# Phosphorus Removal Properties of Blast Furnace Slag and Storm Water BMP Applications

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Testing Data Provided by:
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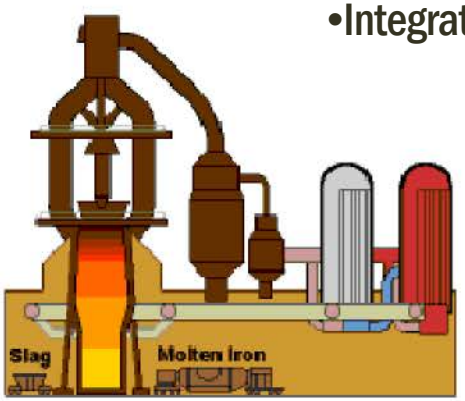
# •What kinds of slag exist in US?

- **All slags generated from high temperature (metals processing) industries**
- **Iron- and Steel-Making Slags (BF, BOF, EAF, Ladle, Stainless)**
  - Highly controlled material by virtue of steel making process.
  - High environmental quality. Granular, but reactive
  - After iron recovery, BF/BOF/EAF slags is crushed and screened to make aggregates.
- **Copper & Lead Smelting Slags**
  - Typically associated with Superfund & RCRA sites (Raritan Bay, NJ, others)
- **Chromium Slags (aka: Chromite Ore Processing Residue; COPR)**
  - Typically associated with Superfund & RCRA sites (New Jersey, Baltimore)
- **Foundry Slags**
- **Power Generation Slags**
  - Incinerator and Bottom Ashes & Slags
- **Scoria & Volcanic Materials**
  - Found in cool places (Hawaii) and great wine destinations (Italy, Greece, Napa)

# •How are iron-and steel-making slags produced?

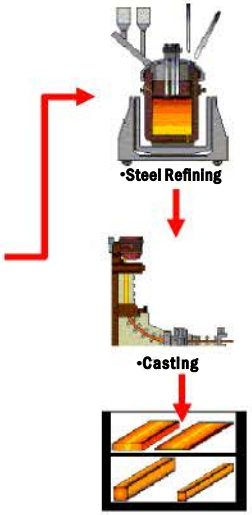
•Integrated Steel Mills




•Blast Furnace

•Liquid Iron

•Basic Oxygen Furnace



•Blast Furnace Slag

Recycled Steel

Steel Furnace Slag

# •Slags are Air and/or Water cooled

- **Blast Furnace Slag**
  - Rapid cooling corresponds to high amorphous mineral content
  - Low Fe content. Good for cements, mineral wool, glass manufacturing
    Light weight aggregates, sorbent, water purification and treatment

# •BF Slag Testing Program – WAC NR 538 , NR 660

- Geochemistry & Leaching
  - XRF & QXRD
  - EPA 1311, 1312, 1313
  - TAL (Metal /Cyanide Target Analyte List )Suite

- Phosphate Immobilization Experiments
  - AASHTO No. 10 (<3/8”)
  - AASHTO No. 67 (1” clean)
  - AASTHO No. 3 (2” x 1”)
  - PO4 concentrations of 1, 5, 10 mg/L
  - Equilibration times (5, 10 min; 1, 8, 24, 72 hours)

- Bulk Density & Water Displacement

# •BF Slag Geochemistry by XRF & QXRD

•XRF Chemical Analysis

| Element | Wt% |
|---|---|
| Ca | 26.42 |
| Si | 17.69 |
| Mg | 6.36 |
| Al | 4.64 |
| S | 1.32 |
| K | 0.51 |
| Fe | 0.44 |
| C | 0.32 |
| Ti | 0.29 |
| Mn | 0.27 |
| Na | 0.22 |
| Cr | 0.02 |
| P | 0.01 |
| Total | 58.50 |

| Total Sample | | Normalized Bemental Composition Amorphous Fraction 1 | | Crystalline Fraction | |
|---|---|---|---|---|---|
| Element | Wt% | Wt% | Distribution ! | Wt% | Distribution |
| Ca | 45.2% | 33.6% | 17.5% | 48.7% | 82.5% |
| Si | 30.2% | 24.0% | 18.6% | 32.1% | 81.4% |
| Mg | 10.9% | 5.5% | 12.0% | 12.5% | 88.0% |
| Al | 7.9% | 16.0% | 47.2% | 5.5% | 52.8% |
| S | 2.3% | 5.9% | 72.0% | 0.8% | 28.0% |
| K | 0.9% | 3.7% | 100.0% | 0.0% | 0.0% |
| Fe | 0.8% | 2.0% | 60.7% | 0.4% | 39.3% |
| C | 0.5% | 2.3% | 100.0% | 0.0% | 0.0% |
| Ti | 0.5% | 2.1% | 100.0% | 0.0% | 0.0% |
| Mn | 0.5% | 1.9% | 100.0% | 0.0% | 0.0% |
| Na | 0.4% | 1.6% | 100.0% | 0.0% | 0.0% |
| Cr | 0.0% | 0.2% | 100.0% | 0_0% | 0.0% |
| P | 0.0% | 0.1% | 100.0% | 0.0% | 0.0% |
| Total | 100.0% | 100.0% | | 100.0% | |

• Quantitative X-Ray Diffraction Analysis Compounds

| •Mineral Name Formula | Wt% |
|---|---|
| •Amorphous Material | 24.4 |
| •Akermanite Ca2Mg81207 | 57.3 |
| Gehlenite Ca2/1123107 | 11.6 |
| Diopside CaMgSi206 | 4.2 |
| Epidote Ca2FeAl2Si3012(OH) | 1.5 |
| •Oldhamite CaS | 0.8 |
| Merwinite Ca3Mg(SiO4)2 | 0.2 |
| •Total | 100.0 |

•Major Oxides

| Oxide | Wt .% |
|---|---|
| Ca° | 37.0 |
| $102 | 37.8 |
| A1203 | 8.8 |
| Fe2D3 | 0.6 |
| MgO | 10.5 |
| LOI | 0.0 |
| Sum | 94.7 |

# •WDNR Testing Suite - DIW Leach

| | NR 538, WI Admin Code, Appendix 1 | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Category 1** | **Category 2&3** | **Category 4** | **Replicate 1** | | **Replicate** 2 | |
| **Water Leach Test (ASTM D3987)** | | | | | | | |
| **Parameter** | **mg/l** | **mg/l** | **mg/l** | mg/l | | mg/1 | |
| Aluminum | 1.5 | -- | - | 1.58 | | 1.54 | |
| Antimony | 0.0012 | 0.012 | -- | 0.005 | **U** | 0.005 | U |
| Arsenic | 0.005 | 0.05 | **--** | 0.01 | **U** | **0.01** | **U** |
| Barium | 0.4 | 4 | | 0.21 | | 0.23 | |
| Beryllium | 0.0004 | 0.004 | -- | 0.0005 | U | 0.0005 | U |
| Cadmium | 0.0005 | 0.005 | 0.025 | 0.0005 | U | 0.0005 | li |
| Chromium, Tot | 0.01 | 0.1 | -- | 0.001 | U | 0.001 | U |
| Copper | 0.13 | -- | -- | 0.0025 | U | 0.0025 | U |
| Total Cyanide | 0.04 | - | - | 0.0015 | U | 0.0015 | U |
| Fluoride | 0.8 | -- | -- | 0.39 | | 0.39 | |
| Iron | 0.15 | 1.5 | 3 | 0.01 | U | 0.01 | U |
| Lead | 0.0015 | 0.015 | 0.075 | 0.01 | **U** | **0.01** | **U** |
| Manganese | 0.025 | 0.25 | -- | 0.0018 | J | 0.0018 | J |
| Mercury | 0.0002 | 0.0002 | 0.01 | 0.0001 | U | 0.0001 | U |
| Nickel | 0.02 | | | 0.0025 | U | 0.0025 | U |
| Selenium | 0.01 | 0.1 | -- | 0.02 | **U** | 0.02 | **U** |
| Sulfate | 125 | -- | -- | 18.4 | | 21 | E |
| Thallium | 0.0004 | -- | -- | 0,048 | | 0,017 | J |
| Zinc | 2.5 | -- | -- | 0.006 | J | 0.007 | J |

•Exceeds Category 1, but satisfies all other categories

•"J" flagged; the analyte was positively identified. The associated numerical value is an estimated quantity.

•"U" flagged: The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

# •WDNR aquifer criteria & SPLP leaching of soil like media

| Metal | WI Ground Water Quality Standard.' | Blast Furnace Slag | Top Soil | Potting Soil 2 | Wood Mulch 2 | Bentonite | Kaolinite | Limestone | RCA | MV |
|---|---|---|---|---|---|---|---|---|---|---|
| Units | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) |
| Aluminum (Al) | 0.200 | 3.72 | 11.70 | 7.93 | 0.279 | 109 | 11.0 | 0.182 | 0.71 | 0.389 |
| Antimony (Sb) | 0.006 | 0.0069 | <0.0345 | <0.0345 | <0.0345 | <0.0345 | <0.0345 | <0.0345 | <0.0345 | <0.0345 |
| Arsenic (As) | 0.010 | <0.010 | <0.0632 | <0.0632 | <0.0632 | <0.0632 | <0.0632 | <0.0632 | <0.0632 | <0.0632 |
| Barium (Ba) | 2.00 | 0.173 | 0.0869 | 0.0834 | 0.0347 | 0.467 | 0.0662 | 0.0192 | 0.218 | <0.001 |
| Beryllium (Be) | 0.004 | 0.0005 | 0.0013 | <0.00106 | <0.00106 | 0.00399 | 0.00148 | <0.00106 | <0.00106 | <0.00106 |
| Cadmium (Cd) | 0.005 | <0.0005 | <0.00169 | <0.00169 | <0.00169 | <0.00169 | <0.00169 | <0.00169 | <0.00169 | 0.00201 |
| Chromium (Cr tot) | 0.100 | 0.0064 | 0.0141 | 0.0148 | <0.00727 | <0.00727 | 0.0141 | <0.00727 | 0.0362 | 0.641 |
| Copper (Cu) | 1.30 | 0.0257 | 0.0304 | 0.0479 | 0.0164 | 0.0279 | <0.0119 | <0.0119 | 0.0251 | 16.2 |
| Iron (Fe) | 0.300 | 0.279 | 10.40 | 4.26 | 0.327 | 37.0 | 1.96 | <0.08 | <0.08 | 61.8 |
| Lead (Pb) | 0.015 | <0.010 | <0.0136 | <0.0136 | <0.0136 | 0.0368 | <0.0136 | <0.0136 | <0.0136 | <0.0136 |
| Manganese (Mn) | 0.300 | 0.303 | 0.0857 | 0.0602 | 0.0277 | 0.19 | 0.017 | <0.00732 | <0.00732 | 10.9 |
| Mercury (Hg) | 0.002 | | <0.00015 | <0.00015 | <0.00015 | <0.00015 | 0.00026 | <0.00015 | <0.00015 | <0.00015 |
| Nickel (Ni) | 0.100 | <0.0025 | 0.0146 | <0.0123 | <0.0123 | <0.0123 | <0.0123 | <0.0123 | <0.0123 | 0.241 |
| Selenium (Se) | 0.050 | <0.0200 | <0.105 | <0.105 | <0.105 | <0.105 | <0.105 | <0.105 | <0.105 | 2.69 |
| Silver (Ag) | 0.050 | <0.0013 | <0.013 | <0.013 | <0.013 | <0.013 | <0.013 | <0.013 | <0.013 | <0.013 |
| Thallium (Tl) | 0.002 | <0.0041 | <0.0339 | <0.0339 | 0.0384 | <0.0339 | <0.0339 | <0.0339 | <0.0339 | <0.0339 |
| Tin (Sn) | NR | | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.0445 |
| Vanadium (V) | 0.030 | 0.0198 | 0.0191 | <0.00888 | <0.00888 | 0.0124 | 0.0729 | <0.00888 | <0.00888 | 0.0168 |
| Zinc (Zn) | 5.00 | 0.0516 | 0.0592 | 0.072 | 0.0971 | 0.151 | <0.0278 | <0.0278 | <0.0278 | 13.0 |

•Notes:

•WI = Wisconsin

•SPLP: = Synthetic Precipitation Leaching Procedure

•"<" represents analytical results not detected at detection limit. Equivalent to "U" in lab report.

•NR = Not regulated; -- = Not tested.

•Color coding: Yellow: = SPLP concentrations above Wisconsin Groundwater Standards.

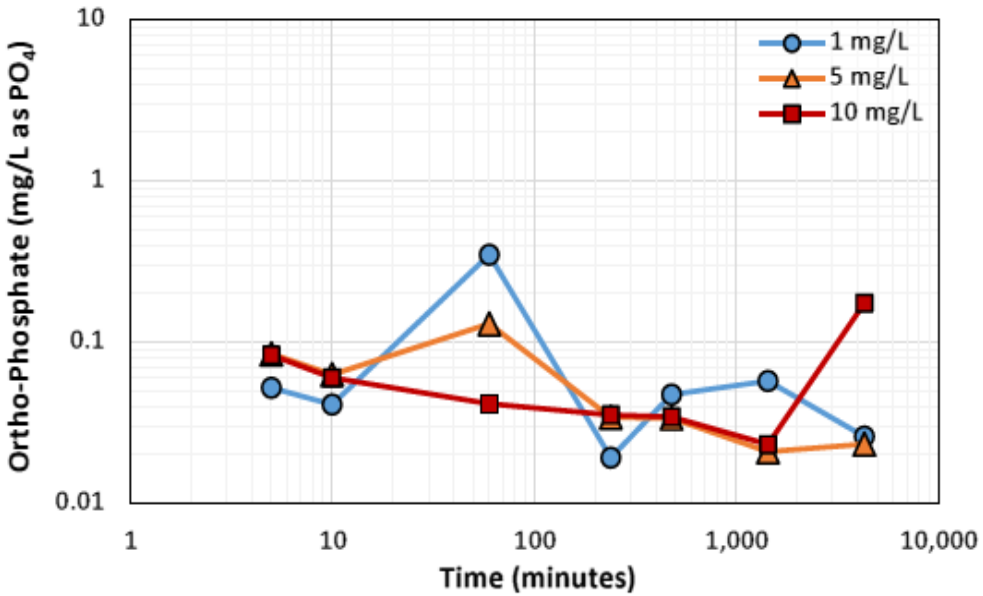
RCA = SHA Recycled Concrete Aggregate

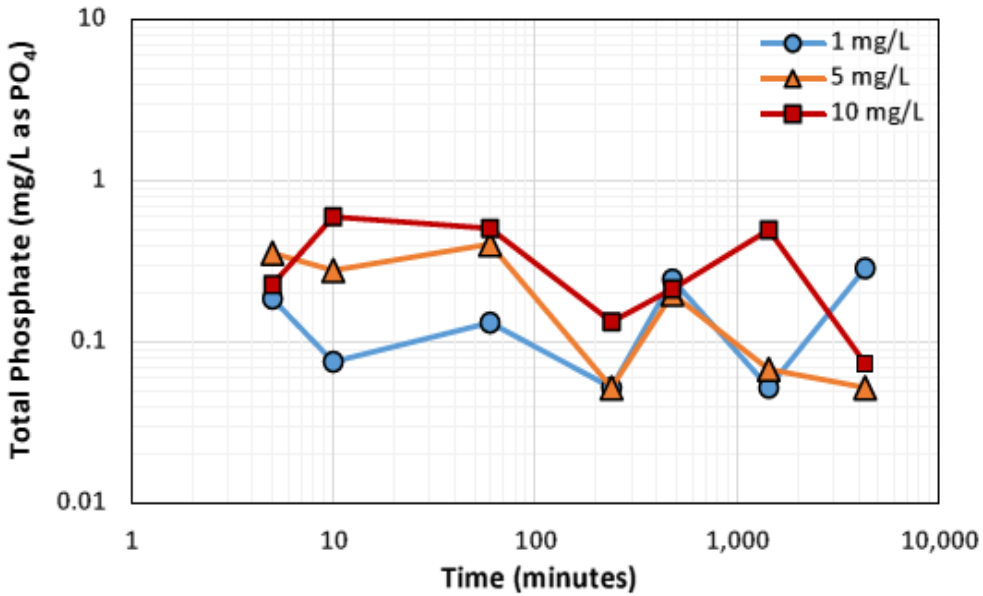
•MV = Multivitamin

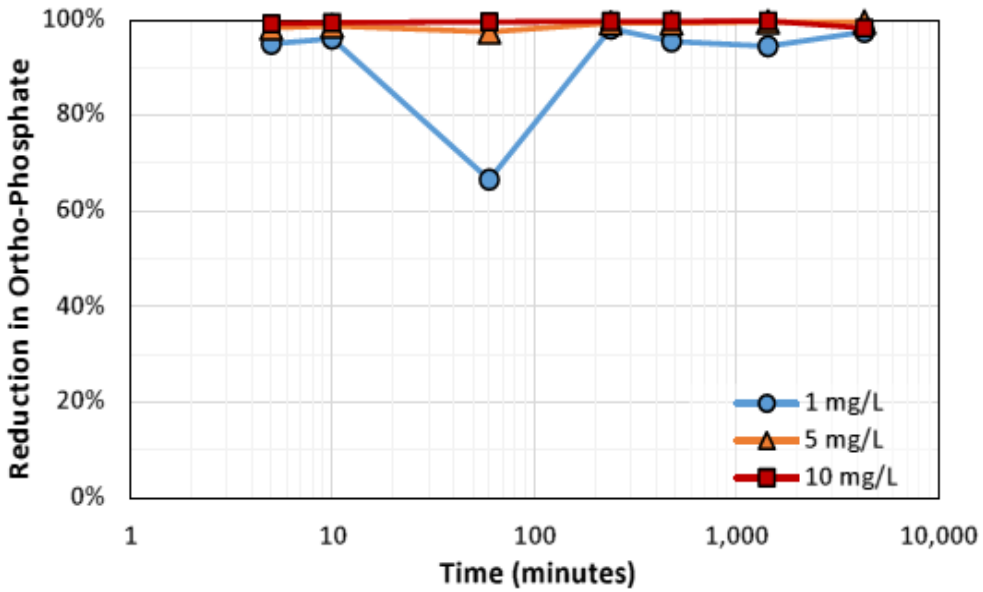
# •BF Slag PO4 Batch Immobilization Experiments

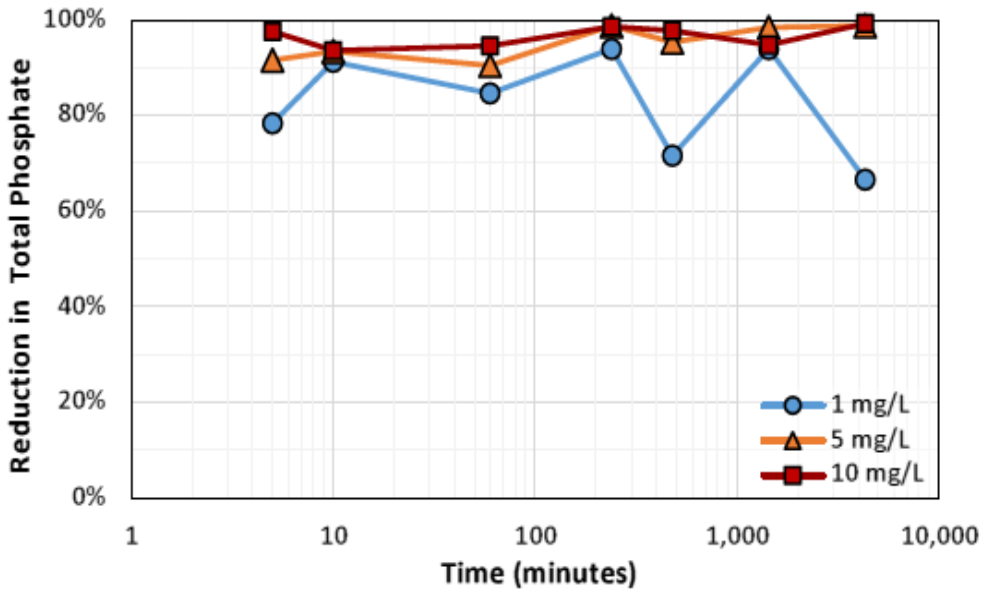
- **Motivation**
  - Bracket PO4 uptake kinetics of BF slag based on expected PAVEDRAIN system residence times and anticipated PO4 levels.
- **Testing Program**
  - <3/8-inch; AASHTO 67, AASHTO 3 sizes
  - PO4 stock solutions: 1, 5, 10 mg/L
  - Contact times: 5, 10 min; 1, 4, 8, 24 and 72 hours
  - L:S ratio 1:1 (in-situ ratio)
  - <3/8 minus & AASHTO 67 on ZHE TCLP tumbler
  - AASHTO 3 on Orbital shaker at 30 RPM

## 3/8"-Minus BF Slag

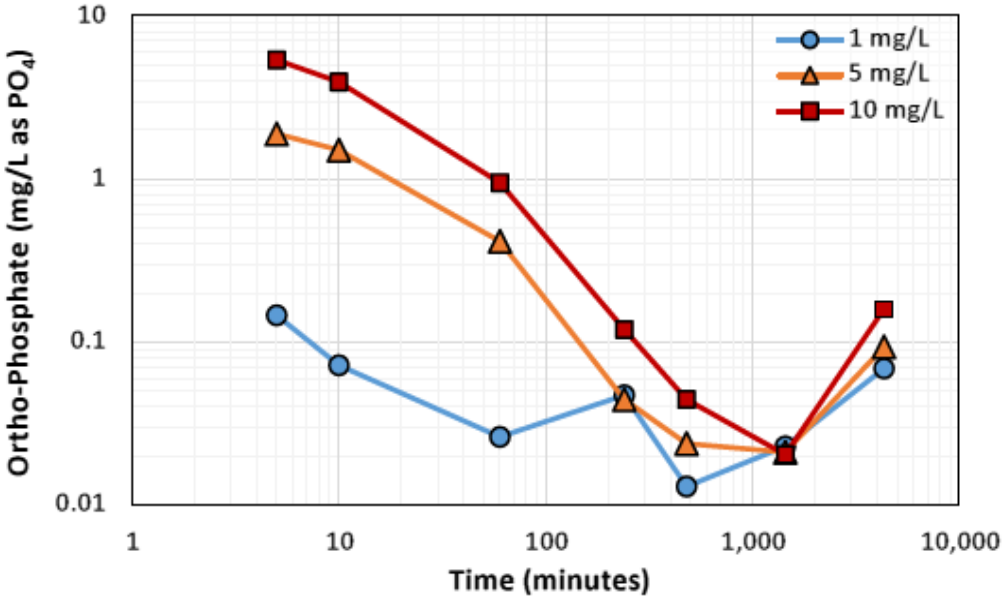


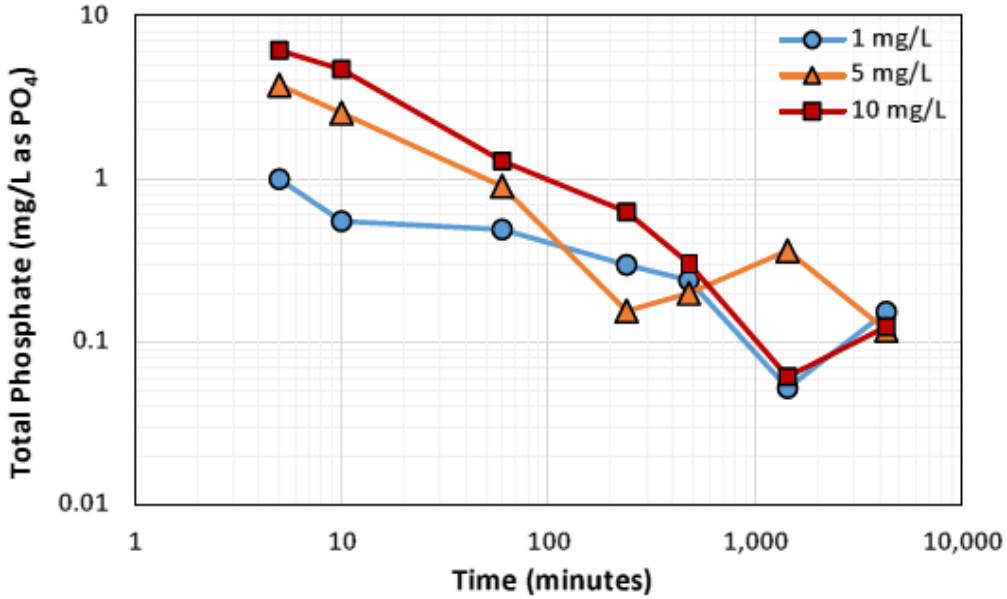



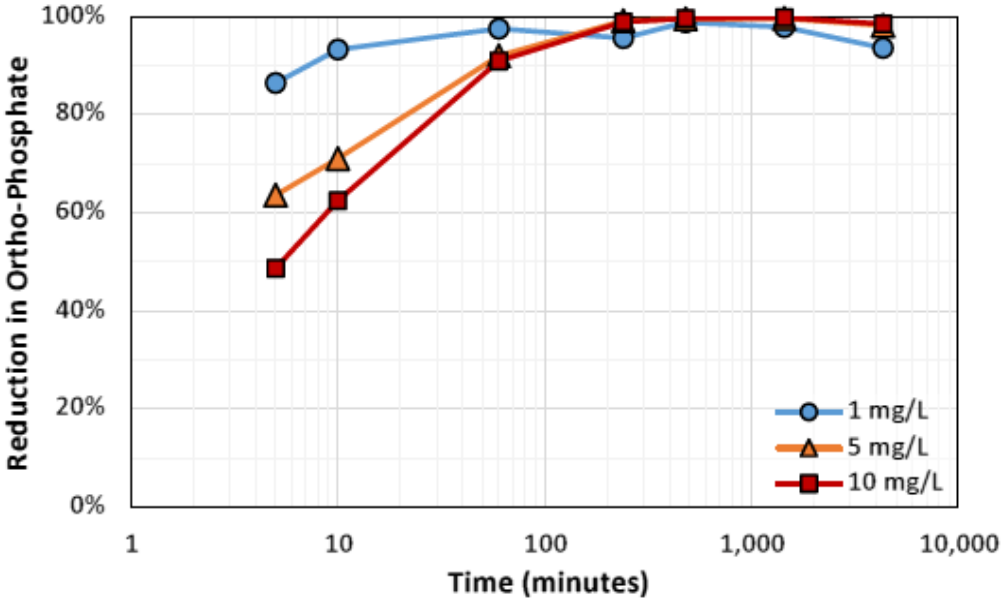



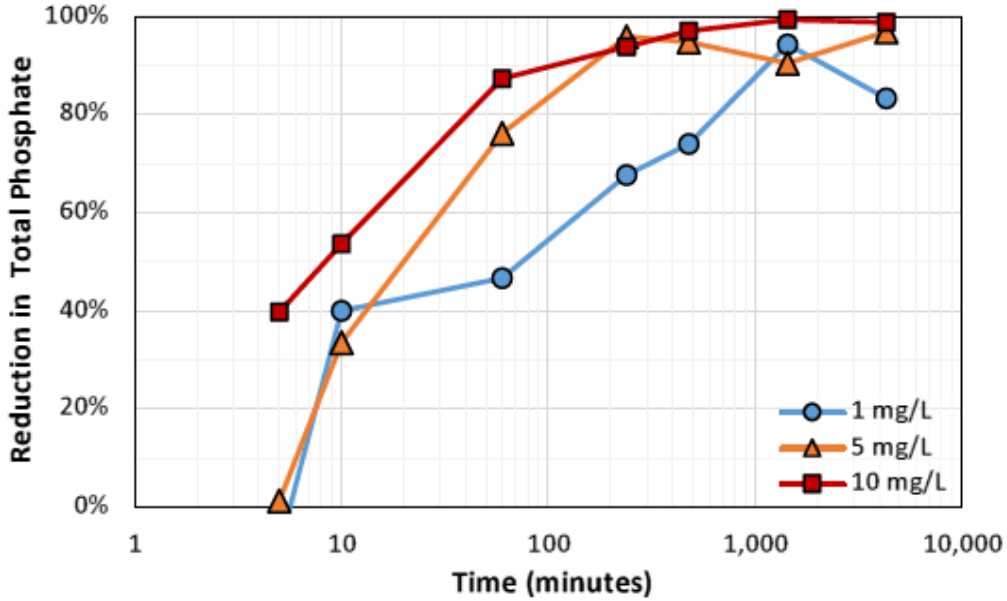



## AASHTO #67 BF Slag

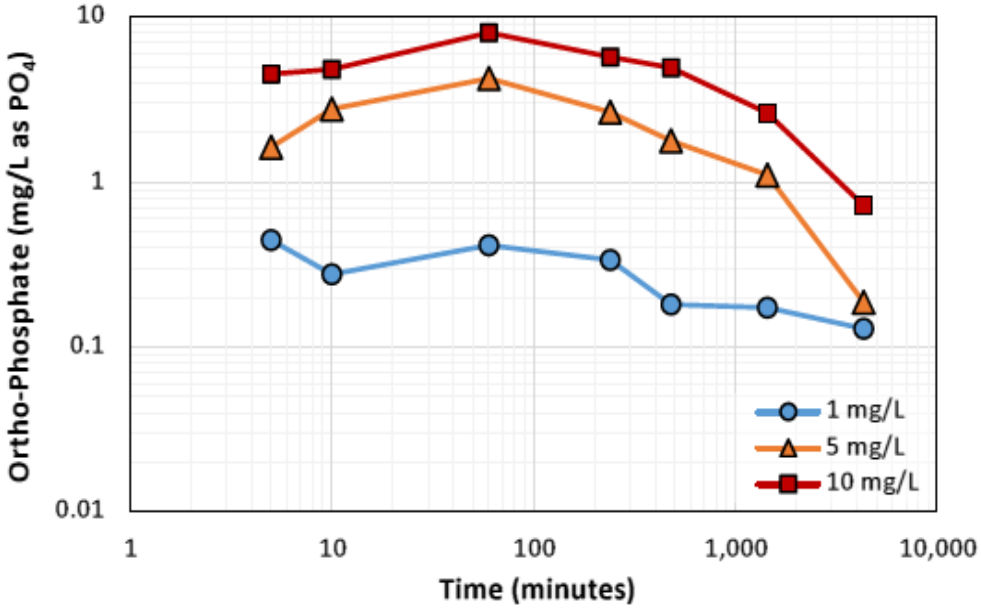


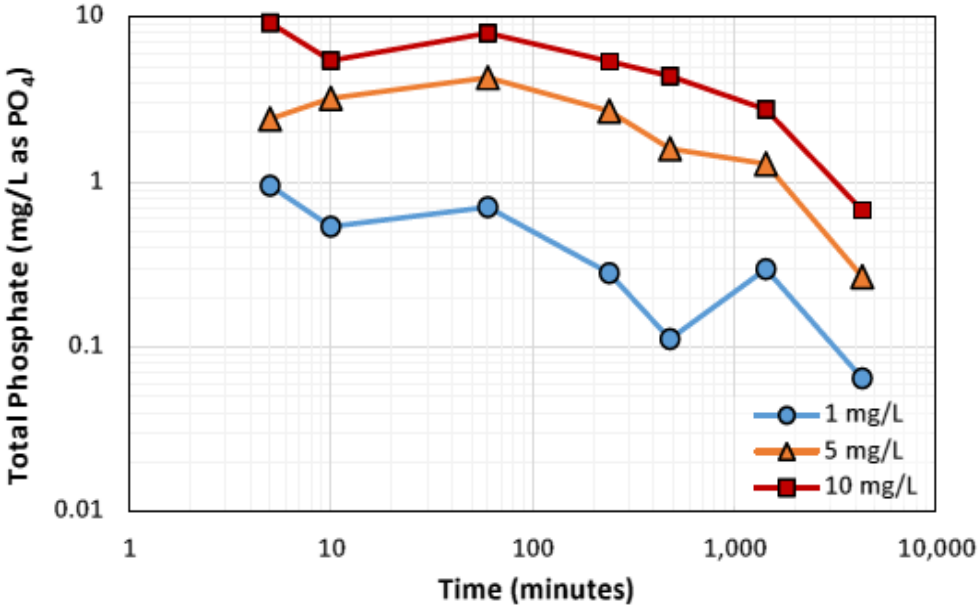



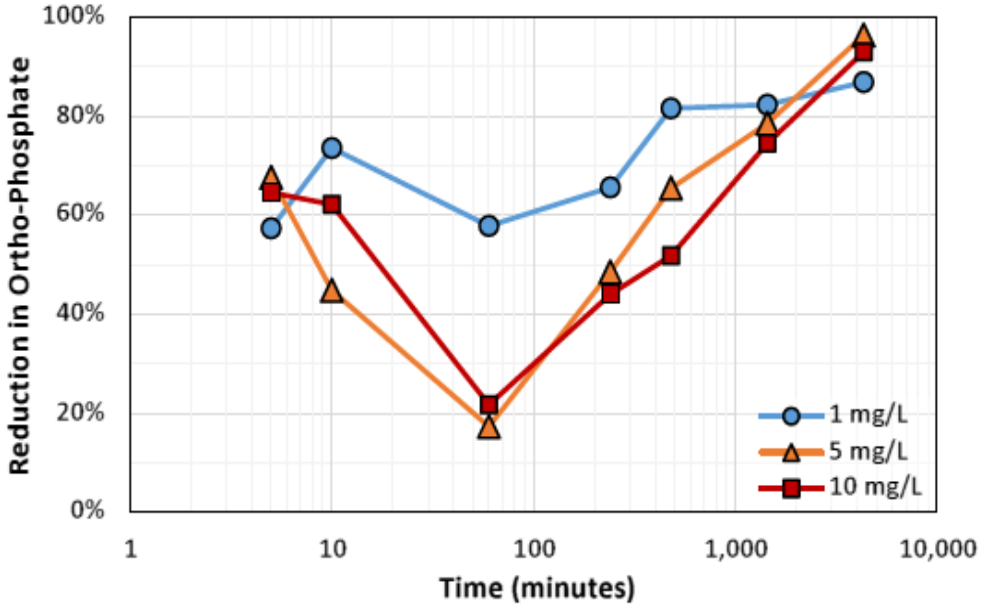



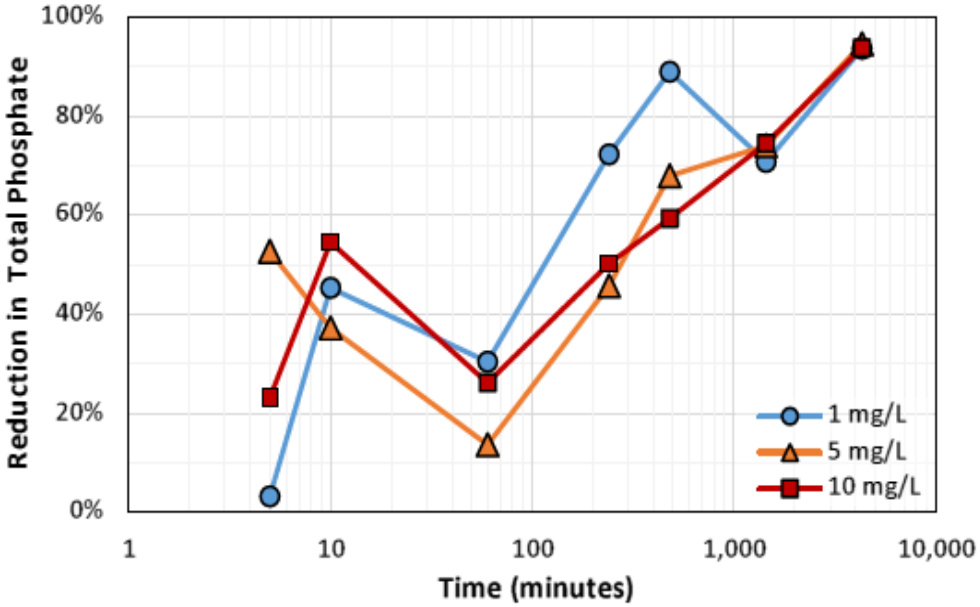



## AASHTO #3 BF Slag

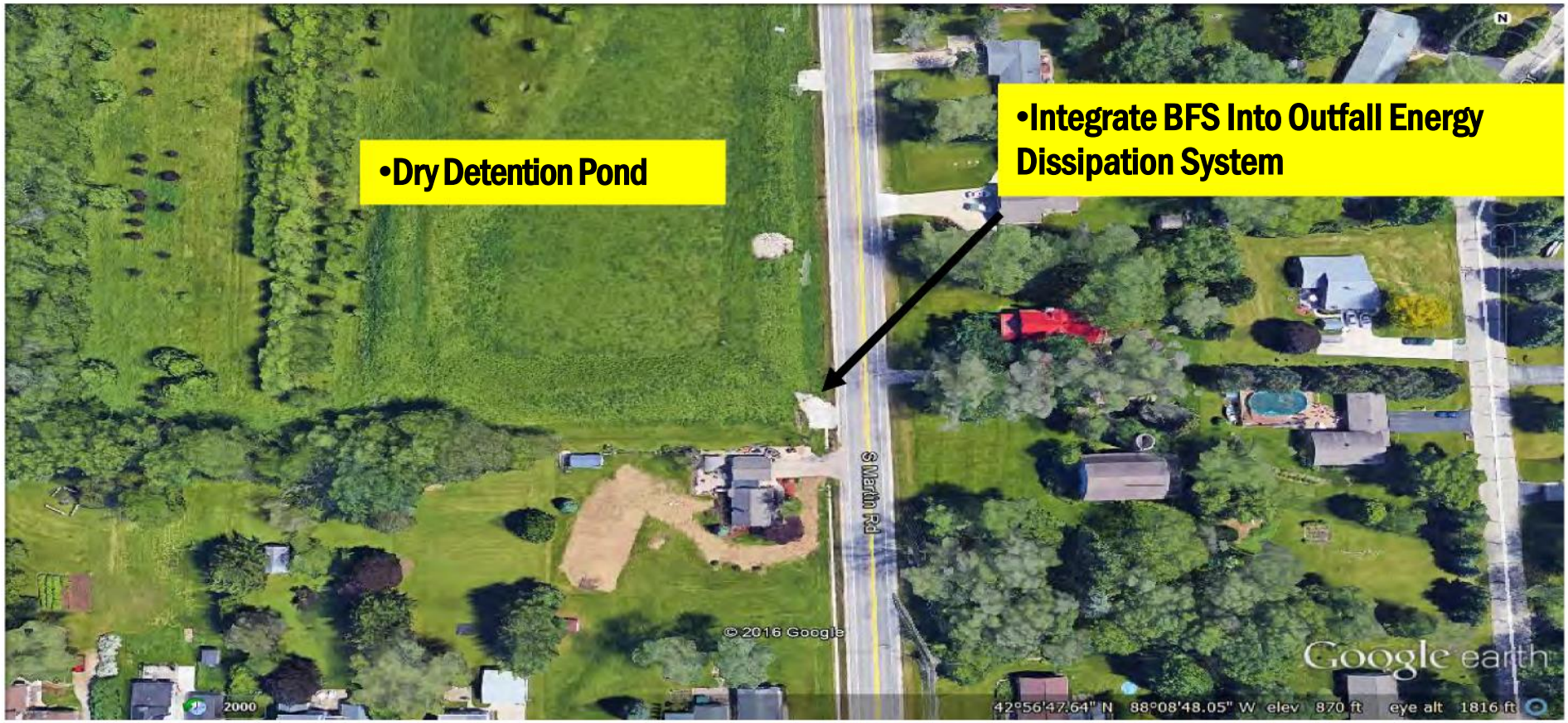


# •Dry Pond Outfall Example

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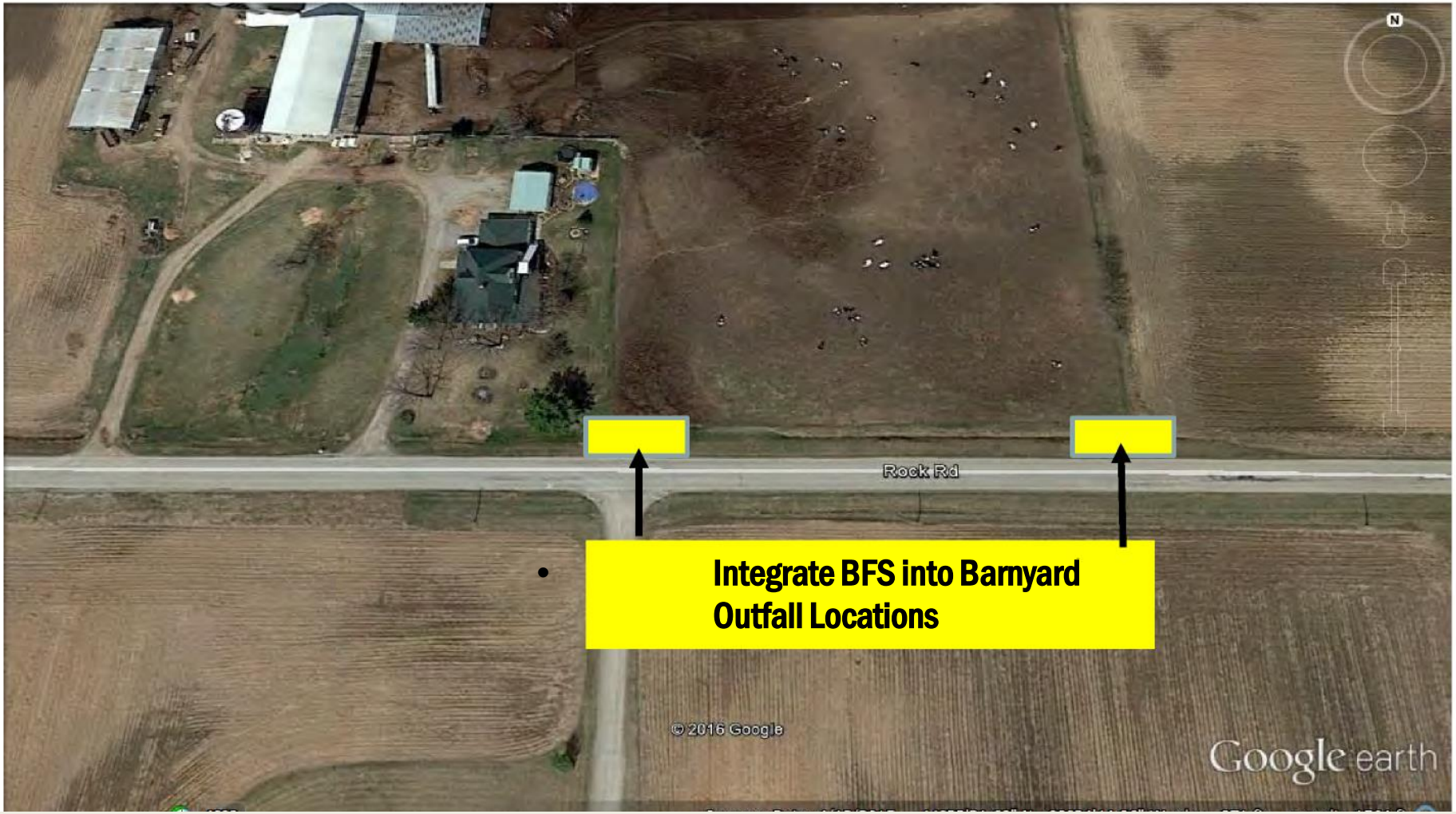
# •Agricultural Runoff/Outfall Example




- **Integrate BFS into Barnyard Outfall Locations**

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# Gabion lined channel

# Rock Check Dams

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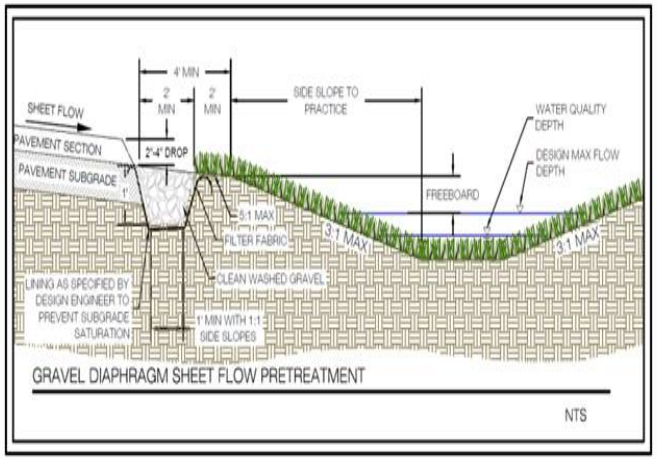
# Outfalls and Shoreline Treatments



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# Permeable Pavement

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# NR 538 Process, Longevity, and Design Considerations

- **NR 538 Process**
  - Draft Exemption Letter
  - Toxicity testing is being performed per the request of WDNR
  - Anticipated submittal of testing results – April 2017
  - Anticipated approvals – June 2017

- **Longevity Testing**
  - 30 bench exchanges – 5mg/l solutions; 24 hour saturation/72 hour dry
  - Considered USGS data from Madison Studies, NURP data and SLAMM models
  - Average 10 year life cycle – dependent on P source concentrations

- **Design Considerations**
  - Contact time
  - Phosphorus source and concentrations
  - Ease of replacement

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# •Summary

- **BF Slag Characterization**
  - BF slag has very high environmental quality.
  - Highly pH buffered, few TAL metals detected, even less leachable.
  - Well suited for filter and PO4 immobilization applications
  - Long term leaching as base/subbase negligible from environmental perspective.

- **PO4 Uptake**
  - BF slag removes substantial PO4 concentrations in short timeframes
  - 3/8”-minus removes > 90% ortho and total PO4 in 10 min for PO4 > 1 mg/L
  - AASHTO 67 removes > 80% ortho and total PO4 in 60 min for PO4 > 5 mg/L
  - AASHTO 3 removes > 60% ortho and total PO4 in 24 hours for PO4 > 5 mg/L

- **Sustainability**
  - BF slag is 100% recycled material.
  - Expended material can be used as aggregate

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# Questions?

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