ASSESSMENT OF REMOTOX FOR PRECIPITATION OF HEAVY METALS IN LABORATORY WASTE STREAM

Performed by Motzz Laboratory, Inc

For Graus Chemicals, LLC

3/3/2015

Approved by: 

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MOTZZ LABORATORY, INC.

Date: March 3, 2015

TITLE: ASSESSMENT OF REMOTOX FOR PRECIPITATION OF HEAVY METALS IN LABORATORY WASTE STREAM

1.0 SCOPE AND OBJECTIVE

1.1 To assess the potential of REMOTOX in cleaning up heavy metals in laboratory waste stream.

1.2 To determine the amount of REMOTOX to be added.

1.3 To determine how much time for the heavy metals to precipitate.

1.4 Determine the effectiveness in reducing laboratory hazardous waste disposal.

2.0 METHOD SUMMARY AND DEFINITIONS

2.1 Two different solutions will be utilized in this study. A certified analytical control standard which contains a mixture of heavy metals and a laboratory waste stream which came from the analysis of chloride which contains Chromium and Mercury.

2.2 REMOTOX will be added into both solutions. Observations will be recorded until reaction is complete. The completion of the reaction will be indicated by a clear supernatant and metals precipitated at the bottom.

2.3 After the completion of the reaction, the supernatant of the samples will be analyzed for their heavy metal content.

2.4 If the heavy metal levels are not below the hazardous waste disposal limit, subsequent additions of REMOTOX and/or acid will be added until the concentrations are below the limits.

3.0 MATERIALS AND SUPPLIES

3.1 REMOTOX: Solution obtained from Graus Chemicals, LLC.

3.2 Sample #1: Analytical Control Standard of Heavy Metals. Certified analytical standard that contains a mixture of Arsenic, Cadmium, Mercury, Lead, and Selenium.

3.3 Sample #2: Laboratory Waste Stream. Laboratory waste from the analysis of chloride which contains Chromium and Mercury.

3.4 Nitric Acid 70% Reagent Grade, ACS

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3.5 Hydrochloric Acid 50% V/V (6M)

4.0 PROCEDURE

First Addition of REMOTOX (First Aliquot)

4.1 Prepare 100 mL of Sample #1 (**3.2**) and Sample #2 (**3.3**) into a 250 mL bottle.

4.2 Add 5 mL of REMOTOX (**3.1**) and wait for the reaction. Record the time when the reaction appears to be complete.

4.3 After the reaction period, mix sample thoroughly. Then immediately take two 25 mL aliquots from each bottle into a 50 mL centrifuge vial.

4.4 Centrifuge samples for 15 min.

4.5 Pipet the supernatant and analyze for heavy metals.

Second Addition of REMOTOX to Sample #2 (Second Aliquot)

4.6 From the centrifuged Sample #2 (**4.4**), take a 20 mL aliquot into a 50 mL centrifuge vial for each vial, respectively.

4.7 Add 2 mL of REMOTOX (**3.1**) and wait for reaction. Record the time when the reaction appears to be complete.

4.8 Centrifuge samples for 15 min.

4.9 Pipet the supernatant and analyze for heavy metals.

Acidification of Sample #2 (Third Aliquot)

4.10 From the centrifuged Sample #2 (**4.8**), decant the supernatant into a 50 mL centrifuge vial for each vial, respectively.

4.11 Add 2 mL of concentrated nitric acid (**3.4**) into one vial and label it “HNO3”

4.12 Add 2 mL of concentrated hydrochloric acid (**3.5**) into the other vial and label it “HCl”.

4.13 Wait for the reaction and record the time when the reaction appears to be complete.

4.14 Centrifuge samples for 15 min.

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4.15 Pipet the supernatant and analyze for heavy metals.

5.0 RESULTS

5.1 **Figure 1** shows the initial color and volume of Sample #1, Sample #2 and the REMOTOX. This is used as a reference. The samples labeled from left to right: Sample #1, Sample #1 before addition of REMOTOX, Sample #2 before addition of REMOTOX, Sample #2, and REMOTOX.

Figure 1: Initial Samples

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5.2 **Figure 2** shows the immediate reaction of the Sample #1 and Sample #2 after the first addition of REMOTOX. Two distinct layers formed in both samples. The samples labeled from left to right: Initial Sample #1, Sample #1 after addition, Sample #2 after addition, Initial Sample #2, and REMOTOX.

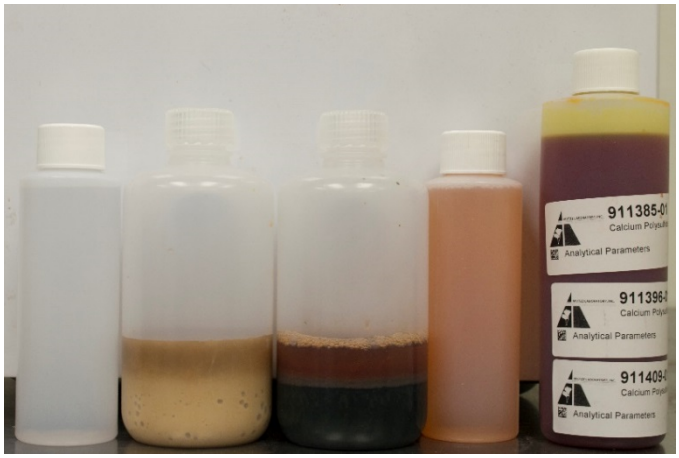

Figure 2: Immediate Reaction After 1st Addition

5.3 **Figure 3** shows the results of the reaction after 1.75 hours of the Sample #1 and Sample #2 after the first addition of REMOTOX. The samples labeled from left to right: Initial Sample #1, Sample #1 after addition, Sample #2 after addition, Initial Sample #2, and REMOTOX.

Figure 3: After Reaction (1.75 hrs)

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5.4 **Figure 4** shows two 25 mL aliquots of Sample #1 and Sample #2. The centrifuged vials labeled from left to right: aliquot of Sample #1, duplicate aliquot of Sample #1, aliquot of Sample #2, and duplicate aliquot Sample #2.

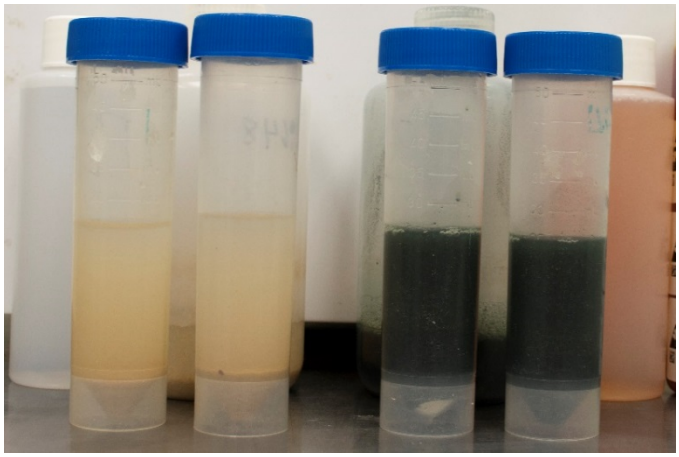

Figure 4: Two 25 mL Aliquots

5.5 **Figure 5** shows two 25 mL aliquots of Sample #1 and Sample #2 after centrifuging the sample for 15 min. There is a clear distinction between the supernatant and the precipitate. The centrifuged vials labeled from left to right: aliquot of Sample #1, duplicate aliquot Sample #1, aliquot of Sample #2, and duplicate aliquot of Sample #2.

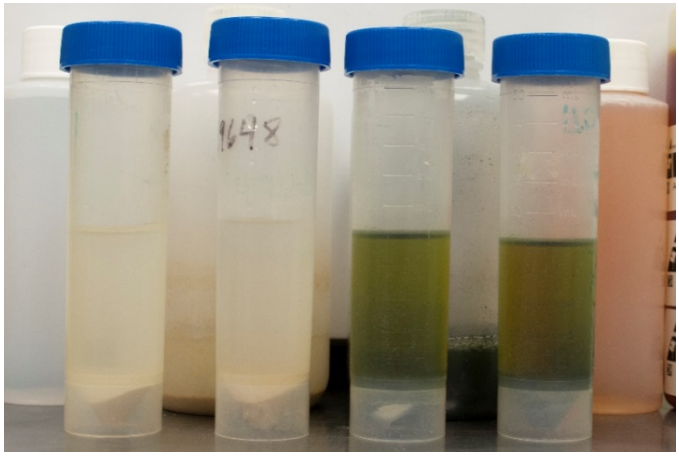

Figure 5: After Centrifuging both 25 mL Aliquots

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5.6 **Figure 6** shows a close-up image of both aliquots of Sample #1 after centrifuging. The supernatant is clear while the precipitate is a light brownish color. Since the volume of the precipitation is below the lowest graduation line (5 mL), the volume can only be approximated at 2.5 mL.

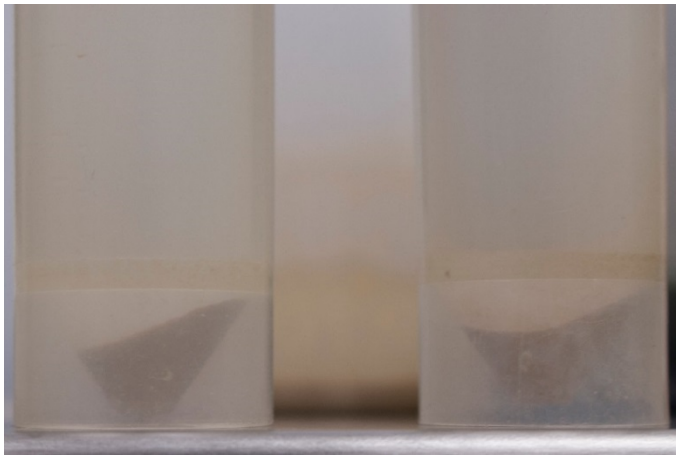

Figure 6: Close-up Centrifuged Aliquot of Sample #1

5.7 **Figure 7** shows a close-up image of Sample #2 after centrifuging. The supernatant is a light green color while the precipitate is a dark grey color. Since the volume of the precipitation is below the lowest graduation line (5 mL), the volume can only be approximated at 2.5 mL.

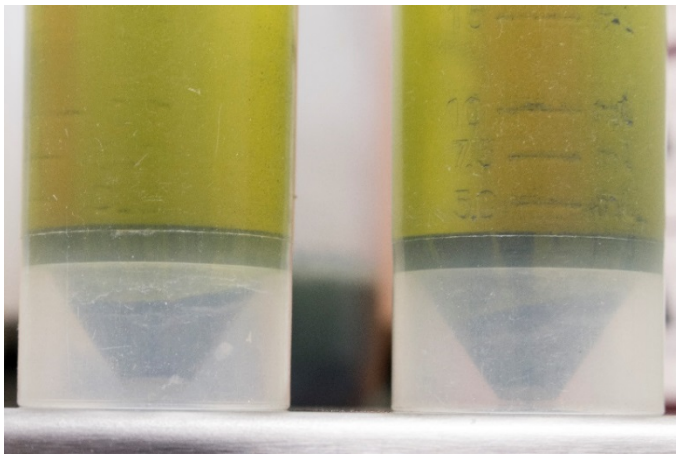

Figure 7: Close-up Centrifuged 1st Aliquot of Sample #2

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5.8 **Figure 8** shows the immediate reaction of the second addition of REMOTOX to Sample #2. There is no distinct formation of layers. The reaction was considered to be complete after 15 mins.

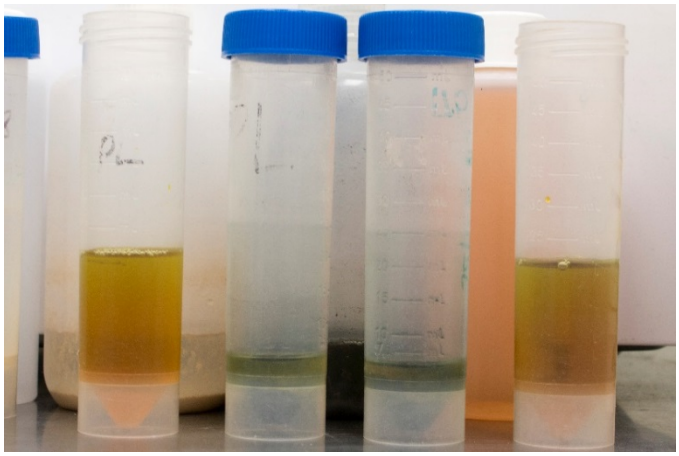

Figure 8: REMOTOX added to 2nd Aliquot of Sample #2

5.9 **Figure 9** shows a close-up of the precipitates formed after the second addition of REMOTOX and centrifuging. The supernatant is a light orange color while the precipitate appears to be black. Since the volume of the precipitation is minimal, the volume will be considered insignificant.

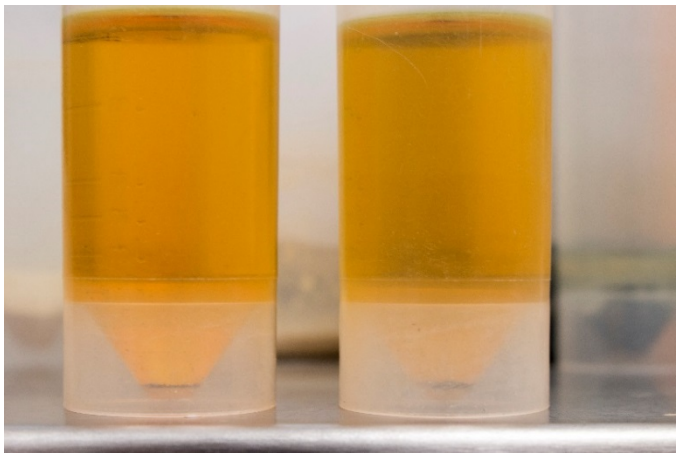

Figure 9: Close-up Centrifuged 2nd Aliquot of Sample #2

5.10 **Figure 10** shows the immediate reaction of adding nitric acid (HNO3) and hydrochloric acid (HCl) to the third aliquot of Sample #2. The centrifuged vials labeled with their respective acid. It is difficult to see any formation of layers in this reaction.

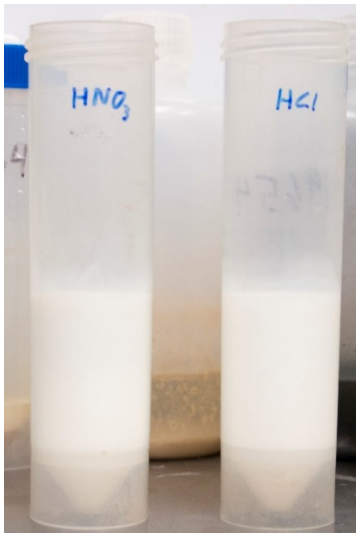

Figure 10: HNO3 and HCl added to the 3rd Aliquot of Sample #2

5.11 **Figure 11** shows a close-up of the precipitates formed after the acidification of the third aliquot. This solution was allowed to stand for one week before centrifuging. The supernatant is a white cloudy color while the precipitate is a greyish color. Since the volume of the precipitation is minimal, the volume will be considered insignificant.

Figure 11:Close-up of Centrifuged 3rd Aliquot of Sample #2

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5.12 **Table 1** shows the heavy metal results from first addition of REMOTOX to Sample #1 after a 1.75 hour reaction time period. The *Initial* column is the starting concentrations of the corresponding metal. The *1st Addition* column is the concentration of the corresponding metals after the first addition of REMOTOX. The percent change is calculated using **Equation 1**.

Sample #1: Control Standard of Heavy Metals			
	Initial	1st Addition	% Change
Ca (%)	<0.001	0.435	-
S (%)	<0.001	0.033	-
As (ppm)	22.735	0.084	-99.6
Cd (ppm)	27.203	0.056	-99.8
Hg (ppm)	0.159	0.004	-97.2
Pb (ppm)	35.718	0.089	-99.8
Se (ppm)	9.658	0.146	-98.5

Table 1: Sample #1 Heavy Metals Results

5.13 **Table 2** shows the heavy metal results from the first addition of REMOTOX to Sample #2 after a 1.75 hour reaction time. The *Initial* column is the starting concentrations of the corresponding metal. The *1st Addition* column is the concentration of the corresponding metals after the first addition of REMOTOX. The percent change is calculated using **Equation 1**.

Sample #2: Laboratory Waste Stream 1st Addition			
	Initial (ppm)	1st Addition (ppm)	% Change
Ca (%)	<0.001	0.431	-
S (%)	<0.001	0.283	-
Cr (ppm)	0.887	0.168	-81.1
Hg (ppm)	152.633	3.805	-97.5

Table 2: Sample #2 Heavy Metals Results for the 1st Addition

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Table 3 shows the heavy metal results from the second addition of REMOTOX to Sample #2 after a 15 min reaction time. The *Initial* column is the starting concentrations of the corresponding metal. The *2nd Addition* column is the concentration of the corresponding metals after the second addition of REMOTOX. The percent change is calculated using **Equation 1**.

Sample #2: Laboratory Waste Stream 2nd Addition			
	Initial	2nd Addition	% Change
Cr (ppm)	0.887	0.103	-88.4
Hg (ppm)	152.633	3.318	-97.8

Table 3: Sample #2 Heavy Metals Results for the 2nd Addition

5.14 **Table 4** shows the heavy metal results after the addition of hydrochloric acid to the third aliquot of Sample #2. The *Initial* column is the starting concentrations of the corresponding metal. The *HCl Addition* column is the concentration of the corresponding metal after the hydrochloric acid addition to the aliquot. The percent change is calculated using **Equation 1**.

Sample #2: Laboratory Waste Stream HCl Addition			
	Initial	HCl Addition	% Change
Cr (ppm)	0.887	0.038	-95.7
Hg (ppm)	152.633	0.079	-99.9

Table 4: Sample #2 Heavy Metals Results for the HCl Addition

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5.1 **Table 5** shows the heavy metal results after the addition of nitric acid to the third aliquot of Sample #2. The *Initial* column is the starting concentrations of the corresponding metal. The *HNO3 Addition* column is the concentration of the corresponding metal after the nitric acid addition to the aliquot. The percent change is calculated using **Equation 1**.

Sample #2: Laboratory Waste Stream HNO3 Addition			
	Initial	HNO3 Addition	% Change
Cr (ppm)	0.887	0.030	-96.6
Hg (ppm)	152.633	0.014	-99.9

Table 5: Sample #2 Heavy Metals Results for the HNO3 Addition

5.2 **Equation 1** is the equation used to calculate the percent change in concentration. The percent change is the difference in concentration divided by the initial concentration multiplied by 100.

$$\%\ Change\ = \frac{Final\ Concentration - Initial\ Concentration}{Initial\ Concentration} \times 100$$

Equation 1: Percent Change Equation

6.0 DATA ANALYSIS

6.1 *Effectiveness and Efficiency of the Precipitation of Heavy Metals*

6.1.1 Observing the physical appearance of the samples: There is an immediate precipitation as the REMOTOX is added. This can be seen in both Sample #1 and Sample #2.

6.1.2 For Sample #1, the initial color was clear (**Figure 1**). After the addition of REMOTOX, there was a distinct two layers of color (**Figure 2**). The top layer was dark brown and the bottom layer was light brown with visible formation of gas bubbles. After the reaction has taken place and the solution was centrifuged, the supernatant was clear and the precipitation was light brownish color (**Figure 6**). Since the formation of the precipitate was below the last graduation line (5 mL) on the centrifuge vial, only an estimate can be made of the total volume of

the precipitate. The total volume of precipitate from both centrifuge vials was approximately 5 mL. Since this was an aliquot of the original volume, the precipitation of the original sample volume is approximately 10 mL. As a result, approximately 10% of the solution has precipitated out of solution after the addition of the REMOTOX. From the physical appearance, it is unclear of the composition of the supernatant and the precipitate.

6.1.3 For Sample #2, the initial color was light orange (**Figure 1**). After the addition of REMOTOX, there was a distinct two layers of color (**Figure 2**). The top layer was light green and the bottom layer was dark grey (**Figure 7**). Similar to Sample #1, the formation of the precipitate was below the last graduation line (5 mL) on the centrifuge vial. Therefore, only an estimate can be made of the total volume of the precipitate. The total volume of precipitate from both centrifuge vials was also approximately 5 mL. Although there was precipitation from the second addition of REMOTOX and the acidification of the third aliquot, the volume could not be approximated. Therefore, it was considered insignificant. Since this was an aliquot of the original volume, the precipitation of the original sample volume is approximately 10 mL. As a result, approximately 10% of the solution has precipitated out of solution after the addition of the REMOTOX. From the physical appearance, it is unclear of the composition of the supernatant and the precipitate.

6.1.4 Reviewing the analysis of the heavy metals analysis: There is a distinct reduction of heavy metals in Sample #1 and Sample #2 from the initial analysis to the 1st addition of REMOTOX.

6.1.5 For Sample #1, the heavy metals of interest were Arsenic (As), Cadmium (Cd), Mercury (Hg), Lead (Pb), and Selenium (Se). The heavy metal concentrations have decreased by 99.6%, 99.8%, 97.2%, 99.8%, and 98.5%, respectively. All concentrations were below the 0.2 ppm limit.

6.1.6 For Sample #2, the heavy metals of interest were Chromium (Cr) and Mercury (Hg). The heavy metal concentrations have decreased by 81.1% and 97.5%, respectively. Cr was below the 0.2 ppm limit. However, Hg was 3.8 ppm which is greater than the 0.2 ppm limit.

6.1.7 In order to bring the Mercury levels below the 0.2 ppm limit, a second addition of REMOTOX was added to the aliquot. However, it only resulted in a decrease of 0.3% in respect to the initial concentration.

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6.1.8 Following the second addition of REMOTOX, two different acids (hydrochloric and nitric) was added to decrease the pH and attempt to bring the Mercury levels below the 0.2 ppm limit. After the acid was added and allowed to stand over 7 days, the Hg concentrations have both decreased by 99.9% with respect to the initial concentration. The Hg concentrations from both acids were below the 0.2 ppm limit.

7.0 CONCLUSION

7.1 From the results of this experiment, the addition of REMOTOX clearly precipitates the heavy metal out of solution effectively. In this experiment, approximately 5% of REMOTOX was added in respect to the volume of the sample.

7.2 For Sample #1, this experiment resulted in approximately 10% precipitation of the sample. The supernatant was analyzed for heavy metals and the concentrations were below the waste disposal limits. As a result, only the precipitations need to follow the hazardous waste disposal protocol.

7.3 For Sample #2, this experiment also resulted in approximately 10% precipitation of the sample. The supernatant was analyzed for heavy metals and the Chromium concentration was below the waste disposal limit. However, after the first addition of REMOTOX the Mercury concentration was still above the waste disposal limit. Even though the concentration is still above the limit, the reduction of Mercury was still significant at 97.5%.

7.4 As a result, a subsequent addition of REMOTOX was added to the remaining supernatant in an attempt bring the mercury limits below the hazardous waste disposal limits. However, this did not have the same efficiency as the first addition and it did not significantly reduce the Mercury concentrations. This may be due to pH of the solution after the first addition. The REMOTOX may have an optimal pH range and the solution was outside of that range.

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7.5 Therefore, to bring the solution to this optimal pH range, two different acids (hydrochloric and nitric) were added to the supernatant after the second addition. Since it was difficult to see the completion of the reaction. The reaction was given one week to take place. The result was a significant improvement over the subsequent addition of REMOTOX. The Mercury concentration decreased by 99.9% with respect to the initial concentration and below the hazardous waste limit. As a result, only the precipitations formed by the subsequent additions of REMOTOX and acid need to follow the hazardous waste protocol.

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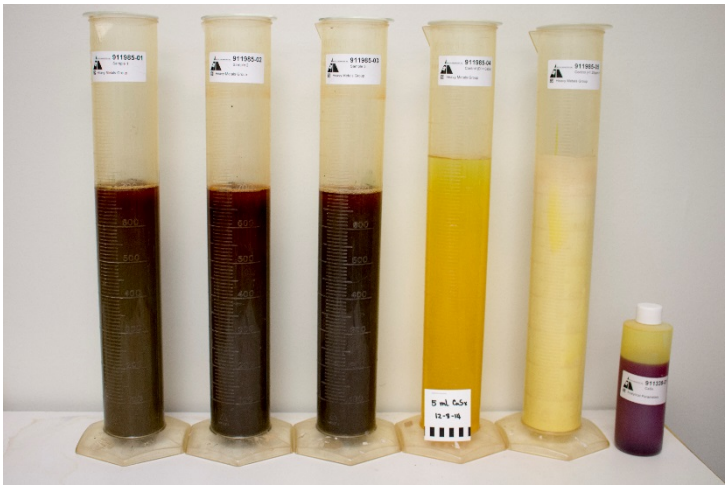
8.0 APPENDIX

8.1 The following pictures are from a similar experiment that was not discussed in this report. The graduation cylinders labeled from left to right: Laboratory Waste Stream # 1, Lab Waste Stream #2, Lab Waste Stream #3, Control Standard, DI Water, REMOTOX. Each image is labeled with the how many days after the first addition of REMOTOX and the number of subsequent additions after.

Appendix 1: Initial Image



Appendix 2: First Addition of REMOTOX

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Appendix 3: Day 1, Addition 1

Appendix 4: Day 2, Addition 1

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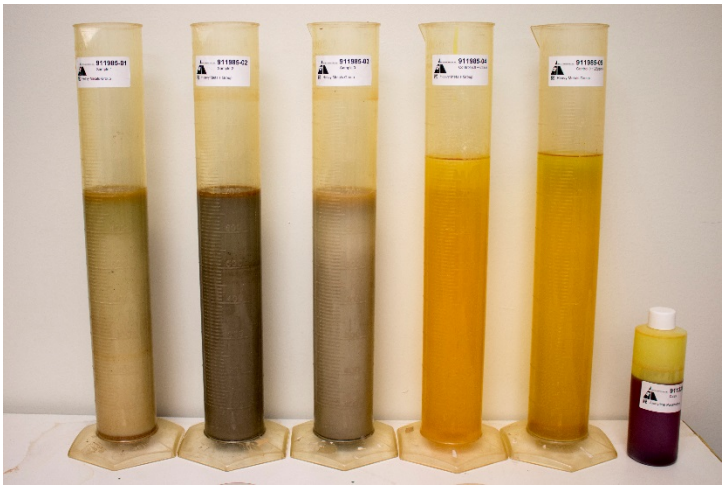

Appendix 5: Day 2, Addition 2

12/12

Appendix 6: Day 3, Addition 2

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Appendix 7: Day 6, Addition 3

Appendix 8: Day 8, Addition 4

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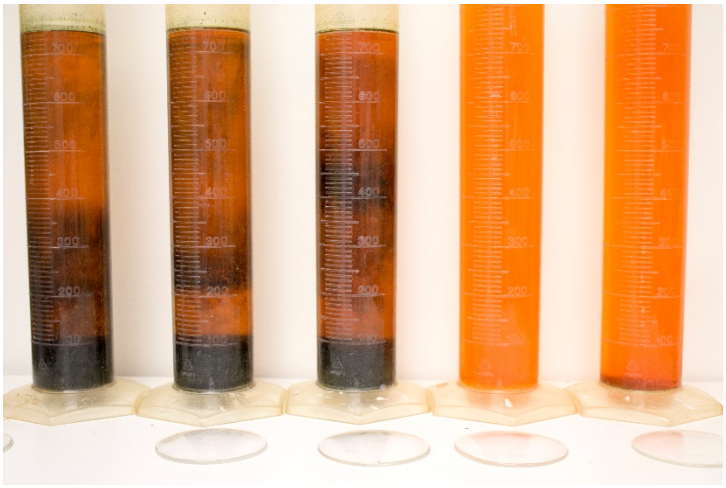

Appendix 9: Day 24, Addition 5

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