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## Treatment of Mine Site Runoff Containing Suspended Solids Using Sedimentation Ponds – Optimizing Flocculant Addition to Ensure Discharge Compliance

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**Abstract** A review of numerous best management practice guidelines for the design and operation of ponds treating mine site runoff to remove total suspended solids and turbidity revealed an absence of a predictive methodology to address regulatory discharge compliance for total suspended solids concentration, turbidity and flocculant-induced toxicity. An essential component of pond design is the need to determine whether flocculants and/or other settling aids are required based on the site-specific soil particle size distributions upslope of the pond. Procedures are provided to predict the need for settling aids and estimate pond discharge quality and downstream impact for total suspended solids, turbidity, toxicity and sub-lethal toxicity.

**Key Words** sedimentation, pond, flocculants, toxicity, compliance

### Introduction

Mining activities typically generate a total suspended solids (TSS) concentration in runoff which may enter receiving waters at soil erosion rates significantly higher than "natural" erosion rates, invariably necessitating the installation of sedimentation ponds. The application of settling aids (particularly flocculants) to settle particles too fine to settle "naturally" needs to be included in best management practice (BMP) guidance documents for the design and operation of ponds. The "fines" in runoff only need to be captured in the pond during a specific rainfall event if they are predicted to cause an exceedance of local regulatory discharge and/or downstream standards for TSS concentration and turbidity. Strategies to yield cost savings and predict discharge compliance can be achieved by (a) ensuring the pond size is optimized; (b) ensuring that a flocculant system is essential; (c) ensuring (a) and (b) are determined by performing settling tests and particle size analyses on representative soil samples; and (d) designing tests which predict pond discharge quality, and define how downstream water quality standards for TSS, turbidity and toxicity will be achieved.

There are numerous examples where this predictive strategy has been absent, and resulted in a variety of problems; for example: (a) installation of a costly flocculant system which subsequently was not required; (b) using flocculants which cause recurring toxicity in the pond discharge, resulting in non-compliance and costly legal action in some jurisdictions; and (c) recurring pond discharge exceedance of TSS concentration because the need for flocculants was not predicted.

An example of pond discharge standards which clearly demonstrate the need for this approach is in Canada: metal mine discharges are required to meet 35 mg/L TSS (on a grab sample) and pass a 96 Hour LC50 using Rainbow Trout (*Oncorhynchus mykiss*), and in BC Canada, stringent receiving water quality standards downstream of the pond discharge apply for TSS and turbidity (and sub-lethal toxicity requirements may apply when downstream dilution is minimal).

### Settling Aids and Soil Particle Size Analyses

Particle size analyses and settling tests performed on representative soil samples from upslope of the pond, provides a predictive tool to determine the need for settling aids. Settling aids may fall into the categories of (a) high/low molecular weight polymers, such as polyacrylamide (i.e. flocculants); (b) coagulants, such as aluminum and ferric salts; and (c) potentially determining ions, such as calcium ions, which have the ability to lower particle surface charge (Zeta potential) as defined by Slater et al. (1968). Kitchener et al. (in Europe) and La Mer and Healey in North America have provided numerous descriptions of the mechanisms that settling aids use to achieve settling of fine suspensions, and this provides an essential basis for the present discussions.

Coagulants, flocculants and potentially determining ions may be used together, or separately, although flocculant use alone is generally more effective in ponds where TSS is the major focus.

TSS is unlikely to cause Rainbow Trout toxicity, while cationic flocculants and coagulant precipitates (and sometimes associated coagulant metal ions) are frequently a cause of pond discharge toxicity.

### **Defining Flocculant Toxicity**

The toxicity potential of flocculants and coagulants is described by Allan 1985, Biesinger 1986, Albassam 1987, and numerous other researchers. Cationic flocculants and coagulants generally exhibit significant toxicity via a “smothering” action on the negatively-charged fish gill and breathing apparatus of other aquatic organisms. Anionic and neutral flocculants typically exhibit low toxicity to aquatic organisms – e.g. 10,000 mg/L may cause no adverse effects, while 1.0 mg/L of cationic flocculant may cause 50% mortality to Rainbow Trout. When cationic flocculant is added to runoff, there is a risk of (a) adding excess flocculant, (b) providing inadequate mixing time, and (c) providing inadequate agitation prior to the entry of runoff into the pond. Under these conditions, as runoff enters the quiescent conditions in the pond, any “excess flocculant” remains in the “supernatant”, or water column, due to the absence of mixing in the pond. High TSS and fines in runoff significantly exacerbates this problem due to the need for adding more flocculant.

### **Flocculant Selection**

It is imperative for a BMP design and operation of ponds to emphasize the selection and application of low toxicity flocculants so that there is a low risk of flocculant-induced toxicity in the pond discharge. This implies diligently searching for lower toxicity and faster-acting flocculants; failure to achieve this may result in the need to install a more complex and costly flocculant addition system (depending on the degree of toxicity risk associated with the selected flocculants).

### **Flocculant Conditioning Time**

The mechanisms controlling the transfer of dissolved flocculant onto suspended particles (as expounded by Kitchener, and La Mer and Healey) need to be incorporated into the design of the flocculant addition system upstream of the pond, to ensure that flocculant is efficiently abstracted from solution by the particles in the runoff. Adequate agitation and conditioning time must also be provided to allow for floc-growth after flocculant moves from the solution phase onto particles. Flocculant testing using soil samples provides guidance on the required time frame a specific flocculant requires to achieve flocculation (the “time frame” is also specific to the TSS concentration and particle size distribution in runoff, which varies with the rainfall event and erosivity of the soils); this defines the challenge the pond operator is tasked with during a rainfall event. Water treatment plants combat this challenge by using a rapid settling test-jar procedure and an on-stream Zeta Meter to control flocculant/coagulant addition; this procedure needs further adaptation if it is applied to a mine site. The centrifuge may also be used to perform “rapid” settling tests on runoff samples, and the centrifuge supernatant is then tested for turbidity, and compared to a turbidity-TSS correlation curve to estimate the pond discharge TSS concentration. Runoff flow rate is also measured, and the retention time in the pond calculated, which then allows the particle “size-cut” required in the pond (and this “size-cut” is used to set the centrifuge rotational speed).

### **Limitations of Sedimentation Ponds**

The need to apply flocculants to runoff flowing into a sedimentation pond is typically a result of “elevated” minus 10 micron particles eroded into the pond from upslope soils. The 10 micron particle is selected based on numerous regulatory requirements to size ponds to achieve this “size-cut” for the 24-hour, 10-year rainfall inflow rate into the pond. Flocculants may also be applied because there is insufficient space at the mine site to size a pond to remove plus 10 microns, or may be used to reduce the size and capital costs of constructing a pond which is only required for the mine construction phase.

### **Flocculant Testing Based on Kitchener’s Scientific Rational**

Flocculant testing of “simulated runoff” is achieved by performing tests on samples prepared from representative soil samples and site water. Test jar suspensions should have a ratio of solids

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to liquids which is representative of the estimated TSS concentrations expected to enter the pond (e.g. for the 24-hour, 10-year rainfall event). For example, storm events may generate approximately 500 to 5,000 mg/L and higher TSS into ponds, and may be estimated by applying a RUSLE calculation (Revised Universal Soil Loss Equation, Terrence 1998). The optimum flocculant dosage varies with the TSS concentration and particle size distribution for a given runoff suspension.

Settling ponds are generally limited to settling particles coarser than about 2 microns (for particles of approximately 2.7 S.G.). Interpretation of particle size analyses of upslope soils provides valuable guidance on the need for flocculants. When this information is combined with appropriate settling tests using TSS loadings which simulate runoff TSS loadings into the pond, this provides a useful procedure to predict the need for settling aids and estimate pond discharge quality for TSS concentration. Larger scale settling tests using approximately 40 litres provides adequate settling test supernatant for Rainbow Trout and *Ceriodaphnia dubia* toxicity testing.

The particle charge of runoff particles is invariably negative, and may be verified by using a Zeta meter. Particle charge is an important factor when selecting flocculants, since the magnitude of the particle charge determines (a) whether fine particles will agglomerate "naturally", and (b) how effective neutral and anionic flocculants are likely to respond. A negative particle Zeta potential of approximately 10 mv has been determined as the universal threshold for the van der Waal's attractive force to allow particles to agglomerate. Some anionic and neutral flocculants are able to attach to negative particles via mechanisms such as adsorption, absorption and chemisorptions, in spite of the repulsive force resulting from like-charges. Cationic flocculants, which have the advantage of lowering particle Zeta potential, are frequently more effective settling aids, but often have higher toxicity. Cationic/anionic flocculant pairs are being used to achieve the most effective settling and clarification, but require testing to establish the "low risk" ratio of cationic to anionic flocculant, and the optimum application conditions, so that toxicity problems are avoided.

Locating effective flocculants of relatively low toxicity is a challenge, and there may be a significant increased cost component when using higher toxicity flocculants, and an increased risk of generating a toxic discharge from the pond. The use of toxic flocculants necessitates installation of a more complex and elaborate flocculant addition system, often referred to as the "Cadillac" system.

### Recommended Settling Tests

The following settling test procedure, which may be varied as needed, has been used for testing runoff at some BC, Canada mine sites, to determine whether flocculants are needed, and to predict pond discharge quality and toxicity:

- a Sample representative soil samples upslope of the pond and synthesize a composite sample to represent the runoff during rainfall events; prepare 8 test suspensions with the appropriate solids to liquids ratio. Use 8 one litre glass cylinders, allow settling to occur 10, 20, 30, 60, 120, 240, 480, and 1440 minutes. Extract a sample from the 100 ml depth of the cylinders and measure TSS and turbidity (also measure particle size distribution if a portable particle size analyzer is available).
- b Calculate the particle size which should settle just below the 100 ml depth for the time elapsed. Compare this calculated particle size with the measured value – typically, the "measured" particle size will be larger due to non-sphericity and particle roughness and density.
- c Typically, the "residual" TSS (for 24 hours, or extended, settling time) in the supernatant above the 100 ml mark will contain particles finer than 2 microns. If the "residual" TSS for the time elapsed to settle a 10 micron particle is above 35 mg/L, this indicates there are sufficient fine particles in the upslope soils necessitating the use of flocculants – this assumes regulators require recovery of the 10 micron particles and require the pond discharge to meet 35 mg/L at the 24-hour, 10-year rainfall inflow into the pond.
- d If the "residual" TSS for the time elapsed to settle a 2 micron particle is above 35 mg/L, this indicates, no matter how long the retention time is in the pond, flocculants will be required. These testing procedures will indicate whether "natural agglomeration" is occurring and whether settling aids are necessary.
- e When measuring turbidity on samples removed from the 100 ml level, these samples can

be diluted, and the resulting turbidity measured, to simulate the expected downstream low-flow dilutions that will be available in the receiving water at the mine site. Similar settling tests should be performed using flocculants on the same soil composite; vary flocculant dosage and mixing time and determine supernatant TSS and turbidity.

- f Select the lowest toxicity effective flocculant and perform a settling test using the optimum dosage in a 40 litre suspension, and allow to clarify, and then use the supernatant to perform a bioassay on Rainbow Trout and *Ceriodaphnia dubia* (using the Environment Canada standard method).

### Estimating the Risk of Generating a Toxic Pond Discharge

A methodology to estimate the risks associated with using a particular flocculant should be applied prior to final selection of flocculants. For example, BC, Canada has used the following method: if  $C_{add}$  mg/L = the flocculant addition dosage and  $C_{floc}$  mg/L = the 96 Hour LC50 concentration of flocculant using Rainbow Trout (which is by definition a 1.0 Toxic Unit concentration of the flocculant), then:

- a if  $[C_{add}] / [C_{floc}] \geq 1.0$ , this could potentially result in a toxic pond discharge; and
- b if  $[C_{add}] / [C_{floc}] \leq 0.25$ , this has a low risk of causing a toxic pond discharge.

The pond operator strives to add the optimum flocculant dosage to the runoff, but without the tools to estimate runoff TSS concentration and particle size distribution, or an alternative tool, insufficient (or excess) flocculant is usually added. Runoff flow rate measurement into a pond is typically used to determine the amount of flocculant addition rate, and this is considered to be inadequate when using toxic flocculants and adding them to runoff containing high TSS loadings. The rapid settling test method applied to the runoff is therefore recommended, until further research develops a more efficient method. Preliminary settling tests can provide supernatant for bioassay testing.

### Conclusion

Procedures have been used successfully in BC, Canada, to predict the need for settling aids and to estimate the pond discharge quality for TSS, turbidity and toxicity. Similar testing procedures are recommended for use in BMP guidance documents for the design and operation of ponds. Additional work is needed to compare “predicted” to “actual” pond discharges and then make the necessary refinements to the methodology, and develop site-specific tools for pond operators to have better control on flocculant addition dosage.

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