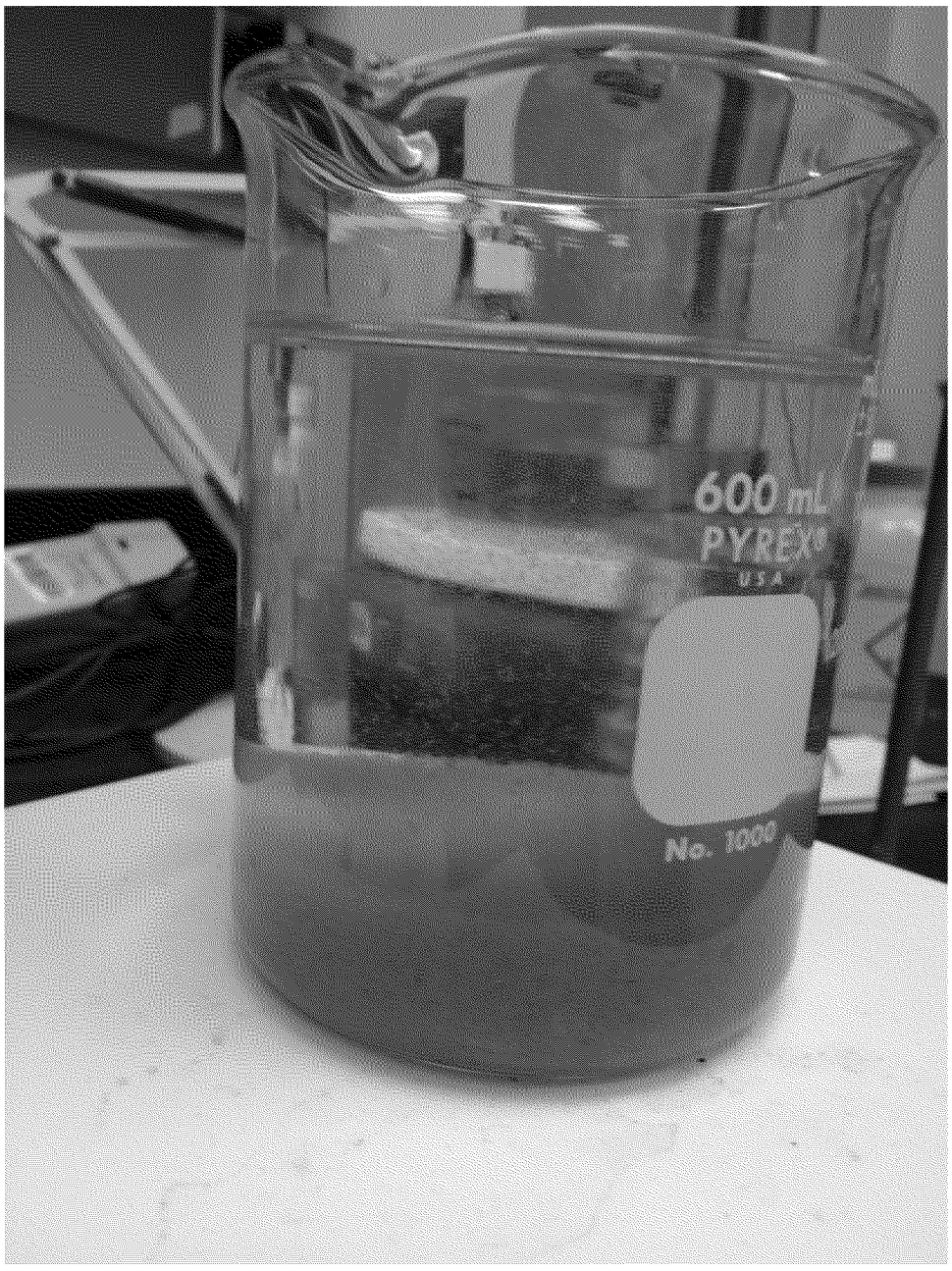
An example of the floc from a viewpoint above the beaker at the pH endpoint during the 9% NaOH titration while the stir bar is off.



An example of the floc at the pH endpoint during the 9% NaOH titration while the stir bar is off and floc is allowed to settle.



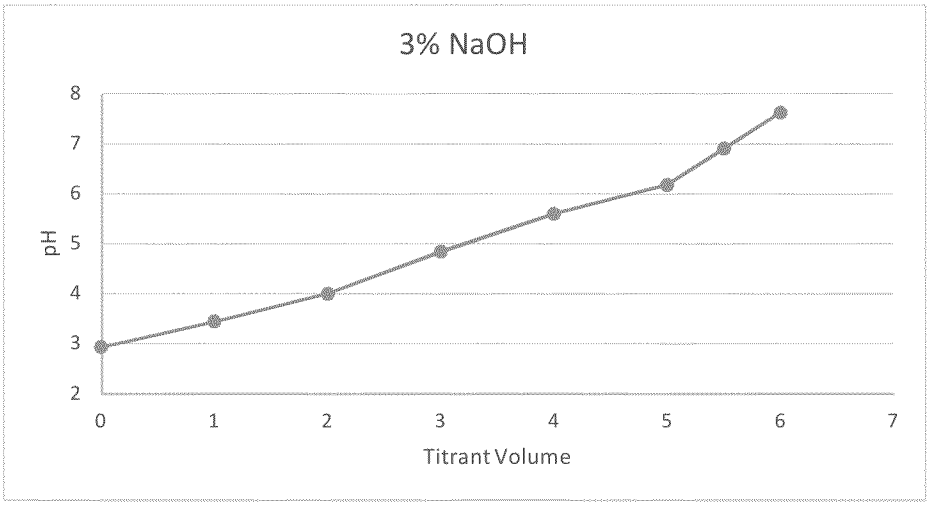
The titration setup during a calcium hydroxide titration. Note the gradient of $Ca(OH)_2$ inside the burette. 3% and 6% $Ca(OH)_2$ solutions were not completely soluble. Therefore, the results of the titration may not be indicative of the target titrant concentration.



An example of the floc at the pH endpoint during the 3% $Ca(OH)_2$ titration while the stir bar is off and floc is allowed to settle.

Appendix C: Titrant Volume vs. pH Graphs for Sodium Hydroxide and Calcium Hydroxide Titrations

Volume of Titrant (mL)	pH
0	2.94
1	3.45
2	4.01
3	4.85
4	5.61
5	6.19
5.5	6.91
6	7.63



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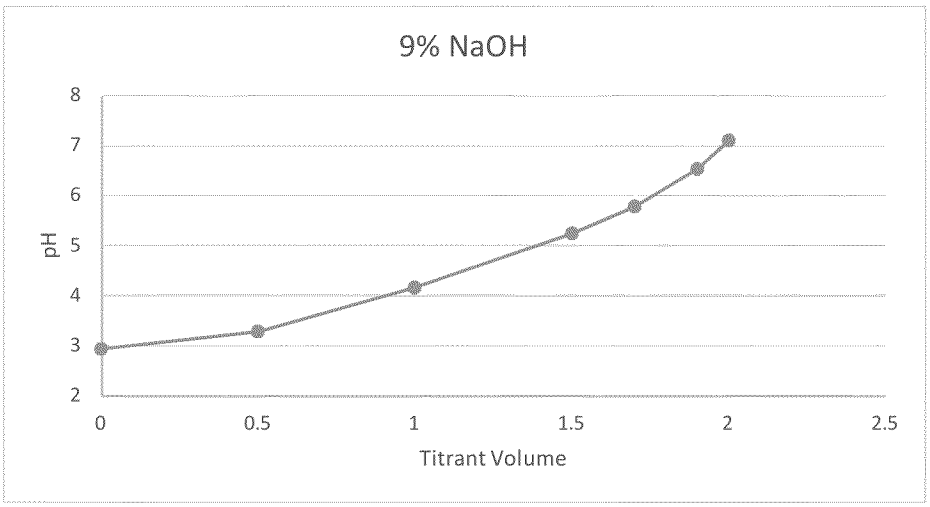

Volume of Titrant (mL)	pH
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0.2	3.24
0.5	3.41
0.7	3.96
1	4.73
1.1	5.23
1.2	5.62
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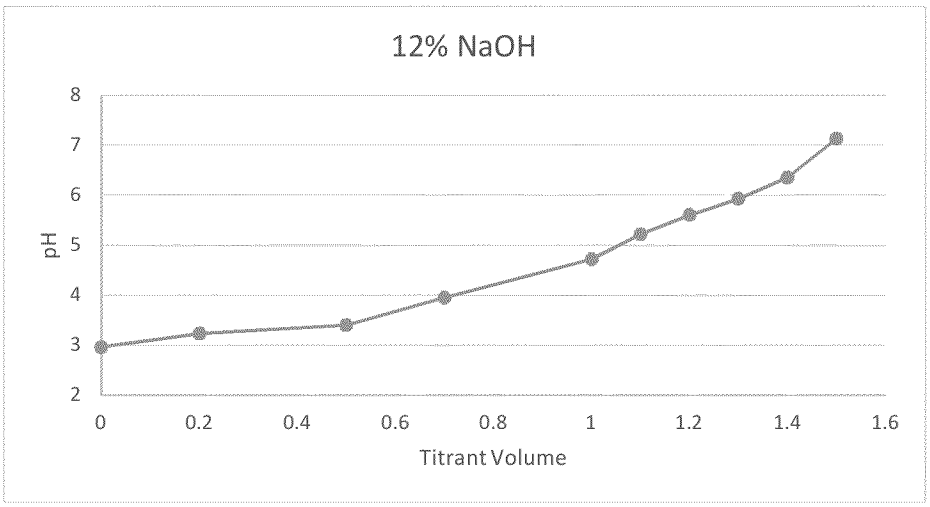

Appendix C: Titrant Volume vs. pH Graphs for Sodium Hydroxide and Calcium Hydroxide Titrations

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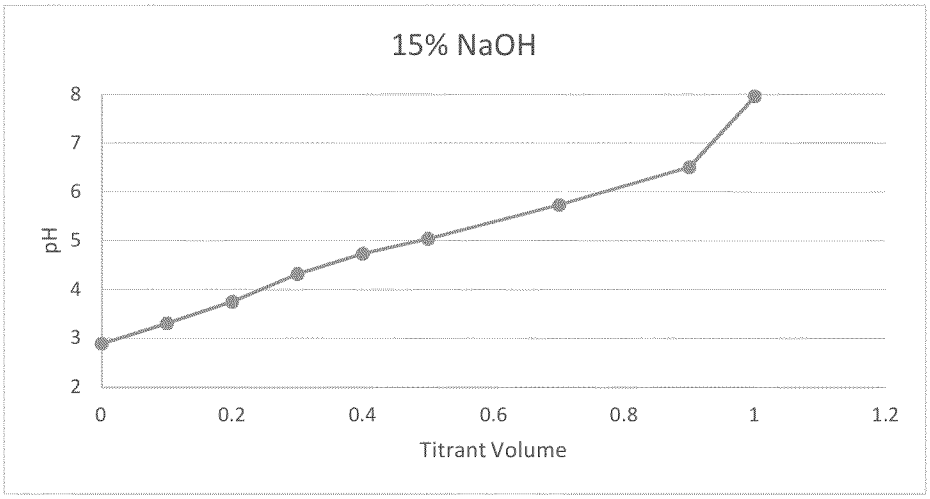
0.1	3.32
0.2	3.76
0.3	4.33
0.4	4.74
0.5	5.05
0.7	5.74
0.9	6.52
1	7.97



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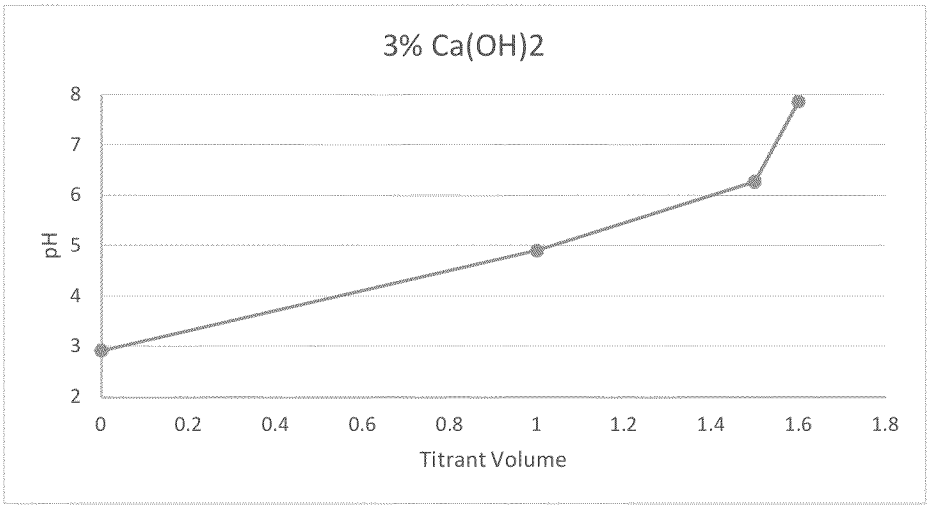
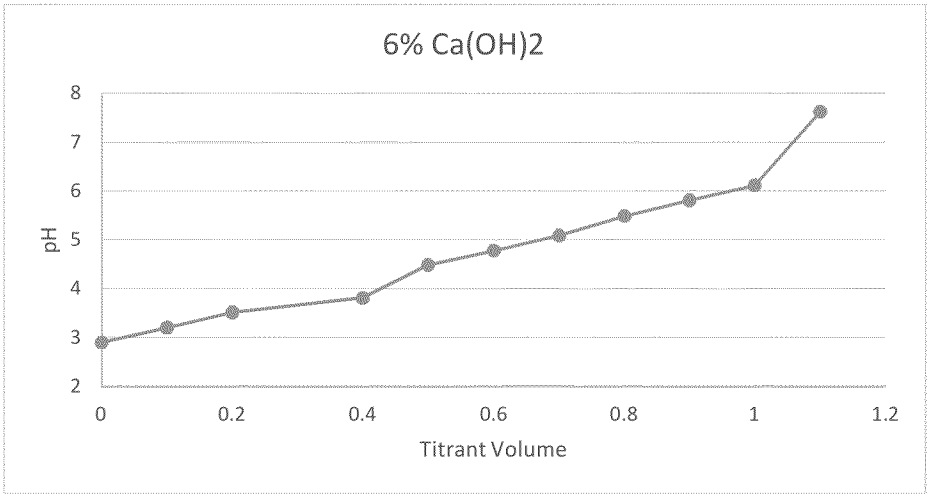
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