Adjustment of High pH Waters at the Soo Locks

Response Summary:

The Detroit District contacted the ERDC Environmental Laboratory Chemistry Branch to determine the chemistry, and possible neutralization pathways, of highly alkaline discharge waters at the Soo Locks construction site. Employees of the Detroit District previously determined the water pH to be >12, outside the acceptable range of 6.5 to 9 to meet state water quality standards (WQS). Aliquots of both the discharge water and North Canal river water were shipped overnight to the ERDC for analysis. The pH and specific conductance of water samples were measured upon receipt of the water samples, which were then stored at <4°C prior to further analysis.

ERDC chemists used potentiometric titration and inductively coupled plasma atomic emission spectroscopy (ICP-AES) to further characterize the waters and suspended material. The titrations demonstrated that the discharge waters can be neutralized with hydrochloric acid (HCl) to an acceptable pH of ~8.5. The neutralization of the discharge water requires approximately 1.3 mL of concentrated hydrochloric acid per liter of alkaline discharge water. The physical separation of solids in the discharge water prior to neutralization only marginally affects the pH adjustment as the solids contribute only approximately 5% of the total alkaline capacity of the turbid water. Analysis of total and dissolved metals in the discharge water demonstrates the suspended solid contains primarily calcium (Ca), magnesium (Mg), and silicon (Si), all commonly associated with concrete. In comparison, the North Canal river water showed lower overall concentrations of these elements, with the total and dissolved fractions being essentially the same, as would be expected in a low turbidity aqueous sample. The full titration of the discharge water showed a linear trend for pH adjustment, indicating the absence of a buffer effect. The physical and chemical characteristics of the samples are consistent with these findings, with the discharge waters exhibiting high pH, high alkalinity, and high turbidity.

Period of Performance:

October 2024

Benefits of the Response to the USACE Dredging/Navigation Program:

Accurate determination of the neutralization capacity of the discharge water is critical to potential response efforts needed to bring chemistry parameters within WQS compliance. The results of these experiments confirm the initial findings by the District and provide specific information on sample characterization and potential neutralization guidance. These efforts will help address the current problem and may prevent future issues.

Deliverable:

The ERDC provided chemical and confirmatory pH analysis of field collected water samples. Based upon this analysis, potentiometric titration demonstrated the neutralization capacity of the waters. Further characterization of the solids suspended in the waters yielded insight into the nature of the elevated alkalinity and demonstrated the aqueous fraction to be the main driver of alkalinity compared to the suspended solid phase. This data allows the District a neutralization option for the discharge water *in situ* to bring the parameters into state WQS compliance prior to release.

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CONNECTING THE DOTS TO INNOVATION

SOO LOCK HIGH PH WATER EVALUATION

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BACKGROUND

1) Detroit District personnel contacted ERDC researchers to evaluate high pH waters found at the Soo Lock and Damn construction site

2) District personnel field pH measurements showed elevated pH values above 12, which were confirmed by ERDC laboratory analyses

3) Neutralization titration studies were quickly performed to quantify the amount of alkalinity measured in the field samples to generate a bulk water below pH 9, suitable for discharge to the river

4) Further evaluation was performed to characterize the nature of the pH adjustment

WATER CHARACTERIZATION

- Total metals in the Davis Sump Pit water and North Canal water were first analyzed by ICP-AES
- Subsequently, fresh aliquots were centrifuged to form a pellet and supernatant from each matrix
  - The supernatant was diluted and analyzed for dissolved metals by ICP-AES
  - The pellet was dissolved in 10% nitric acid and analyzed by ICP-AES to confirm the differences observed between total and dissolved metals measured and reported separately in the Analytical Report

Metals Concentration in Davis Sump Pit water and separately in solid and aqueous phase						
24J2501-02	**Ca (mg/L)**	**K (mg/L)**	**Mg (mg/L)**	**Na (mg/L)**	**S (mg/L)**	**Si (mg/L)**
Supernatant 1	195.6	86.7	0.1	87.2	2.8	2.9
Supernatant 2	196.6	86.4	0.1	86.8	2.8	2.8
Supernatant 3	196.2	87.1	0.0	87.3	2.8	2.9
Pellet 1	143.1	27.7	22.2	2.9	0.1	134.6
Pellet 2	135.6	27.0	22.4	5.8	0.1	134.3
Pellet 3	143.2	26.5	21.9	3.1	0.1	129.2
Concentrations in Solid Phase (mg/kg wet weight)						
Pellet 1	21677.3	4201.0	3369.4	443.1	15.2	20394.1
Pellet 2	20237.7	4026.3	3343.0	866.7	17.5	20041.7
Pellet 3	27017.9	5006.0	4128.3	589.2	26.2	24374.9

TITRATION ANALYSIS

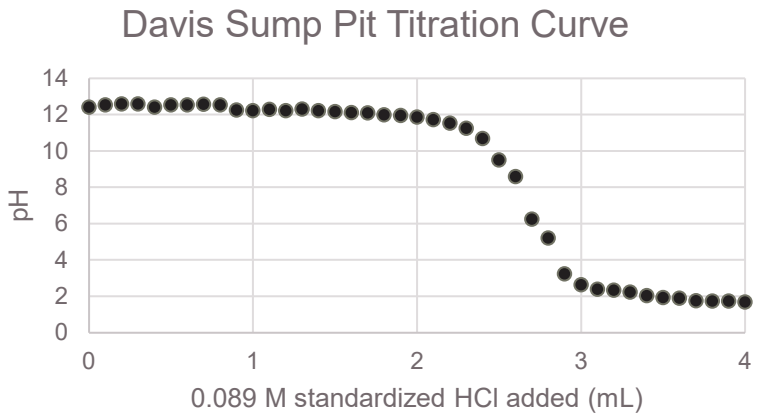
Davis Sump Pit whole water	
Final Neutralization Capacity (mmol HCl)	
AVG	± SD
0.234	0.005

Davis Sump Pit Supernatant	
Final Neutralization Capacity (mmol HCl)	
AVG	± SD
0.217	0.003

Davis Sump Pit Reconstituted Solids	
Final Neutralization Capacity (mmol HCl)	
AVG	± SD
0.010	0.001

- Neutralization capacity of the discharge waters was determined by titration using standardized 0.089 M HCl to a titration endpoint of pH ~8.5
- Similar to the metals analysis, separate sample aliquots (15mL) were centrifuged to form a pellet and supernatant in each sample.
  - The supernatant was titrated with the standardized HCl solution
  - 15 mL of deionized was added to each pellet, followed by shaking for 30 minutes to resuspend the material, prior to titration with standardized HCl
- Titration curve indicates no significant buffer effect
- Titration was done in triplicate for each matrix type
- Neutralization to pH ~ 8.5 requires 1.3 mL of concentrated hydrochloric acid per 1 L of Davis Sump Pit water

HCl needed (mmol)	Davis Sump Pit water treated
0.234	15 mL
15.6	1 L
59.1	1 gal
Assuming starting HCl stock concentration of 37% or 12.06 M then	
0.001	L of HCl to treat 1 L
1.294	**mL of HCl to treat 1 L**



CONCLUSIONS

1) High pH turbid waters from the Davis Sump Pit were evaluated for pH neutralization

2) Suspended solids contribute marginally to the bulk sample alkalinity and contain mostly concrete-related constituents (Ca, Mg, Si)

3) Neutralization with strong acid yields a standard titration curve

4) Neutralization requires approximately 1.3 mL of concentrated hydrochloric acid per liter of Davis Sump Pit water to yield a final pH of ~8.5

5) No other specific hazards or constituents were noted in the samples evaluated