

Whole effluent toxicity assessments and experimental considerations for evaluating coagulation agents and polymers for wastewater treatment of coal combustion

Alexandra N. Steele¹, Konrad J. Kulacki¹, Margaret L. Fleming¹, and William L. Goodfellow, Jr.²

¹Exponent, Inc., 1 Mill and Main Place, Suite 150, Maynard, MA 01754; ²Exponent, Inc., 1800 Diagonal Road, Suite 500, Alexandria, VA 22314

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ABSTRACT

Coal-powered utilities' compliance with the Federal Coal Combustion Residual (CCR) Rule requires the closure or retrofit of facilities that do not meet the Rule's technical criteria for the structural integrity of surface impoundments, or that cause exceedances of groundwater protection standards. The principal closure options require dewatering of the surface impoundment. Dewatering of ash basins often generates effluents with elevated levels of total dissolved solids (TDS). These effluents are typically monitored for individual concentrations of various cations or anions but are seldom evaluated in their entirety. For facilities that have whole effluent toxicity (WET) limits in their NPDES permits, only monitoring specific chemical constituents in the effluent may lead to compliance issues, as elevated TDS in total may be toxic to aquatic organisms. When toxicity to these organisms is observed during WET testing, a toxicity reduction evaluation (TRE) is often required. These methodologies and other toxicity testing methods can be important for facility operators to consider with regards to cases of intermittent toxicity scenarios. This paper will elaborate on the strategies dischargers can consider when intermittent toxicity occurs while facilities are treating CCR impoundment wastewater for ash pond closures. These strategies relate to: (1) the evaluation of potential toxicity exhibited by coagulation agents use in wastewater treatment processes; (2) the evaluation of effluent chemistry using a toxic unit approach; and (3) the evaluation of potential toxicity exhibited by specific cations and anions in effluent through the construction and testing of mock effluents.

Introduction

Following the burning or combustion of coal for power production residues from burnt coal remain. This type of industrial waste is referred to as coal combustion residuals or more commonly CCR. CCR can include different types of by-products such as fly ash, bottom ash, boiler slag, and others ([75 FR 35137](#)).¹ Chemical constituents of CCR can include metals such as boron, cadmium, chromium, mercury, selenium, and silver as

well as other inorganic constituents often expressed as total dissolved solids (TDS).² The chemical constituents contained in CCR vary depending on the type and source of the coal as well as the types of CCR by-products that were produced ([75 FR 35137](#)).

The production of CCR industrial waste prompts the reuse or disposal of these by-products. CCR can be reused or recycled into different products and materials such as concrete cement and construction products.³ It has been estimated that roughly 44% of CCR produced in the U.S. is recycled for beneficial uses, as the reuse of CCR offers environmental, economic, and product benefits ([80 FR 21301](#)).^{2,4,5} CCR reuse can also reduce the cost of coal ash disposal at coal-fired facilities.⁵ If not recycled, CCR is most commonly disposed of in surface impoundments or landfills at coal-fired facilities ([80 FR 21301](#)). CCR stored in on-site surface impoundments and landfills can pose risks to human and environmental receptors in the possible scenario of a catastrophic failure of the impoundment resulting in CCR leachates entering into surrounding groundwater or into the air as fugitive dust ([75 FR 35127](#)).^{3,4,6,7} Due to these potential risks, the CCR rule of 2015 ([40 CFR § 257 subpart D](#); [80 FR 21301](#)) requires structural stability assessments of surface impoundments and landfills, as well as groundwater monitoring. CCR disposal units that do not meet the technical criteria for stability or cause exceedances of groundwater standards are required to be closed. Closure options for these disposal units include close-in-place through the installation of a final cover system or removal of CCR and decontamination of the disposal unit ([80 FR 21301](#)).² Surface impoundments can collect water and therefore are often referred to as “ash ponds.” Any standing water in ash ponds must be removed prior to impoundment closure. To ensure that water removed from ash basins is safe prior to its release to surface waters, wastewater from the ash ponds is often managed by physical and/or chemical treatment and the subsequent effluent is then discharged via a National Pollutant Discharge Elimination System (NPDES) regulated outfall (Figure 1). NPDES compliance typically requires limitations on specific parameters in effluents, and may also include whole effluent toxicity (WET) testing ([40 CFR Part 122](#)).⁸



Figure 1. A coal-fired power plant facility generating CCR. CCR is disposed of in a landfill and/or surface impoundment (ash pond). Potential landfill leachate is regulated through groundwater monitoring. Ash pond wastewater is treated and discharged from a NPDES regulated outfall.

Rather than evaluating the potential effects of individual effluent chemicals, WET testing integrates the effects of all chemical constituents in an effluent into one test.^{8,9} Monitoring or regulating only chemical-specific parameters of an effluent has limitations, as the chemicals in the effluent must be known in order to evaluate their concentrations and potential to exhibit toxicity. To overcome this limitation and account for the effects of chemical mixtures, WET testing can be used to more effectively determine whether the effluent is potentially toxic to aquatic organisms. WET testing can be used to measure acute toxicity or chronic toxicity of an effluent and uses standardized test organisms and exposure durations.^{8,10,11} Biological organisms used as the analytical detector ensure that toxic effluent constituents do not pass into receiving waters, even if the identity of the toxic chemical constituents is not immediately known. Common organisms used as indicators in freshwater systems include water fleas, *Ceriodaphnia dubia*, *Daphnia pulex*, and *D. magna* and fish species, *Pimephales promelas* (fathead minnow), *Oncorhynchus mykiss* (rainbow trout), and *Salvelinus fontinalis* (brook trout). For estuarine and marine systems, the opossum shrimp, *Americamysis bahia*, and fish species, *Cyprinodon variegatus* (sheepshead minnow), *Menidia beryllina* (inland silverside), *M. menidia* (Atlantic silverside), and *M. peninsulae* (tidewater silverside), are commonly used.

When toxicity to these organisms is observed during WET testing, a toxicity reduction evaluation (TRE) is often required.¹² The tool most often employed as part of the TRE is the toxicity identification evaluation (TIE), in order to identify toxic agents and reduce the toxicity of effluents.¹³ TREs are site-specific studies of effluent or wastewater from treatment sites that use a stepwise process to systematically fractionate the complex wastewater, allowing further assessment of potentially toxic subsets of the effluent.¹² This approach aims to identify and isolate the chemical class or individual chemical constituent(s) that is causing the effluent to be toxic to aquatic organisms. Once the

toxic agent is identified, available actions that can reduce or treat the effluent toxicity are evaluated.¹³

TRE/TIE methodologies and other toxicity testing methods can be important for facility operators to consider with regards to cases of intermittent toxicity scenarios. In these situations, intermittent toxicity refers to an ash pond effluent or a more broadly effluent at a facility, which results in *occasional* WET test failures. Intermittent toxicity can be a common occurrence at facilities; however, this type of toxicity can be difficult to trace or capture for further analysis due to its fleeting nature. Therefore, the driver(s) of this type of toxicity can be difficult to characterize and identify. This paper will elaborate on the strategies dischargers can consider when intermittent toxicity occurs while facilities are treating CCR impoundment wastewater for ash pond closures. These strategies relate to: (1) the evaluation of potential toxicity exhibited by coagulation agents use in wastewater treatment processes; (2) the evaluation of effluent chemistry using a toxic unit approach; and (3) the evaluation of potential toxicity exhibited by specific cations and anions in effluent through the construction and testing of (“mock”) effluents.

Evaluation of coagulation agents

In accordance with NPDES permitting, the dewatering process involves treating ash pond water prior to discharge. A common step in wastewater treatment is the coagulation/flocculation step, used to remove suspended solids as well as some dissolved solids. Coagulating agents are added to wastewater to cause particles to destabilize and stick together. This destabilization can occur through several different mechanisms depending on the coagulating agent and dosage used. For both inorganic (i.e., aluminum and iron salts) and organic (i.e., surfactants) coagulating agents, destabilization is commonly achieved through adsorption and charge neutralization. Briefly, particles in solution that have the same surface charge are considered stable because repulsive forces will prevent them from sticking together. Adding a coagulant agent with the opposite surface charge will cause attraction and attachment between the coagulant and particles in the solution. Through this attachment, the overall surface charge of the coagulant-particle aggregate will be neutralized, allowing for additional collisions and further particle adsorption. The purpose of particle destabilization is to create aggregated flocs that are heavy enough to settle out of the solution quickly, decreasing the level of suspended and dissolved solids that may be contributing to excessive solids (e.g., turbidity) in the effluent discharge or contributing to the toxicity of the waste stream.

While organic polymers are commonly used in water treatment, water flea species used in WET tests have demonstrated sensitivity to surfactants.^{14,15,16} The metric used to quantify acute toxicity to water flea species is the concentration that results in the death of 50% of organisms exposed over a 48-hr period (48-hr median lethal concentration [LC₅₀]). Hall and Mirenda exposed *D. pulex* to 31 different wastewater treatment polymers in standard U.S. Environmental Protection Agency (EPA) moderately hard reconstituted water and found 48-hr LC₅₀ values spanning three orders of magnitude, from 0.06 to 70 milligrams per liter (mg/L).¹⁵ Fort and Stover also observed toxic effects on water flea species at low coagulant concentrations, with exposure of *C. dubia* to four

different polymeric coagulating agents in standard EPA moderately hard reconstituted water resulting in 48-hr LC₅₀ values ranging from 0.07 to 0.12 mg/L.¹⁶ In a mixed liquor solution (2,300 mg/L suspended solids and 1,350 mg/L volatile suspended solids), *C. dubia* were less sensitive to the four coagulating agents, with 48-hr LC₅₀ values ranging from 2.74 to 7.06 mg/L.¹⁶

These studies show not only that water flea species can be sensitive to the polymers used in wastewater treatment, but that sensitivity is both coagulant and solution specific. Certain polymer characteristics can help inform predictions of aquatic toxicity, including polymer charge (with cationic polymers typically exhibiting the greatest toxicity to aquatic organisms), length, and the extent of branching.^{17,18,19} Toxicity is also dependent on environmental factors, including water hardness, temperature, and the presence of other substances (including organic matter such as humic acid). Because unbound polymer may exhibit significantly greater toxicity than polymer bound to organic matter, EPA's Office of Pollution Prevention and Toxics considers the presence of organic carbon a mitigating factor in the evaluation of cationic polymer toxicity.

In wastewater treatment operations, the amount of coagulating agent added to the wastewater is based on the desired level of removal of the chemicals of concern, typically without consideration of the potential toxicity posed by excess, unreacted coagulant. This oversight can result in intermittent toxicity issues, especially if influent conditions are fluctuating, resulting in inconsistent levels of unreacted coagulant in the treated effluent. According to the TRE Guidance Manual for Municipal Wastewater Treatment Plants published by the EPA, water treatment polymers are among the most common toxicants found in effluents discharged from publicly owned treatment works.²⁰ Furthermore, water treatment polymers are often some of the most difficult effluent constituents to evaluate analytically, thus WET tools are often necessary to characterize toxic agents.¹²

If dewatering of an effluent demonstrates intermittent toxicity during WET testing, we recommend several strategies that can be used to determine whether the observed toxicity is related to unbound coagulating agents: (1) a review of safety data sheets (SDS), (2) bench-scale toxicity testing, and (3) in-process toxicity testing.

The first strategy is to perform a preliminary assessment based on a review of available ecotoxicological data provided in the SDS for the coagulants of interest. Because the review of SDS is not time or resource-intensive, it can be used as a screening step to identify or rule out treatment chemicals that may be contributing to overall toxicity. The efficacy of this step is dependent on the level of information provided in the SDS. In some instances, 48-hr LC₅₀ values for relevant organisms may be provided, allowing assessors to develop informed evaluations of anticipated toxicity at the applied treatment dose. However, ecotoxicological data are not always provided by the SDS and site-specific toxicity concerns typically cannot be assessed solely through SDS review.

The second strategy is to perform bench-scale toxicity testing with coagulants that have been identified as possible sources of toxicity. Alternative coagulants can be selected

for parallel testing based on coagulation/flocculation efficiency, ease of dosing, the volume of polymer required, and overall cost, as well as toxicity considerations. Polymers should be tested in a solution that mimics the facility's wastewater, such as ash pond water mixed with sediment from the basin to provide additional total suspended solids. We recommend testing polymers at levels 4 to 10 times the anticipated operational dose in order to observe the impact of unbound coagulants on exposed organisms. WET testing organisms should be exposed to a series of dilutions of the coagulant-treated effluent (e.g., 12.5%, 25%, 50%, and 100% effluent) to compare the toxicity of the different polymers. Table 1 provides an example of how the results of acute toxicity testing may be used for easy comparison between polymer types.

Table 1 An example data table for water flea survival following 48-hr exposure to a series of polymer dilutions.

Polymer	Type	Charge	Water Flea Survival (%)			
			12.5% Effluent	25% Effluent	50% Effluent	100% Effluent
A	Dry	Cationic				
B	Dry	Non-Ionic				
C	Dry	Anionic				
D	Emulsified	Anionic				

The third recommended strategy is to evaluate chosen coagulants through full-scale, in-process toxicity testing. Initial in-process toxicity testing should be conducted over the span of at least several weeks, to account for day-to-day fluctuations in effluent water quality and facility operations. Over the course of several days, hourly samples of the effluent should be collected for 48-hr testing with the water flea species of interest. This strategy allows for the direct evaluation of the coagulant agent as a component of the treatment process.

In summary, polymeric coagulants can be a significant source of organic compounds in a treated effluent and may act as a toxic stressor if not adequately evaluated and managed. When dosing a system, operators need to be sure that they are adding enough coagulants to remove all of the chemicals of concern from the waste stream, but not so much that excess, unreacted polymers may contribute toxicity of their own. Often these decisions are only made through the eyes of the wastewater treatment operator, who is solely focused on the removal efficiency of the constituent of concern.

Some level of coagulant over-dosing is inevitable under most wastewater treatment situations as effluent characteristics fluctuate over time.

Coagulant toxicity effects can be identified through (1) SDS review, (2) bench-scale testing, and (3) in-process toxicity testing. SDS by themselves are typically not enough to appropriately inform toxicity evaluations because they often lack sufficient ecotoxicological data and do not offer site-specific insights. Bench-scale and in-process toxicity testing performed with elevated doses of the coagulant of interest allows for direct observations of the effects of unbound coagulant on exposed WET testing organisms. These strategies, along with long-term monitoring, can help to determine the relationship between coagulant use and observations of intermittent toxicity.

Evaluation of effluent chemistry

Regardless of whether WET testing requirements are included on a permit, dischargers regulated under the NPDES program are subject to chemical-specific limitations for effluent constituents; therefore, dischargers routinely monitor individual analytes as part of their NPDES permit requirements. Suspended and dissolved solids found in an effluent are targets of ash pond wastewater treatment prior to discharge, as mentioned above. TDS is also frequently used as a measure of common ions in freshwater²¹ and are often monitored in facility effluents regulated under NPDES, as ions in TDS can act in concert as a stressor to aquatic organisms if concentrations reach levels of concern. Organism sensitivity to TDS varies depending on the species.^{21,22} For example, among water flea species, *C. dubia* and *D. pulex* exhibit greater sensitivity to TDS compared to *D. magna*.²²

If dewatering of an effluent demonstrates intermittent toxicity during WET testing and there are not individual chemical constituents present at concentrations that indicate toxicity, we recommend evaluating whether the observed toxicity may be caused by high levels of TDS. One method to address this issue is the calculation of Toxic Units (TU) for the effluent in question. TU are a measure of species-specific toxicity of an effluent and can be used in the evaluation of acute (TU_a) or chronic toxicity (TU_c).⁹ This method can be used to examine the potential toxicity of chemical constituents in an effluent that have similar modes of action and are commonly used in toxicity tests involving mixtures. The calculation of TU for a given chemical constituent scales the measured concentration of the constituent to the compound's inherent toxic concentration. Therefore, the effect of a single constituent can be compared to others within an effluent or TU for multiple effluent compounds can be added to evaluate the potential collective toxicity of multiple constituents present in an effluent mixture.²³ Acute TU for a given effluent constituent are calculated as follows:

$$TU_a = [48\text{- or }96\text{-hr } LC_{50} \text{ of the constituent}] / [\text{the concentration of the constituent in the wastewater}]$$

The use of a 48-hr LC₅₀ compared to a 96-hr LC₅₀ value depends on the test organism used in toxicity testing (e.g., for water fleas, standard toxicity values are 48-hr LC₅₀

values, whereas 96-hr LC₅₀ values are common toxicity values for fish species) and can be derived from the literature.

When calculating TU_c for WET testing, the following formulae is used:

$$TU_c = [\text{7-day NOEC of the constituent}] / [\text{the concentration of the constituent in the wastewater}]$$

The no-observed-effect-concentration (NOEC) is used in place of the LC₅₀ value.^{9, 23} TU_a or TU_c values for individual constituents measured in an effluent can be added together to derive a cumulative sum TU (ΣTU) for an effluent mixture.

When calculating TU for the evaluation of potential toxicity of an effluent exhibited by TDS and effluent chemistry, multiple TDS compounds should be considered. Additionally, common TDS constituents in ash pond effluents, such as mercury, copper, chromium, and silver, may be particularly important to monitor and include in TU calculations due to their inherent toxicity to some aquatic organisms classically used in toxicity testing, such as *C. dubia* or *D. magna*. For example, the above listed constituents have LC₅₀ values ranging from 3 to 31 µg/L for water fleas. Table 2 provides an example of how the results of a TU_a calculation may be used for easy comparison between effluent constituents and the calculation of ΣTU.

Table 2. An example data table for the calculation of TU_a for common effluent constituents.

Parameter	Units	Concentration	Water flea ^a Acute LC ₅₀	Acute Toxic Units
Mercury	µg/L (dissolved)	X ₁	3 ²⁵	X ₁ / 3
Copper	µg/L (dissolved)	X ₂	17 ²⁶	X ₂ / 17
Chromium	µg/L (dissolved)	X ₃	31 ²⁷	X ₃ / 31
Silver	µg/L (dissolved)	X ₄	3 ²⁸	X ₄ / 3
Manganese	µg/L (dissolved)	X ₅	14,500 ²⁹	X ₅ / 14,500
Constituent A	µg/L (dissolved)	X ₆	Y	X ₆ / Y

^aWater flea species used in this evaluation included *Ceriodaphnia dubia*, *C. reticulata*, *Daphnia magna*, and *D. pulex*.

²⁵U.S. EPA 1996

²⁶U.S. EPA 2007

²⁷Dorn et al. 1987

²⁸U.S. EPA 1980

²⁹U.S. EPA 1986

The derived TU for each effluent constituent can also be displayed graphically to visually evaluate potential collective toxicity exhibited by the constituents in the effluent

mixture. Figure 2 provides an example graphical representation of a Σ TU for a hypothetical effluent mixture.

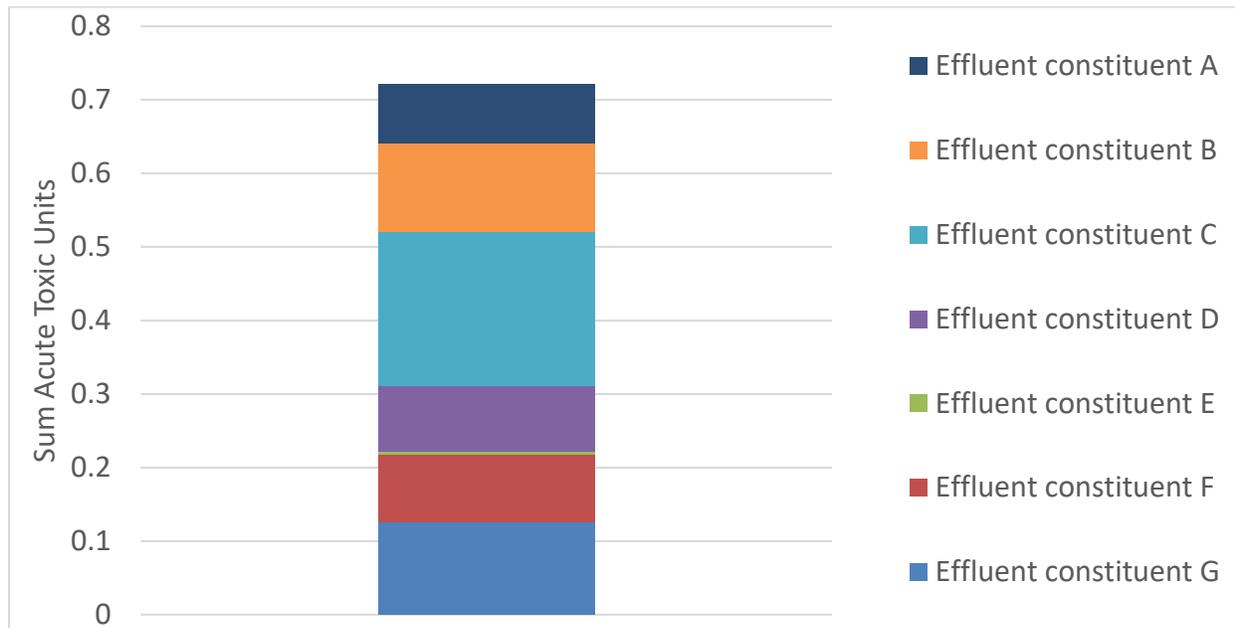


Figure 2. Graphical representation of individual TU_a, calculated for hypothetical effluent constituents A to G and Σ TU calculated for an effluent mixture.

The cumulative toxicity assessment presented in Figure 2 is an example evaluation of chemical-specific impacts to overall toxicity. As the TU value for a given constituent increases, toxicity also increases.⁹ In the case of TU_a calculations, when the Σ TU for an effluent exceeds 1.0, 48-hr exposure to the effluent is expected to result in 50% mortality in the test organisms. Similarly, when calculating TU_c, a Σ TU exceeding 1.0 would indicate a toxic response by the test organisms (dependent on the endpoints measured for the development of the NOECs used) is expected. In the example above (and as seen in Figure 2 above), the most toxic individual component of the hypothetical effluent is effluent constituent C; however, the effluent mixture has a Σ TU below 1.0, therefore this effluent is not expected to cause 50% mortality in the test organism population with the measured concentrations of effluent constituents A to G. This example cumulative toxicity assessment uses the measured concentrations of seven individual effluent components; however, this assessment may be more informative if concentrations of additional effluent constituents were also monitored and used in TU calculations. The calculated Σ TU and any conclusions drawn from this analysis are inevitably based on the number and identity of analytes measured.

When using this strategy for the evaluation of the potential toxicity of an effluent caused by TDS and effluent chemistry, one must also consider laboratory detection limits for the analytes in question. The derivation of TU associated with a complex mixture can, at times, be driven by analytical chemistry limitations. Analytes used to determine Σ TU in an ash pond wastewater effluent may not be present above their associated laboratory method detection limits or the laboratory reporting limit. As a conservative approach,

when the concentration of an analyte is below its detection limit, the detection limit value can be used as the concentration to generate TU. Detection limits for different analytes can vary both within and among laboratories based on several factors, including analytical equipment, methodology, matrix limitations, and sample dilutions. If a detection limit is high enough to be near the LC₅₀ or NOEC value for a given analyte, this could contribute to an artificially (and perhaps incorrectly) elevated ΣTU. As a precaution against misinterpretation of results, we recommend that in cases where concentrations of effluent constituents are known to be at or near analytical detection limits, users review their contribution to the ΣTU to understand if these analytes may be biasing the ΣTU value.

It is also important to consider calculating an average concentration of effluent constituents contributing to TDS over the span of several weeks, to account for day-to-day fluctuations in effluent water quality and facility operations. In the event of intermittent WET testing failure, concentrations of effluent constituents can also be averaged over a smaller time frame (i.e., over the WET test duration or when facility operation changes came into effect) for a more focused evaluation of effluent chemistry.

Evaluations of anions and cations using mock effluents

One of the most challenging classes of compounds to characterize toxicity using the EPA TIE methods are TDS.^{12, 21} This is because they are largely left “untouched” by the various TIE fractionation treatments. Experience has shown that there can be non-TDS sources of toxicity in the effluent even if there are indications of TDS as the primary source of toxicity.¹² It is important to determine whether or not there is an additional toxicant(s) hiding under the toxicity response that is assumed to be only due to the effluent TDS level. Therefore, being able to characterize other toxicants in an effluent can offer important insights.²¹ Since TDS does not bioaccumulate and many of these constituents are essential minerals for aquatic life the anions and non-heavy metal cations are not considered to be as much of an environmental concern as other toxicants (e.g., cations representing heavy metals).

The objective of a mock effluent assessment is to determine whether the toxicity associated with the effluent can be attributed to its TDS or ion composition. Briefly, this is accomplished by conducting chronic toxicity tests with combinations of an actual and a synthetic mock effluent, the latter prepared to be similar to the former, specifically in the composition of major cations and anions other than heavy metals. Tests can be performed with the WET test organism that is most sensitive to the effluent, for example, *C. dubia*, *D. magna*, or *P. promelas*. It is generally considered that the chronic sensitivity of these three standard test organisms to TDS is *C. dubia* > *D. magna* > *P. promelas*.²¹ Results of these tests provide lines of evidence in a weight-of-evidence approach to support or refute the hypothesis that effluent toxicity is due solely to TDS or ion composition rather than a more persistent toxicant.

Before toxicity testing, a detailed chemical analysis of the effluent and laboratory control water should be performed in order to determine the composition and concentrations of the major anions and cations.

An effluent sample and laboratory control water will be evaluated for the following parameters:

Anions (using ion chromatography procedures, e.g., EPA Methods 9056A, 300.0)

- bicarbonate
- chloride
- carbonate
- nitrate
- sulfate

Cations (using ICP procedures, e.g., EPA Method 200.8)

- calcium
- magnesium
- potassium
- sodium

Other chemical parameters (using standard EPA methods)²⁴

- conductivity
- pH
- alkalinity
- hardness

Mock Effluent Preparation

Using the chemical characterizations of the effluent and laboratory control water listed above, a synthetic mock effluent is developed to mimic the anions and cations in the effluent sample.²¹ Reagent salts, including but not limited to sodium chloride, sodium bicarbonate, calcium chloride, magnesium chloride, sodium sulfate, potassium chloride, and sodium nitrate, are combined in an effort to match the various anions and cations in the effluent and create a mock effluent with a reasonably close ionic balance.

The EPA moderately hard and hard water laboratory control recipes can be used as the base stock of the mock effluent, with additional salts added to increase the anions and cations in the mock effluent to mimic the effluent. These additional salts should be added to the mock effluent in the appropriate order for the laboratory water recipe to ensure solubility of the salts in the mock effluent. The pH of the mock effluent can be further refined using sodium hydroxide or hydrochloric acid (e.g., 1 N) to match the effluent pH level as close as possible without substantially increasing the conductivity of the effluent. The mock effluent is also evaluated for conductivity, alkalinity, and hardness.

Effluent and Mock Effluent Experimental Design

A strategy that we have used is an experimental design using a series of five separate samples created using the actual effluent and mock effluent preparations. These samples include:

- 100% effluent / 0% mock effluent
- 75% effluent / 25% mock effluent
- 50% effluent / 50% mock effluent
- 25% effluent / 75% mock effluent
- 0% effluent / 100% mock effluent

Chronic toxicity tests are performed with each of the above samples, for example, with *C. dubia*. Toxicity tests are performed using the standard EPA protocol for *C. dubia*; each sample is evaluated for chronic toxicity with serial dilutions (100%, 75%, 50%, 25%, and 12.5% of the sample and a laboratory control water).^{10,11} Endpoints measured during the toxicity testing should include both survival and reproduction. Thus, effluent toxicity can be expressed in three ways: as a 48-hrLC₅₀ using the survival endpoint, as a NOEC at the end of the exposure (e.g., 7 days) using survival and reproduction endpoints, and as a 25% inhibitory concentration (IC₂₅) at the end of exposure using survival and reproduction endpoints. Since the EPA *C. dubia* chronic toxicity test is normally a three-brood test, it is important that all tests are run for the same exposure duration (e.g., 7 or 8 days) in order to treat all of the samples the same and allow for direct comparison.

If toxicity testing shows similar toxicity across all of the treatments (effluent, mock effluent, and integrates of the two), this indicates that toxicity is being driven primarily by the major anions and cations of the effluent's dissolved solids. If testing shows substantial differences across treatments (e.g., increasing toxicity with the increasing proportion of effluent in the series of samples), it provides evidence that something other than the effluent's TDS or ion composition is responsible for the principal toxicity. Including the 75%/25%, 50%/50%, and 25%/75% splits, rather than simply comparing the effects of 100% effluent versus 100% mock effluent, provides the additional weight of evidence to the test conclusions.

Conclusions

Ash pond dewatering effluent contains a complex mixture of analytes. The NPDES permits regulating the discharge of these effluents are typically subject to not only restrictions on concentrations of analytes known to be toxic to aquatic organisms, but also successful passing of WET testing. This combination of approaches provides greater certainty that the effluent is "safe" but puts a greater burden on the discharger to prove this point.

Exposure to ash pond dewatering effluent can cause toxicity to exposed organisms if not properly treated. As this effluent is unlikely to be of uniform composition over time as impoundments are dewatered, toxicity may be variable over time. Occurrences of

intermittent toxicity can impose additional challenges on dischargers and treatment methods should be adjusted accordingly. We have elaborated on multiple strategies that dischargers can consider when intermittent toxicity occurs while facilities are treating CCR impoundment wastewater for ash pond closures.

TDS can be an important (and variable) component of ash pond dewatering effluent that may not be resolved by existing treatments or identified definitively by TIEs and may cause intermittent toxicity issues. The strategies we have discussed also generate lines of evidence that TDS may be responsible for toxicity associated with exposure to ash pond dewatering effluents. Facility managers can use these strategies to identify TDS as a cause, and then discuss with their regulators what options they may use to mitigate or otherwise account for this toxicity. The use of different WET testing organisms is one option that could be discussed, depending on what makes the most sense for the protection of receiving waters. In the end, these are all tools in a facility manager's toolbox, and the choice of which to use will be case-specific based on the needs of the facility.

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