

REVIEW OF MUNICIPAL WASTEWATER EFFLUENT

Chlorination/Dechlorination

PRINCIPLES, TECHNOLOGIES AND PRACTICES

1 PROJECT BACKGROUND AND OBJECTIVES

Municipal wastewater contains pathogenic microorganisms, i.e. bacteria, viruses and protozoa. The safe discharge of municipal wastewater back into the receiving water is perhaps the most important function of the treatment plant since the receiving water is expected to be safe for both human and aquatic life. Failure to provide due diligence to the treatment and disinfection of the wastewater can result in the spread of waterborne disease and lead to significant health risk.

Risk of waterborne disease can occur through the contamination of the potable water supply, recreational water use and/or consumption of shellfish that can concentrate the pathogens. Under normal conditions, the waterborne pathogens are naturally controlled by decay, predation or dilution. However, the high concentration of these microorganisms in wastewater makes in-plant treatment, i.e. disinfection, prior to discharge, essential in these situations.

Since the early 1900's, disinfection of municipal wastewater has typically been done through the use of some form of chlorine. Chlorination, as this type of disinfection is called, has often been selected on the basis of its relatively low cost, the availability of a wide range of chlorine-related disinfectant chemicals and its effectiveness in achieving the required pathogen kills.

While much good has come about from the use of chlorination, in recent years there have been concerns raised about the downsides of chlorination. In particular, concerns about the toxicity of even very low levels of chlorine residuals to fish and other aquatic life have been raised, especially under Section 36(3) of the Federal Fisheries Act, (i.e. the "no deleterious substances" clause). In addition, there have been operator safety issues raised regarding certain types of chlorination. This has led to increased attention to disinfection practises and efforts to improve disinfection technologies and equipment.

The problems with chlorine residuals have been addressed, with mixed success, through the control of chlorine addition and the use of dechlorination chemicals, introduced after the required chlorine contact time has been achieved. Over time, there have been significant improvements to chlorination and dechlorination equipment, testing procedures, and control equipment.

Despite the improvements in chlorination and dechlorination technology, Environment Canada, Fisheries and Oceans Canada, and the BC Ministry of Water, Land and Air Protection (MWLAP) know that there are still problems. Many chlorination/dechlorination systems currently in use are either not adequately designed or operated to consistently meet their target effluent pathogen

content or chlorine residual levels. In many cases, especially at the smaller treatment plants, the chlorination/dechlorination equipment is complex and automated, and is often beyond what can be operated and maintained by the plant operators. In addition, variations in both flow rates and chlorine demand, inaccurate testing procedures and poor facilities maintenance, make proper operation of the chlorination/dechlorination system difficult. For this reason, Environment Canada and Fisheries and Oceans Canada, have been encouraging the use of non-chlorine-based disinfection technologies such as ultraviolet (UV) irradiation.

While the eventual move to other forms of disinfection such as UV may occur, the fact remains that, to many wastewater treatment plant owners and/or operators, chlorination involves relatively low capital and operating costs, reliability, low maintenance, and a “well known” technology. At present, there are over 40 municipal wastewater treatment plants in B.C. that chlorinate and over 20 of these also dechlorinate. While new wastewater treatment plants are discouraged from including chlorination/dechlorination systems, it will likely be some time before these existing plants that chlorinate or chlorinate and dechlorinate make the switch to another disinfection technology.

Where disinfection is required and chlorine is used, the regulation requires the residual chlorine is to be limited to 0.01 mg/L (10 µg/L) (Waste Management Act - 1999 Municipal Sewage Regulation (MSR) - Part 8: Effluent disinfection). Ensuring that this level is met is one concern of the Georgia Basin Ecosystem Initiative (GBEI).

The Georgia Basin ecosystem extends as far north as Pemberton, as far east as Boston Bar, Yale and Hope and south, past the US border. The GBEI has identified that liquid waste management programs need to be developed and implemented to arrest and reverse pollution trends and, therefore, minimize health risks in the Georgia Basin. Many of the plants that discharge into the Georgia Basin use chlorine to protect the public from waterborne diseases that are concentrated in the wastewater effluent. Unfortunately, this same chlorine poses a potential risk to the aquatic biota in the Georgia Basin ecosystem.

An ultimate goal of the GBEI is to reverse pollution and minimize public health risks in the Georgia Basin. To this end, optimal control of chlorine to protect the public and optimal control of the final chlorine residual to protect the aquatic life falls well into the GBEI mandate.

Given that chlorine and chlorine residuals are toxic to fish and other aquatic life, and the likelihood that current chlorination and dechlorination installations are not going to be abandoned overnight, it was appropriate that a review of chlorination/dechlorination principles, technologies and practises be conducted. To this end, this report has been developed. This has included a comprehensive review of the current state-of-the-art methods for chlorine-based disinfection, residual chlorine control, dechlorination chemicals and procedures, and the related chlorination and dechlorination equipment used in the wastewater treatment.

The report summarizes chlorination/dechlorination theory and documents a wide range of chlorination and dechlorination chemicals that are available in the marketplace. The survey of BC plants found that the chemicals used in chlorination and dechlorination of wastewater treatment plant effluent are a function of plant size and safety concerns. For larger plants, with more trained staff and resources, chlorine gas (Cl_2) for chlorination and sulphur dioxide gas (SO_2) for dechlorination have been popular, due to their lower bulk chemical costs and fast reaction rates. However, the high equipment costs associated with these gas-based systems are typically considered to be prohibitively expensive for smaller plants. Additionally, safety concerns surrounding the storage and handling of the pressurized gas have forced some larger capacity treatment plants away from the use of gas. In addition, the complexity of gas storage and dosing systems also requires more experienced and highly trained operators. As a result, for smaller treatment plants, either sodium or calcium hypochlorite for disinfection and sodium sulfite, thiosulphate, bisulphite or metabisulphite for dechlorination are preferred based on ease of handling and relatively low hazards. While calcium hypochlorite is typically 1.5 to 2 times the cost of liquid sodium hypochlorite, it may be preferred by smaller users since it requires less infrastructure for transport, storage, and handling. This is especially true of the newer “puck”-type calcium hypochlorite systems.

There are difficulties measuring chlorine and sulphite residuals accurately at very low levels. As a result, the operators of these plants could consider using alternate chemicals for dechlorination that will have little or no impact on receiving environment if spilled or overdosed. Two such options are ascorbic acid and hydrogen peroxide. However, hydrogen peroxide reacts very slowly with combined chlorine and may not meet the technical requirements, i.e. it may require more contact time than is normally available. Ascorbic acid is very expensive in comparison with other dechlorination methods. However, safety issues and protection of the environment may justify its use.

Regardless of treatment plant size, chlorination and dechlorination chemical feed systems need to be designed so that spills of toxic chemicals do not enter the environment. Secondary containment and spill containment need to be incorporated into each design. Consideration should be given to chemicals that present low risk to the surrounding environment.

3 CHLORINE AND SULPHITE RESIDUAL TESTING

While the methods of measuring chlorine residual in wastewater are essentially the same as those used for potable water, the larger concentrations of dissolved and suspended solids in wastewater create increased interferences. The target of less than 10 $\mu\text{g/L}$ (0.01 mg/L) total chlorine residual is much higher than that required for potable water analysis. Control to these low levels is at the current limit of feed and measurement technology.

In order to properly monitor and control chlorination and dechlorination, operators require simple, accurate techniques for determining chlorine and sulphite residuals. Several field test kits are commercially available that duplicate laboratory procedures including the diethyl-p-

phenylenediamine (DPD), amperometric, and iodometric methods. Each methodology and associated field test kit has particular strengths and weaknesses in terms of accuracy, precision (reproducibility), interferences, ease of use, and applicability for use in municipal wastewater treatment plants.

The Free Available Chlorine Test-syringaldazine (FACTS) method of chlorine residual measurement provides a simple and accurate test for free available chlorine but is not commercially available as a field test kit. The method is limited to free chlorine analysis, therefore it is of limited use for wastewater, as most chlorine is in a combined form. The orthotolodine method, despite previous widespread use, has been discontinued in favour of other measurement techniques. The iodometric method is only suitable for measurement of high strength chlorine (hypochlorite) solutions and is not suitable for measuring levels of chlorine residual below 1 mg/L.

The amperometric titration method of determining chlorine residual was concluded to be the most accurate method of determining chlorine residual. However, the off-line manual method requires a high level of training and skill to produce the required accuracy. Portable test instruments using amperometric titration are commercially available and can be used on grab samples from both large and small treatment plants, provided the operators have the skill and training to use the equipment. There are many cases in BC where the treatment plants have amperometric titration equipment that was once used but now sits under the equipment dust cover while other, easier, but less accurate, methods are used on a regular basis to measure the chlorine residual. This may change with the commercial release of small automated amperometric titration devices that should be suitable for use in small treatment plants.

The DPD colourimetric test was found to be the simplest, most versatile field test available on the market for the measurement of chlorine residual. It can be a very simple test based on a hand-held colour comparator or it can be more sophisticated based on spectrophotometer techniques. In either case, the operator must take care to minimize interferences and possible false positive values, particularly in the presence of organic chloramines. While the DPD method is relatively accurate, it is only accurate above concentration of approximately 30 to 50 µg/L for chlorine residual measurement. Since the objective of chlorine residual is 10 µg/L in the BC Waste Management Act - Municipal Sewage Regulations - Part 8 Effluent Disinfection (provided in Appendix A), one can not assume the required low chlorine level is being met by using a DPD method.

Low chlorine limits required for municipal effluent discharge are at the lowest detection limits of chemical feed and control equipment. Though published data indicates that devices can measure chlorine residuals down to levels as low as 1 µg/L, control at these levels is not practical. Feed and measurement of a slight sulfite or sulphate residual represents a more practical means of dechlorination. A slight sulfite/sulfate residual is an indication that the

chlorine has been neutralized. The detection limits and control for meeting discharge limits are well within the ability of current chemical feed technology.

Sending a grab sample of wastewater effluent to a lab off-site for more accurate measurement of chlorine residual is unacceptable. The chlorine residual will completely dissipate between the time the grab sample is captured and the time when the lab does the analysis.

4 ON-LINE CONTROL OF CHLORINE RESIDUALS

On-line measurement of chlorine residuals in wastewater is based on techniques that have been developed for on-line measurement of chlorine residuals in potable water. However, many of the units commercially available for residual chlorine measurement are not acceptable for use in wastewater. Manufacturers promote their use in wastewater; however, most of these installations are only for high quality tertiary applications. Care is required in applying technology and where possible, a long term pilot study of the unit should be completed. In all cases of on-line monitoring, it is also important that the sample lines between the sampling point and the measurement cell be continuously cleaned and flushed if accurate results are to be achieved.

For tertiary wastewater treatment plants and high quality secondary plants, membrane- type residual chlorine analyzers represent the best combination of accuracy and ease of operation for on-line residual chlorine measurement. However, these units will be quickly biologically and chemically fouled if used on lower quality effluents. In addition, when used at treatment plants that are nitrifying, any changes in nitrogen levels will cause significant inaccuracy in the measured residual.

Gas phase and Oxidation Reduction Potential (ORP) analyzers are suitable for primary and low quality secondary effluents. They have demonstrated success with the higher solids contacts involved.

Bare electrode, amperometric, on-line analyzers provide the most accurate indication of chlorine residual for both free and combined chlorine. Units with the 3-probe sensors provide better accuracy and better stability as the units are designed to adjust to background interferences. The units are, however, more difficult to operate and require the highest level of operator intervention.

5 THE CURRENT PRACTICES SURVEY

The study began with the initial understanding that chlorination and dechlorination practises vary throughout the province and within the Georgia Basin. In order to provide a full picture of the existing situation, it was necessary to conduct a survey on current chlorination and dechlorination practises. In determining the plants to be surveyed, all BC wastewater treatment plant discharge permits were initially reviewed to determine which plants were required by permit to disinfect. Further information was obtained from the GBEI report EC/GB-99-022 that was compiled from MWLAP data. Since, in the GBEI study, plants under 10 m³/day were eliminated from the inventory, the same has been done in this study. This current study also added known BC installations outside of the Georgia Basin in order to get as large a database for equipment verification as possible. Fifty-six plants were surveyed, forty-four in the Georgia Basin and twelve outside the Basin.

Chemicals used for chlorination and dechlorination in BC tend to be a function of the economies of scale and the operator training and certification level related to treatment plant size. Chlorine gas for disinfection and sulphur dioxide for dechlorination have been the chemicals of choice for the medium to larger capacity wastewater treatment plants that disinfect by chlorination. Sodium hypochlorite for disinfection and liquid sulphate/sulfite compounds for dechlorination tend to be used at the smaller plants. Due to safety concerns regarding chlorine gas and improvements in the accuracy of calcium hypochlorite systems, many operators are moving away from chlorine gas to sodium hypochlorite at larger plants and from sodium hypochlorite to calcium hypochlorite “pucks” at smaller plants. It is not clear what chemicals will be preferred for dechlorination. For the smaller plants, there are some chemicals such as ascorbic acid that present little or no environmental impact if overdosed. For the larger plants, it is not clear that those moving from chlorine gas will also abandon sulphur dioxide gas as the dechlorinating agent. In any event, there are several non-gas methods of dechlorination.

Of the most commonly used test methods available for chlorine residual measurement, the most accurate method is amperometric titration. However, since this method has required considerable operator training and skill to be accurate, other methods, particularly the DPD colourimetric method, have been widely used in B.C. While the simplicity and relative accuracy of the DPD method typically ensures that the test will be done regularly, the detection limit of the DPD method makes it impossible to positively confirm that the chlorine residual is meeting the 10 µg/L target level set out in the 1999 BC Municipal Sewage Regulations (BC MSR). Many B.C. operators typically deal with this by slightly over dosing their dechlorination chemicals since a dechlorination chemical residual is not as harmful as chlorine residuals above 10 ppb. New automatic amperometric chlorine residual measurement units will provide the accuracy of the amperometric devices, with the simplicity of the DPD measurement devices. The units are only available for chlorine measurement; however, they will have sulfite/sulfate measurement ability by early 2003. The use of this device should allow plants large and small to have more accurate monitoring and control of plant effluent.

There is not a strong trend in BC to use on-line chlorine residual monitoring devices since they tend to only work reliably at plants with tertiary treatment effluent. Since there are very few plants in BC that produce this quality effluent, most chlorination systems are flow-paced rather than chlorine residual-paced. Some (three plants) use a combination of flow and chlorine residual feedback. It is very common to set the dechlorination equipment to pace the chlorination equipment so that a slight excess of dechlorination chemical is added at all times. This trend is expected to remain in the future.

The majority of the measurement and/or confirmation of chlorine residuals in BC is done through the DPD method even though the method is not accurate enough to measure the BC MSR target of 10µg/L. The majority of these DPD tests are done colourimetrically using a spectrophotometer. This trend may change when automated amperometric chlorine and sulphite residual analyzers are installed into the plants.

6 OVERALL SUMMARY

Based on the above, the following are evident:

- Chlorination of wastewater effluent in B.C. will continue for some time in the future.
- The trend in chlorination/dechlorination in B.C. will be towards safer to handle and easier to use chemicals, despite increases in costs.
- While the amperometric titration method is the most accurate means of measuring chlorine and sulphite residuals, the test requires time and operator skill that is often beyond the plant resources available.
- The DPD method of manual chlorine residual measurement is easy to use, but it isn't accurate enough to actually measure a 10 µg/L chlorine residual.
- Operators tend to slightly overdose dechlorination chemicals to ensure that the chlorine residual is "zero".
- New automated amperometric titration systems may permit easy measurements of low chlorine residual levels.
- Selection of on-line residual monitoring is dependent on effluent quality.