Biofilm Control Study

Darigold, Inc.

Darigold Lynden, WA
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1 Background

Darigold operates a milk products facility in Lynden, Washington. Production processes include evaporation of milk, which generates what is referred to as condensate of whey (COW) water. COW water contains low molecular weight organic compounds including traces of lactic acid, alcohols, acetoin, and non-protein nitrogen (Möslang, 2017).

COW water and non-contact cooling water from the Darigold Lynden facility are currently discharged to Outfall 001, which combines with stormwater and the City of Lynden's wastewater treatment plant (WWTP) effluent discharge to the Nooksack River through the City's outfall. Darigold's discharge is regulated under National Pollutant Discharge Elimination System (NPDES) Permit No. WA0002470 administered by the Washington Department of Ecology (Ecology). In the future, Darigold's COW Water and non-contact cooling water will be directly discharged to the Nooksack River in a new outfall pipe (Outfall 002) currently being constructed by the City. The current permit became effective January 1, 2019 and includes effluent limits shown in Table 1. Additional effluent limits for biochemical oxygen demand (BOD) and total suspended solids (TSS) become effective January 1, 2022 as indicated in Table 1.

Table 1. Effluent limits for Darigold Lynden facility COW water and non-contact cooling water direct discharge to Nooksack River via Outfall 002

Parameter	Limit	Minimum Sampling Frequency
Flow	Max Day: 1 million gallons per day (mgd)	Continuous
Temperature	Max Day: 80°F	Continuous
pH	6.5 – 9.0	Continuous
Effluent Limits effective January 1, 2022:		
Biochemical Oxygen Demand (BOD)	Average Monthly: 30 mg/L (250 lb/d) Average Weekly: 45 mg/L (375 lb/d)	1/week
Total Suspended Solids (TSS)	Average Monthly: 30 mg/L (250 lb/d) Average Weekly: 45 mg/L (375 lb/d)	2/month

During normal operation, the COW water is expected to meet the permit limits in Table 1. However, elevated BOD and TSS are observed occasionally when cracks in the whey evaporator occur. Darigold is challenged in how to address these occurrences because the milk processing cannot be easily stopped for sustained periods and cracks in the whey evaporator are difficult to locate and quickly repair. At the same time, the COW water discharge has yielded a biofilm growth in downstream COW water discharge components including the COW buffer tanks, effluent flume, and discharge outfall pipeline. Nuisance slimy biofilm growth is known to occur for COW waters (Möslang, 2017). Floating biofilm mats have occasionally been observed on the Nooksack River during times of excessive biofilm growth. Biofilm growth is present under routine operating conditions but limited such that excessive biofilm growth and biofilm mats on the Nooksack River are not commonly observed.

Ecology is aware of the biofilm issue and has included compliance activities in the recently-issued permit requiring Darigold to assess methods to prevent or minimize biofilm growth in the COW water and discharge pipe. This study serves as an initial assessment of reasonable methods to control such biofilm growth and comply with permit requirements. The study is intended to be an initial step leading to a more detailed engineering report where up to four alternatives will be evaluated in greater detail. Subsequent sections of the study provide an overview of Darigold facilities, evaluation of biofilm control alternatives, and recommendations for alternatives to be carried forward in the future engineering report.

2 Overview of Facilities

A process flow diagram of the COW water system is included as Appendix A. An overview of the COW water system components and features is provided below.

Hot COW water originating from the milk evaporation process is collected in CRT-1 (commonly referred to as “Hot COW Tank” or Tank 48 by staff). Hot COW water is pumped to the SEP.PRE-HE.PHE heat exchanger (commonly referred to as “Sep Press” by staff), which warms the incoming milk and cools the hot COW water. Cooled COW water is typically between 45 and 60°F. Cooled COW water is pumped to either of two locations with different end-uses. A portion of the cooled COW water goes to the COW Water Tank CWT-3 (commonly referred to as “Cold COW Water Tank” by staff) and ultimately to cooling towers or to the cream cooling heat exchanger and boiler feed water. COW water sent to the cooling towers and boiler is one-time use and not recycled to the COW system. The majority of the cooled COW Water goes to the COW Water Shock Tank (commonly referred to as “COW Buffer Tank” by staff) and is subsequently discharged from the facility. There is no recirculation within the COW water system. The facility discharge is typically 300,000 to 400,000 gallons per day (210 – 280 gpm). At 250 gpm, the hydraulic residence time (HRT) in the 9,000 gal COW Water Shock Tank or “COW Buffer Tank” is 36 minutes. COW water pH ranges from 6.3 to 8.5 standard units. 10^{th}, 50^{th}, and 90^{th} percentile pH values are 6.5, 7.1, and 8.0 standard units based on four years of operating data through 2018. COW water is characterized by low ionic strength and pH buffering capacity meaning small doses of chemical may significantly impact pH.

As described in Section 1, Darigold’s COW water will be directly discharged to the Nooksack River in a new outfall pipe (Outfall 002) in the near future. The pipe material and approximate length of discharge pipe segments are summarized in Table 2. The future discharge pipe alignment to Outfall 002 is shown in Figure 1. Assuming an average velocity of 2 feet per second in the discharge pipe, the approximate HRT in the discharge pipe is 45 minutes. More detailed information on pipe diameters and slopes would be needed for a more accurate estimate of discharge pipe HRT. The above estimate provides an order-of-magnitude approximation based on typical pipe velocity in gravity flow systems.

Although BOD and TSS discharge exceedences occurred in the past, effluent BOD and TSS concentrations since the beginning of 2018 have been consistently below discharge limits. Modifications to plant maintenance practices were made and are anticipated to reduce the likelihood of equipment leaks believed to be the root cause of BOD and TSS exceedences. At the same time, biofilm growth has been much lower than in the past based on observations by Darigold facility staff.

Table 2. Summary of main segments of discharge pipe to Outfall 002

Segment	Description	Approximate length (ft)
A	Darigold plant to Judson Alley Original piping believed to be clay.	1,800
B	Judson Alley to Riverview Road and Riverview Road to Hannegan Road New PVC pipe.	1,400
C	Along Hannegan Road Original asbestos/concrete pipe lined with cured-in-place resin-impregnated tube.	1,600
D	Hannegan Road to Nooksack River New PVC pipe.	400
E	Nooksack River outfall HDPE including stainless steel diffuser fitting and neoprene check valves.	200
n/a	Various cement concrete manholes between Judson Alley and Nooksack River.	n/a
Total	---	5,400

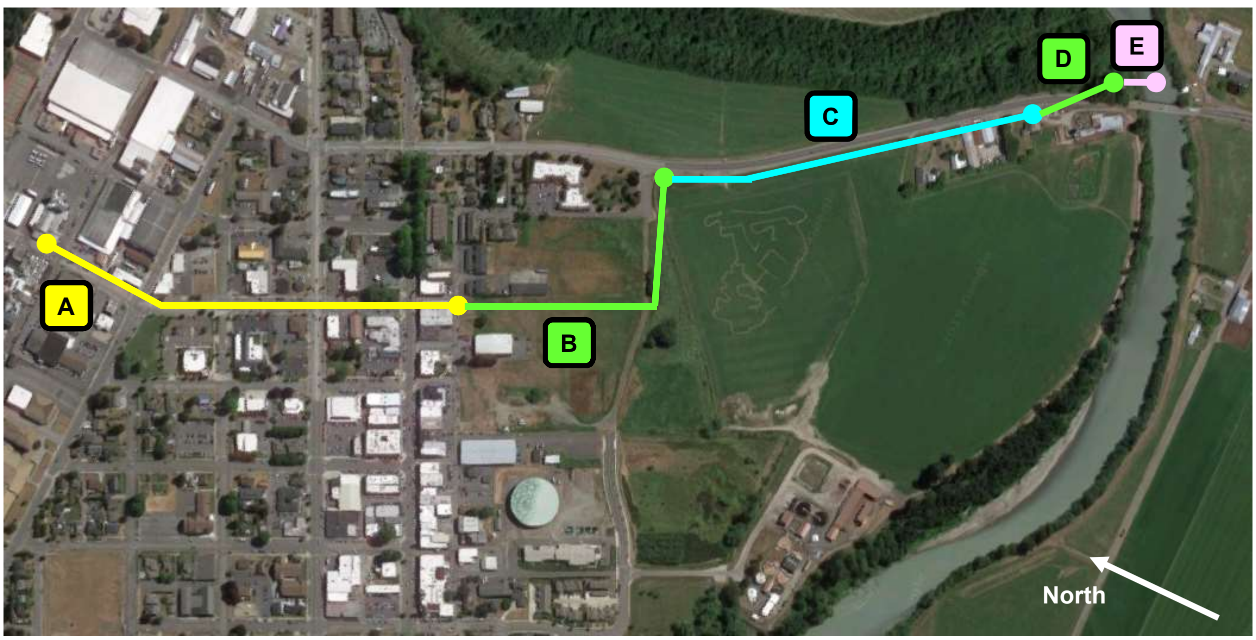

Figure 1. Discharge pipeline alignment and segments

Note: Pipe alignment and lengths approximate. Not to scale.

3 Biofilm Control Alternatives

Darigold's permit stipulates that biofilm control alternatives that use "nontoxic or low toxicity methods" should be considered. Ultraviolet (UV) light, ozone, peracetic acid, and hydrogen peroxide are specifically named in the permit. The permit also allows other methods to be considered.

Alternatives are identified and screened for potential viability in this section. General considerations broadly applicable to biofilm control approaches are first discussed to provide context for alternatives screening.

3.1 Biofilm Control Considerations

Several considerations are discussed below as a point of reference prior to alternatives screening.

Biofilm microbial composition: Past analyses aimed at identifying the biofilm microbial composition yielded inconclusive results. Analyses suggested that the biofilm may be due to fungal and/or bacterial growth. The efficacy of control methods in general or a given chemical dose may be affected by the type of microbial growth (e.g., fungal versus bacterial).

Growth in discharge pipeline: Even if biofilm growth is controlled within the Darigold facility "fenceline", there is potential for biofilm growth in the discharge pipeline. Growth may originate from the existing discharge pipeline biofilm if substrate (e.g., BOD) is available to support microbial growth and no chemical disinfectant residual is present to control biological growth. Such growth may occur even if efforts to clean the discharge pipeline are made because it is difficult to completely remove established biofilm in a pipeline. It is conceivable that sloughing events of pipeline biofilm growth may result in floating "mats" in the river. It is also conceivable that biofilm control approaches lacking the ability to maintain a residual disinfection dose in the discharge pipeline may be sufficient to control discharge pipeline biofilm growth to levels such that floating "mats" do not occur. However, approaches that allow a residual disinfectant in the discharge pipeline are more likely to control biofilm growth in the discharge pipeline, all other considerations being equal.

Need for quenching: Certain chemical biofilm control approaches may require quenching prior to river discharge. For example, dechlorination would be required if chlorination is used for biofilm control. Darigold does not have legal authority to maintain or operate such chemical quenching facilities near the outfall riverbank; therefore, chemical quenching would need to be done within the facility fenceline. Furthermore, regardless of access near the riverbank, locating chemical quenching facilities near the outfall is not preferred for security reasons due to its accessibility to the public.

Materials compatibility: Potential for corrosion or degradation of Darigold equipment and discharge pipeline materials must be considered.

3.2 Alternatives Screening

Alternatives were screened based on relative capital cost, operations cost, operator safety, and other considerations as discussed below. Alternatives were given a "Pass" or "Fail" screening grade with respect to being carried forward for further evaluation in the future Engineering Report. Where relevant, Hazardous Materials Identification System (HMIS) III and National Fire Protection Association (NFPA) 704 rankings are provided. HMIS III and NFPA 704 provide hazard rankings for various categories on a scale of zero (0) to four (4) with zero corresponding to no hazard and four corresponding to the greatest hazard. Refer to Appendix B for details on HMIS and NFPA ranking classifications.

3.2.1 UV irradiation

UV irradiation inactivates microbial cells by damaging cellular DNA. UV irradiation does not involve chemical addition and could be applied using a closed-vessel element on the downstream (cold COW water) side of the Sep Press if space allows. In this manner, the entire cold COW water stream including streams going to the COW Buffer Tank (to discharge) and Cold COW Water Tank (to facility uses) could be treated. If effective, this could reduce plant clean-in-place operations on the line to the Cold COW Water Tank. If space does not allow, UV could also be applied in separate locations or only on the line to the COW Buffer Tank and facility discharge. Closed-vessel low-pressure high-output elements such as Wedeco LBX or Trojan UVFit are recommended. Such elements have flanged connections and would require some pipe modifications for installation in the existing COW water system. By itself, UV irradiation would not provide a residual in the discharge pipeline.

Relative capital cost: Low, assuming UV transmittance (UVT) and required dose are reasonable, thus requiring one UV element similar to pipe line size.

Relative operations cost: Low, assuming UVT and required dose are reasonable.

Operator safety: Lowest risk. No chemical exposure or handling.

Screening grade: Passes alternatives screening for further evaluation as biofilm control alternative.

Further considerations: Additional testing on COW water UVT is recommended. This can be measured in-house with a UVT meter. It is also common for UV vendors to measure UVT as part of application screening and design development. In instances where the target organism is known and can be reliably quantified, microbial inactivation can be studied in bench-scale dose-response or collimated beam tests. Such tests are not feasible for Darigold because the biofilm microbial specie(s) of interest are not identified. However, UV units can be leased from manufacturers and used in full-scale field demonstration testing on a temporary basis. A full line-size unit could be used, or a smaller unit and sacrificial test pipe segment could be compared to the larger existing system. Full-scale field testing would provide insight on the ability control biofilm growth within the Darigold facility fenceline, but the test duration may not allow the effects on discharge pipeline biofilm growth to be fully realized due to response time and dynamics of microbial growth and decay in the discharge pipeline.

3.2.2 Ozone

Ozone is commonly found at water treatment plants where it used for disinfection, removal of taste and odor compounds, and oxidation of trace organics that are recalcitrant to other types of treatment. The electrical discharge method is used for ozone generation in water treatment processes. Ozonation is not widely used in conventional wastewater treatment. It is more complex than chlorination or UV irradiation. Ozone is highly corrosive and reactive. Disinfection byproducts (DBPs) may be formed through reactions with bromide, aldehydes, and organic acids. By itself, ozone would not provide a residual in the discharge pipeline.

Relative capital cost: High. Not easy to retrofit in Darigold COW Water system. Complex system requiring ozone generation, ozone dissolution reactor, ozone quenching and off-gas thermal destruction system.

Relative operations cost: High due to energy for ozone generation, dissolution, and chemical quenching.

Operator safety: Moderate to high risk. Worker safety is a concern. Ozone is a strong irritant. Although ozone itself is not flammable, as a strong oxidant it may accelerate or even initiate combustion or cause explosions. Acute exposure to high concentrations can be lethal. Requires ozone gas detection, however, the threshold of odor detection for most persons is below concentrations that are hazardous to health. NFPA rankings for pure ozone gas are as follows: Health (4); Flammability (0); Reactivity (4); Special (Oxidizer).

Screening grade: Fails alternatives screening for further evaluation as biofilm control alternative.

3.2.3 Peracetic acid

Peracetic acid (PAA) is a strong oxidizer and broad spectrum antimicrobial agent. PAA has been widely used in food and pharmaceutical applications for decades, but its use in wastewater treatment applications is comparatively newer and less common. PAA results from the equilibrium reaction of hydrogen peroxide and acetic acid. PAA is commercially available in different solution concentrations. Commonly-used solutions contain 12-15% PAA, 20-25% hydrogen peroxide, 15-25% acetic acid, and 0.5-1% sulfuric acid. These PAA solution strengths are less flammable than higher strength solutions. PAA manufacturers and product trade names include Solvay Proxitane WW-12 and FMC VigorOx WWT II. PAA is not known to produce DBPs. PAA can be used to maintain a residual in the Darigold discharge pipeline. The residual decomposes into non-toxic compounds (water and acetic acid), and quenching is not usually required. Ideally, PAA could be added at the Darigold facility such that PAA residual is exhausted or at very low concentration at the outfall discharge.

Relative capital cost: Low. Requires chemical feed system. May also require static or mechanical mixing depending on turbulence at dose point.

Relative operations cost: Moderate. Can be comparable to chlorination-dechlorination depending on doses required.

Operator safety: Moderate to high risk. Liquid and mist are corrosive (causing burns); direct contact could cause irreversible damage to eyes including blindness and/or irreversible destruction of skin tissue. Vapor/mist will irritate nose, throat and lungs but will usually subside when exposure ceases. May be corrosive to metals. Flammable, but with relatively high flash point above 200°F. HMIS and NFPA rankings are given below for 12-15% PAA solutions:

HMIS III: Health (3); Flammability (1); Physical Hazard (2)

NFPA 704: Health (3); Flammability (1); Reactivity (2); Special (Oxidizer)

Screening grade: Passes alternatives screening for further evaluation as biofilm control alternative.

Further considerations: Materials compatible with 12-15% PAA include 304L stainless steel (pickled and passivated), Teflon, PVDF, HDPE, and LLDEPE. Chemical equipment must be placed close to the point of use with no buried piping. Corrosivity issues at typical applied doses less than 2 mg/L have not been widely reported but requires further evaluation. Darigold indicated that PAA was used in the past as a biocide for cooling towers, but that PAA addition caused corrosion in the cooling tower system. Details on Darigold's past operating practice including PAA dose are not known. If corrosion is due to low pH resulting from PAA addition in the low ionic strength COW Water, addition of chemicals to provide pH buffering capacity may be a means to control pH-associated corrosion.

Such pH buffering should avoid excessively alkaline conditions where PAA tends to dissociate (pKa = 8.2) and have lower efficacy.

Full-scale field testing would provide insight on the ability control biofilm growth within the Darigold facility fenceline and discharge pipeline due to the potential to maintain a PAA residual in the discharge pipeline. Locally, PAA is used at the Snohomish, WA wastewater treatment facility; this facility may be a source of practical operating experience as PAA is considered in future phases at Darigold.

At a PAA dose of 2 mg/L, hydrogen peroxide in the PAA solution should be rapidly quenched by reduction of organics (BOD) in the COW Water. Addition of acetic acid with PAA addition is not anticipated to result in significant increases in Darigold discharge BOD concentration due to the reaction of interaction of hydrogen peroxide and organics as described above.

3.2.4 Hydrogen peroxide

Hydrogen peroxide is used in water treatment applications including disinfection, advanced oxidation processes, odor removal, and metal removal. Hydrogen peroxide rapidly reacts with oxidizable compounds including organics and metals. Hydrogen peroxide decomposes to oxygen and water; many commercial solutions include stabilizers to limit decomposition at typical storage and handling conditions. By itself, hydrogen peroxide would not provide a residual in the discharge pipeline.

Relative capital cost: Low. Requires chemical feed system similar to chlorination. May also require static or mechanical mixing depending on turbulence at dose point.

Relative operations cost: High, due to hydrogen peroxide cost itself exacerbated by high doses required for disinfection due to scavaging of hydrogen peroxide by organic compounds (e.g. BOD).

Operator safety: Moderate to high risk. Highly corrosive material. Containers may explode when heated. Oxidizer: contact with combustible/organic material may cause fire. In the event of fire and/or explosion do not breathe fumes. Thermal decomposition can lead to release of irritating gases and vapors. May ignite combustibles (wood paper, oil, clothing, etc.). HMIS and NFPA rankings are given below for 30% hydrogen peroxide solution commonly used in industrial settings:

HMIS III: Health (3); Flammability (1); Physical Hazard (3)

NFPA 704: Health (3); Flammability (1); Reactivity (3); Special (Oxidizer)

Screening grade: Fails alternatives screening for further evaluation as biofilm control alternative.

3.2.5 Chlorination-dechlorination

Chlorination is widely used for disinfection and to control microbial growth. Dechlorination or quenching of residual chlorine is also widely practiced when discharges are to surface waters or groundwaters. Sodium hypochlorite and sodium bisulfite are commonly used for chlorination and dechlorination, though other chemicals may be used. Chlorination efficacy is affected by pH due to the speciation of hypochlorite and hypochlorous acid, the latter of which is the more effective disinfectant. Chlorination may form DBPs depending on a variety of complex factors including background water composition, water chemistry, and chlorine dose. For practical purposes described earlier, dechlorination would need to occur within the Darigold fenceline; therefore, a chlorine residual would not be provided in the Darigold discharge pipeline.

Relative capital cost: Low. Requires chemical feed systems for chlorination and dechlorination chemical addition. May also require static or mechanical depending on turbulence at dose points.

Relative operations cost: Low. Exact cost depends on chemical doses necessary for biofilm control.

Operator safety: Moderate risk. Causes severe skin burns and eye damage. May be corrosive to metals. Widely used in water treatment industry. HMIS and NFPA rankings are given below for 12.5% sodium hypochlorite and 15-44% sodium bisulfite solutions:

12.5% sodium hypochlorite:

HMIS III: Health (2); Flammability (0); Physical Hazard (1)

NFPA 704: Health (2); Flammability (0); Reactivity (0); Special (None)

15-44% sodium bisulfite:

HMIS III: Health (2); Flammability (0); Physical Hazard (1)

NFPA 704: Health (2); Flammability (0); Reactivity (1); Special (None)

Screening grade: Passes alternatives screening for further evaluation as biofilm control alternative.

Further considerations: Full-scale field testing would provide insight on the ability control biofilm growth within the Darigold facility fenceline. Effects on discharge pipeline biofilm growth may be able to be evaluated depending on test duration. DBP formation could also be evaluated in pilot testing.

3.2.6 Bromination-debromination

Bromination-debromination is generally similar to chlorination-dechlorination with respect to many disinfection principles including the potential to form DBPs. Bromine is typically supplied as bromodimethylhydantoin tablets or cartridges which dissolve slowly to release hypobromous acid, which can be quenched with sodium bisulfite or similar chemicals commonly used for dechlorination. Brominated water has an unpleasant taste. The operations cost is anticipated to be higher than chlorination-dechlorination due to the higher cost of bromine and higher anticipated doses due to bromine’s reactivity.

Screening grade: Fails alternatives screening for further evaluation as biofilm control alternative.

3.2.7 Filtration

Filtration would physically remove biofilm particles rather than prevent biofilm growth. A variety of filtration processes are available including media and membrane filtration. Filtration is not easy to fit in the existing Darigold COW Water system and would carry a high capital cost compared to other alternatives. Filtration also increases energy demand for pumping and backwashing. Chemicals are also required for membrane cleaning if membrane filtration is used; thus, chemical handling is not necessarily eliminated. Furthermore, without other biofilm prevention methods, the risk of filter biofouling and/or plugging is high. Biofouling of this nature increases backwashing/cleaning frequency. It also decreases the hydraulic capacity, further increasing the extent of filtration facilities and capital cost required.

Screening grade: Fails alternatives screening for further evaluation as biofilm control alternative.

3.2.8 Potassium permanganate

Potassium permanganate is a strong oxidant used in water treatment for removal of hardness, iron, manganese, and taste and odor compounds. Permanganate can also be used for controlling the formation of DPBs by oxidizing DBP precursors and reducing the demand for other disinfectants.

Due to the limited disinfection capabilities of permanganate, it is not commonly used as a disinfectant (US EPA Water Treatability Database, 2019).

In industrial applications, potassium permanganate is supplied in dry form and fed with a dry chemical feeder. Water turns a characteristic pink color if a potassium permanganate residual is present, even at low residual concentrations less than 0.5 mg/L. Residual can be quenched with iron salts, inorganic reductants like sodium thiosulfate, powdered activated carbon, or hydrogen peroxide. NFPA 704 ratings are as follows: Health (3); Flammability (1); Reactivity (1); Special (Oxidizer). Stainless steels have a high corrosion rate when chlorides are present in permanganate solutions.

Darigold has experience using potassium permanganate for cooling tower biofilm control. A high dose was required to control the cooling water tower biofilm at the time, turning water a dark pink color characteristic of solutions with high permanganate residual.

For application to the COW Water system discharging to Outfall 002, dry permanganate could be added to the COW Buffer tank. Mechanical or pumped mixing in the COW Buffer Tank would be required for good dispersion and dissolution of the dry chemical. Either permanganate addition would need to be controlled such that no residual is present in the discharge, or residual permanganate quenching would be required to ensure that a discharge plume of pink-colored water does not occur. Capital cost for a permanganate system would be much lower than high capital cost alternatives such as ozonation or filtration and in the same order or magnitude as other alternatives such as UV, PAA, or chlorination-dechlorination. Operations costs are difficult to evaluate without knowing the dose needed for effective biofilm control. However, based on past Darigold operating experience where a high permanganate dose was required, operating cost is expected to be higher than alternatives such as PAA or chlorination-dechlorination.

Considering the likely need for quenching, anticipated doses for biofilm control, and desire to avoid unintended transport or dispersion of dry permanganate powder residues to other locations in the food production facility, other biofilm control approaches are preferred over permanganate addition.

Screening grade: Fails alternatives screening for further evaluation as biofilm control alternative.

3.2.9 Isothiazolone

Isothiazolone biocides are sold under the trade name KATHON™ WT by Rohm and Haas Company and have been used in industrial settings as broad-spectrum biocides effective against bacterial, fungi, and algae. Isothiazolone biocides inhibit certain dehydrogenase enzymes which disrupt metabolic activity and stop cell growth within minutes (Williams, 2004). Different isothazolone compound formulations are available, but they all act in a similar manner as biocides. Studies have shown that isothiazolones are biodegradable with half-lives less than 24 hours in aquatic environments, and degradation products are four to five orders of magnitude lower in toxicity than the starting parent compounds (Williams and Jacobson, 1999). Formation of halogenated byproducts has not been observed with isothazolone addition (Williams and Jacobson, 1999). Toxicity studies exposing bluegill sunfish to isothiazolone for a 96-hour period showed no mortality at 0.2 mg/L but complete mortality within 24 hours at 2 mg/L (Williams and Jacobson, 1999).

Aspects of isothiazolone biocides seem attractive; however, information on the fate of isothiazolone in aquatic environments and impacts on aquatic species is limited to a small collection of studies primarily authored by the chemical vendor. It does not appear that impacts to sensitive species such as salmonids have been studied. Due to uncertainties regarding these considerations and lack of a more substantive body of research and documented full-scale experience with discharge to surface waters, isothiazolone is not considered a viable alternative at this time.

Screening grade: Fails alternatives screening for further evaluation as biofilm control alternative.

3.2.10 Temperature adjustment (cooling)

Cooled COW water is typically between 45 and 60°F. It is conceivable that the COW water temperature could be further lowered closer to 32°F such that microbial biofilm growth is limited or prevented completely. This approach would involve adding a water chilling system, which would have a high capital cost and high energy demand. Furthermore, the chilled water temperature may not be maintained after discharge from the Darigold facility due to heat gain in the discharge pipeline. As such, biofilm control by temperature adjustment is not considered a viable alternative at this time.

Relative capital cost: High, due to equipment needed for water chilling system.

Relative operations cost: High, due energy demand for water chilling.

Operator safety: Moderate risk. Chemicals likely required for occasional water chilling system cleaning.

Screening grade: Fails alternatives screening for further evaluation as biofilm control alternative.

3.2.11 pH adjustment

It may be possible to control biofilm growth by adjusting COW water pH to levels that limit or prevent biofilm growth. Such an operation could seek to maintain a constant target pH within the discharge limits of 6.5 to 9.0 standard units or involve a “shock” pH treatment and neutralization prior to discharge. As noted earlier, the HRT in the COW Buffer Tank is approximately 36 minutes, and this could possibly serve as shock pH location, with neutralization occurring downstream prior to the discharge flume. The efficacy of either pH adjustment approach would need to be tested and demonstrated because the biofilm microbial composition is not known. Furthermore, a different biofilm microbial community may develop at different pH conditions. Biofilm growth in the discharge pipeline after neutralization and discharge remains a possibility. Acid and base storage and dosing systems required.

Relative capital cost: Low, with relatively simple chemical storage and feed systems.

Relative operations cost: Not evaluated, but expected to be low due to low ionic strength of COW water and thus low pH buffering capacity.

Operator safety: Moderate to high risk. Strong acid and base likely used for pH adjustment.

Screening grade: Passes alternatives screening for further evaluation as biofilm control alternative. Efficacy and ability to control biofilm growth in the discharge pipeline needs to be tested and demonstrated.

4 Summary and Recommendations

Results of the biofilm control alternatives screening (Section 3) are summarized in Table 3. UV irradiation, PAA, chlorination-dechlorination, and pH adjustment passed the screening evaluation and are recommended to be carried forward for consideration in a more detailed Engineering Report described in Darigold's permit.

Table 3. Biofilm control alternatives screening summary

Alternative	Capital cost	Operation cost	Operator safety	Other comments	Pass / Fail
UV irradiation	Low	Low	Low risk	UVT of COW water needs to be evaluated. No residual in discharge pipeline.	**PASS**
Ozone	High	High	Moderate to high risk	High capital and operations cost. Complex system.	FAIL
Peracetic acid (PAA)	Low	Moderate	Moderate to high risk	Possible to maintain residual in discharge pipeline.	**PASS**
Hydrogen peroxide	Low	High	Moderate to high risk	High doses anticipated due to peroxide scavenging by other organics.	FAIL
Chlorination-dechlorination	Low	Low	Moderate risk	No residual in discharge pipeline if dechlorination is within Darigold fenceline.	**PASS**
Bromination-debromination	Low	High[1]	Moderate risk	Similar to chlorination-dechlorination but with higher operation cost and risk of impact to potable water taste.	FAIL
Filtration	High	Varies	Low risk[2]	High capital cost, exacerbated by biofouling in absence of other control methods.	FAIL
Potassium permanganate	Low	Medium	Moderate to high risk	High dose required based on past Darigold experience. Quenching likely required. Risk of dry chemical powder residue transport and dispersion in food facility.	FAIL
Isothiazolone	Low	Not evaluated	Not evaluated	Aquatic toxicity to salmonids not well-characterized. Lack of substantive research and full-scale experience with direct discharge to surface waters.	FAIL
Temperature adjustment (cooling)	High	High	Moderate	High energy demand for chilling wastewater. Temperature increase in discharge pipe expected.	FAIL
pH adjustment	Low	Not evaluated	Moderate to high risk	Biofilm control viability unknown and would require demonstration. Biofilm growth in pipeline after neutralization and discharge from Darigold facility must be investigated.	**PASS**

[1]Versus comparable chlorination-dechlorination alternative

[2]Low risk for media filtration with no chemical addition. Higher risk with chemical handling for membrane filtration.

Pending a more detailed cost evaluation, UV irradiation is particularly attractive if it is proven to be effective at controlling biofilm growth without chemical addition. COW water UVT needs to be measured to confirm UV as a potentially viable solution. Ideally, a full-scale test can be performed to evaluate whether UV alone is effective at controlling biofilm in the Darigold facility and discharge pipeline. UV elements can be leased from vendors; however, the duration of full-scale test necessary to evaluate biofilm control in the entire system including discharge pipeline may render a long-term lease not cost effective compared to outright purchase and installation. Thus, outright installation of a UV system presents a risk in terms of “sunk cost” if not effective at controlling biofilm growth. It may be possible to construct a smaller-scale pilot test system simulating the retention time in the Darigold facility and discharge pipe.

PAA is attractive because it is not known to produce disinfection byproducts, decomposes into non-toxic compounds, is not anticipated to require quenching, and can be dosed at the Darigold facility such that a residual is exhausted or at very low concentration at the outfall discharge. In this manner, PAA offers greater potential to control biofilm growth in the discharge pipeline by providing a residual. Further investigation of material compatibility considerations is required in next steps to confirm that PAA remains a potentially viable solution. Compared to UV irradiation, a full-scale PAA trial is much easier to accommodate.

Combining PAA and UV in a hybrid system could also be considered. PAA addition prior to UV is expected to increase UVT and thus UV irradiation efficacy. The hybrid approach may also reduce required PAA dose for biofilm control. Preferably, UV or PAA alone is sufficient for biofilm control; however, the hybrid system provides flexibility and enhanced disinfection capability. Should a pilot or full-scale UV demonstration study proceed, provisions for temporary PAA addition during the study period are recommended.

Chlorination-dechlorination, while requiring chemical addition, is widely practiced, familiar to operators, and uses chemicals of lower hazard ranking than other alternatives including PAA. No chlorine residual in the discharge pipeline would be provided if dechlorination occurs within the Darigold fenceline, which is the most practical point for dechlorination. A full-scale trial would be easier to accommodate than UV irradiation but more complex than PAA due to the need to add two chemicals and control dechlorination.

Adjustment of COW water pH – either at a constant target pH within the discharge limits of 6.5 to 9.0 standard units or with a shock pH treatment and neutralization prior to discharge – could potentially be a “nontoxic or low-toxicity” method for biofilm control. The efficacy of either pH adjustment approach would need to be tested to demonstrate that biofilm can be controlled not only within the Darigold facility but also in the discharge pipeline after a potential pH neutralization step.

5 Peracetic Acid Trial

Based on findings of the biofilm control alternatives screening and discussions with Ecology, Darigold will be proceeding with a full-scale peracetic acid trial. The preliminary framework of a trial and considerations for full-scale trial design were documented in separate trial plan memorandum and previously submitted to Ecolgoy in draft form. This memorandum is attached as Appendix C. The trial plan also included some bench-scale testing of the impacts peracetic acid addition on COW water pH. Design and construction of the full-scale trial system is ongoing.

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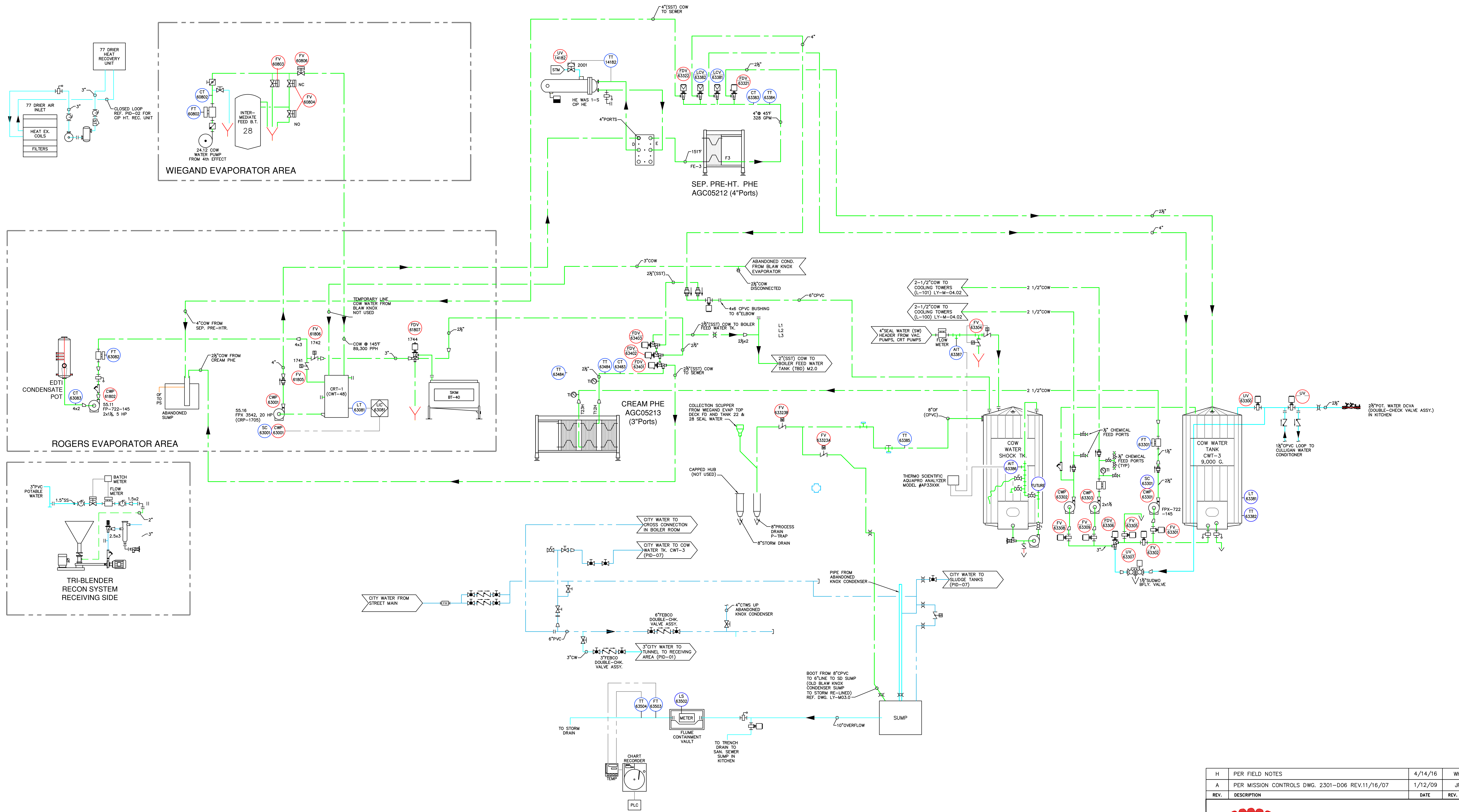
Appendix A. Darigold Lynden Facility COW water system process flow diagram



LEGEND

XX XXXXX — DEVICE # ADDRESS	120VAC DISCRETE
XX XXXXX — DEVICE # ADDRESS	24VDC ANALOG

COW, City, Cooling Tower Water

REV.	DESCRIPTION	DATE	REV. BY
H	PER FIELD NOTES	4/14/16	WHM
A	PER MISSION CONTROLS DWG. 2301-D06 REV.11/16/07	1/12/09	JRJ

DARIGOLD, INC.
1130 RAINIER AVE. S. SEATTLE, WA 98144
P.O. BOX 34377 SEATTLE, WA 98124

SCALE: SCHEMATIC 3/4xp	APPROVED: R.TAYLOR	PLANT: LYNDEN	
DATE: 6/3/02	DRAWN BY: J.R.JAMES		
MECHANICAL-UTILITY PIPING COOLING TOWER/COW WATER DETAILS		DRWG. NO.: LY-M03.0	

Appendix B. HMIS III and NFPA 704 ranking classifications

Table B1. HMIS III rating summary table.

Health	Comments
4	Life-threatening, major or permanent damage may result from single or repeated overexposures.
3	Major injury likely unless prompt action is taken and medical treatment is given.
2	Temporary or minor injury may occur.
1	Irritation or minor reversible injury possible.
0	No significant risk to health.
Flammability	**Comments**
4	Flammable gases, or very volatile flammable liquids with flash points below 73°F, and boiling points below 100°F. Materials may ignite spontaneously with air.
3	Materials capable of ignition under almost all normal temperature conditions. Includes flammable liquids with flash points below 73°F and boiling points above 100°F, as well as liquids with flash points between 73°F and 100°F.
2	Materials which must be moderately heated or exposed to high ambient temperatures before ignition will occur. Includes liquids having a flash point at or above 100°F but below 200°F.
1	Materials that must be preheated before ignition will occur. Includes liquids, solids and semi solids having a flash point above 200°F.
0	Materials that will not burn.
Physical Hazard	**Comments**
4	Materials that are readily capable of explosive water reaction, detonation or explosive decomposition, polymerization, or self-reaction at normal temperature and pressure.
3	Materials that may form explosive mixtures with water and are capable of detonation or explosive reaction in the presence of a strong initiating source. Materials may polymerize, decompose, self-react, or undergo other chemical change at normal temperature and pressure with moderate risk of explosion.
2	Materials that are unstable and may undergo violent chemical changes at normal temperature and pressure with low risk for explosion. Materials may react violently with water or form peroxides upon exposure to air.
1	Materials that are normally stable but can become unstable (self-react) at high temperatures and pressures. Materials may react non-violently with water or undergo hazardous polymerization in the absence of inhibitors.
0	Materials that are normally stable, even under fire conditions, and will not react with water, polymerize, decompose, condense, or self-react. Non-explosives.
Personal Protection	**Comments**
No ranking	Specific personal protection equipment may be recommended but is site-specific

Table B2. NFPA 704 rating summary table.

Health	Comments
4	Very short exposure could cause death or major residual injury.
3	Short exposure could cause serious temporary or moderate residual injury.
2	Intense or continued but not chronic exposure could cause temporary incapacitation or possible residual injury.
1	Exposure would cause irritation with only minor residual injury.
0	Poses no health hazard, no precautions necessary and would offer no hazard beyond that of ordinary combustible materials.
Flammability	**Comments**
4	Will rapidly or completely vaporize at normal atmospheric pressure and temperature, or is readily dispersed in air and will burn readily. Includes pyrophoric substances. Flash point below room temperature at 73°F.
3	Liquids and solids (including finely divided suspended solids) that can be ignited under almost all ambient temperature conditions. Liquids having a flash point below 73°F and having a boiling point at or above 100°F or having a flash point between 73 and 100°F.
2	Must be moderately heated or exposed to relatively high ambient temperature before ignition can occur and multiple finely divided suspended solids that do not require heating before ignition can occur. Flash point between 100 and 200 °F.
1	Materials that require considerable preheating, under all ambient temperature conditions, before ignition and combustion can occur. Includes some finely divided suspended solids that do not require heating before ignition can occur. Flash point at or above 200°F.
0	Materials that will not burn under typical fire conditions, including intrinsically noncombustible materials such as concrete, stone, and sand. Materials that will not burn in air when exposed to a temperature of 1,500°F for a period of 5 minutes.
Reactivity	**Comments**
4	Readily capable of detonation or explosive decomposition at normal temperatures and pressures.
3	Capable of detonation or explosive decomposition but requires a strong initiating source, must be heated under confinement before initiation, reacts explosively with water, or will detonate if severely shocked.
2	Undergoes violent chemical change at elevated temperatures and pressures, reacts violently with water, or may form explosive mixtures with water.
1	Normally stable, but can become unstable at elevated temperatures and pressures.
0	Normally stable, even under fire exposure conditions, and is not reactive with water.
Special	**Comments**
OX	Oxidizer, allows chemicals to burn without an air supply.
~~W~~	Reacts with water in an unusual or dangerous manner.
SA	Simple asphyxiant gas. The SA symbol shall also be used for liquefied carbon dioxide vapor withdrawal systems and where large quantities of dry ice are used in confined areas.

Appendix C. Peracetic Acid Test Plan and Preliminary Bench Testing

Peracetic Acid Test Plan and Preliminary Bench Testing

Darigold, Inc.

Darigold Lynden, WA
February 14, 2020

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1 Background

Production of evaporated milk products at the Darigold facility in Lynden, WA generates what is referred to as condensate of whey (COW) water. COW water and non-contact cooling water from the Darigold Lynden facility are currently discharged to the Nooksack River. The discharge is subject to regulation under National Pollutant Discharge Elimination System (NPDES) Permit No. WA0002470 administered by the Washington Department of Ecology (Ecology). The most recent permit included special conditions for studying and implementing systems for control of filamentous bacteria growth in the discharge.

This test plan memo builds on a preceding Biofilm Control Study (HDR, 2019), which identified peracetic acid (PAA) as a potentially feasible alternative to biofilm control within the Darigold facility and discharge pipeline to the Nooksack River outfall. HDR and Darigold staff viewed PAA addition as the preferred biofilm control approach and want to move forward with a full-scale trial. Ecology is supportive of the Biofilm Control Study findings and progression of the full-scale PAA trial.

Darigold is permitted to discharge up to 1.0 million gallons per day (mgd) maximum daily flow. Current COW water discharge is typically between 0.3 and 0.4 mgd as shown in Figure 1.

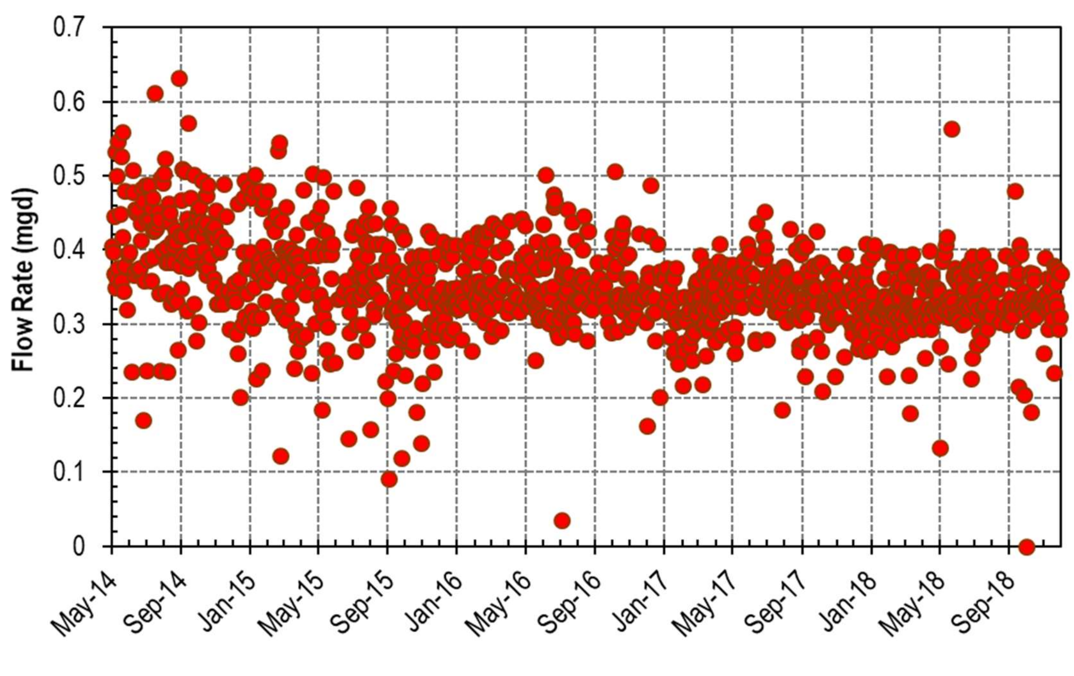

Figure 1. Darigold Lynden COW Water Flow

2 Peracetic acid general information

PAA is a strong oxidizer and broad spectrum antimicrobial agent. It has been widely used in food and pharmaceutical applications for decades, but its use in wastewater treatment applications is comparatively newer and less common. PAA results from the equilibrium reaction of hydrogen peroxide and acetic acid and thus exhibits some pH dependence. PAA tends to dissociate (pKa = 8.2) and have lower efficacy under excessively alkaline conditions.

PAA is commercially available in different solution concentrations. Commonly-used PAA solutions for wastewater disinfection and industrial process biofilm control contain 12-15% PAA, 20-25% hydrogen peroxide, 15-25% acetic acid, and 0.5-1% sulfuric acid. Several PAA manufacturers and product names are listed in Table 1. PAA solution composition and physical properties for the commonly-used VigorOx WWT II by PeroxyChem are summarized in Table 2.

Table 1. Examples of commercially-available PAA solutions in 12-15% strength

Manufacturer	Trade Name(s)
PeroxyChem, LLC	VigorOx WWT II
Solvay Chemicals, Inc.	Proxitane WW-12
BioSafe Systems, LLC	SaniDate 12.0, SaniDate 15.0
Evonik Industries	Peraclean 15
EnviroTech Chemical Services, Inc.	BioSide HS 15, Peragreen 15, Peragreen WW

Table 2. Composition and physical properties of PeroxyChem VigorOx WWT II

Parameter	Value
PAA (%)	15
Hydrogen peroxide (%)	23
Acetic acid (%)	16
Sulfuric acid (%)	1
Specific gravity	1.15 at 20°C
Freezing point (°C)	-49
Flash point, closed cup (°C)	68
Boiling point (°C)	108
Autoignition temperature (°C)	251-254
Decomposition temperature (°C)	>55

Information from vendor Safety Data Sheet dated March 2019

PAA is not known to produce DBPs. PAA can be used to maintain a residual in the Darigold discharge pipeline. The residual decomposes into non-toxic compounds (water and acetic acid), and quenching is not usually required. Ideally, PAA could be added at the Darigold facility such that PAA residual is exhausted or at very low concentration at the outfall discharge.

3 Preliminary basis for PAA dose

Typical PAA doses for disinfection of municipal wastewater secondary effluent are 1 to 2 mg/L. Darigold's biofilm control treatment objectives and industrial wastewater matrix are different, but municipal secondary effluent disinfection experience provides a point of reference for PAA doses that may be expected at Darigold. A preferred outcome is that low PAA doses in or below this range are effective at controlling biofilm growth such that PAA doses are well below PAA discharge limits, thus making PAA discharge monitoring simple or possibly allowing indirect monitoring approaches as described above.

It should be noted that PAA dosing directions for EPA registration number 65402-8, the registration number for the PAA product "VigorOx 15/23 Antimicrobial Agent", suggest initial PAA doses up to 17 mg/L of PAA for control of slime-forming bacteria and gradual reduction of PAA dose to a level sufficient to maintain biofilm control. The expectation at Darigold is that a once initial biofilm control is established, the maintenance dose will be similar to municipal wastewater disinfection doses.

For purposes of this trial, an initial "shock" dose is not recommended to minimize the risk of an instantaneous dramatic sloughing event. A sustained lower dose is recommended to favor more gradual sloughing as the established biofilm is slowly eliminated. Sloughing in this regime is expected to resemble natural sloughing that occurs currently with low levels of biofilm growth and where microbial "mats" are not observed on the Nooksack River.

Consequently, preliminary PAA demand was based on doses in the range of 0.5 to 3 mg/L and 15% PAA solution. The basis for doses and corresponding PAA solution demand are summarized in Table 3. Although Darigold has a permitted maximum flow of 1.0 mgd, such flows are not currently produced and are not expected to be produced by future facility operations. Therefore, a maximum flow rate of 0.4 mgd and PAA dose of 3.0 mg/L represents the maximum design scenario.

Table 3. Conceptual PAA solution demand range

Parameter	Low-Low Dose	Low Dose	Medium Dose	High Dose
COW water flow rate (mgd)	0.30	0.30	0.35	0.40
PAA dose (mg/L)	0.5	1.0	2.0	3.0
15% PAA solution demand (gpd)	0.9	1.7	4.1	7.0
30 days storage (gal)	26	52	122	209

Based on the estimated PAA solution demands in Table 3, delivery of 300-gal totes will provide sufficient storage and appropriate chemical turnover. 55-gal drums may also be appropriate if a lower biofilm control dose near 1 mg/L is shown to be effective.

4 PAA discharge and monitoring considerations

It is anticipated that some of dosed PAA will be consumed by oxidation/disinfection processes occurring from the dosing point at the Darigold facility and throughout the discharge pipeline to Nooksack River outfall. Therefore, the discharged PAA concentration is anticipated to be less than the PAA dose. Should no PAA demand exist, the discharge concentration will equal the PAA dose concentration.

A challenge in Darigold's situation is that the existing permit compliance monitoring is inside the facility but biofilm control is desired throughout the discharge pipeline. Darigold does not have access to a permanent and secure monitoring point near the Nooksack River discharge, which complicates PAA dosing and discharge monitoring approaches.

Guidelines for residual PAA discharge were included as part of EPA registration number 65402-8, the registration number for the PAA product "VigorOx 15/23 Antimicrobial Agent". The guidelines are shown below in Figure 2 (excerpt from EPA registration number 65402-8). The Fact Sheet for NPDES Permit No. WA0002470 indicates that the chronic mixing zone dilution factor for the Darigold Lynden facility is 37 as determined by Ecology. Based on the chronic dilution factor and guidelines for residual PAA discharge, the corresponding maximum PAA discharged concentration is 3.3 ppm. Based on this analysis, absent additional information from Ecology, a maximum PAA dose of 3.3 mg/L would comply with EPA-approved PAA discharge guidelines in the event that PAA concentration does not decrease between the dose point and river outfall.

The maximum amount of peracetic acid that can be discharged is:

i. 0.09 * DF, when DF ≥ 12 and

$$DF = \frac{\text{plant effluent discharge + receiving stream 7Q10}}{\text{plant effluent discharge}}$$

where 7Q10 is the minimum average 7-day flow expected to occur once every 10 years for the receiving stream; or

ii. 1 ppm if the 7Q10 is unknown or DF < 12

Figure 2. Guidelines for residual PAA discharge

Excerpt from EPA registration 65402-8 for the PAA product "VigorOx 15/23 Anitmicrobial Agent"

If PAA addition is effective at controlling biofilm growth and permanently implemented at full-scale, a PAA discharge limit may be incorporated into future NPDES discharge permits. Such a limit may require direct measurement of PAA concentrations. Various online PAA probes are available (see examples in Figures 3 and 4). A full review of the features, advantages, and disadvantages of such probes is beyond the scope of this test plan. Separate laboratory wet chemistry methods are also available to quantify PAA concentration (see example colorimetric analyzer in Figure 5). It is also conceivable that alternative approaches not involving direct PAA measurement but other parameters such as monitoring and reporting PAA chemical flow rate may be acceptable to Ecology. For example, the PAA chemical flow rate may indirectly show that discharge PAA is inherently below discharge limits under the conservative assumption of no PAA consumption in the facility and discharge pipeline (e.g., less than 3.3 mg/L PAA dose using example limit above).

Figure 3. Online submersible PAA probe by PeroxyChem

Figure 4. Panel-mounted PAA analyzer by ECD

Figure 5. Benchtop colorimetric PAA analzer by PeroxyChem

5 PAA system implementation considerations

PAA system implementation considerations are discussed in this section to frame decisions on the test system design. PAA system implementation considerations were primarily based on information from PeroxyChem, a leading PAA vendor in the United States. PeroxyChem can offer VigorOx WWT II as “chemical only” or turnkey complete PAA systems including chemical supply, storage, feed and control equipment, installation, startup, and maintenance services.

5.1 Tote storage

Tote or drum storage is expected to be sufficient at Darigold. Considerations related to tote storage and location include the following:

- Secondary containment is required.
- Do not store near reducing agents or combustibles (20 ft minimum distance). Do not store o wooden pallets.
- Do not block vents.
- Typically stored outside; freezing is not commonly an issue due to low freezing point. Ventilation required if stored indoors. Minimum ventilation rate of 1 cfm/ft^2.
- NFPA classification IV organic peroxide; does not support a flame.
- Intrinsically safe electrical components recommended for areas that are not well-ventilated.

5.2 Pumps

An example PAA pump skid furnished by PeroxyChem for LOTT Alliance in Olympia, WA is shown in Figure 6. Considerations related to PAA pumping systems include the following:

- Peristaltic, diaphragm, or solenoid pumps acceptable

- Placed close to the point of use if carrier water is not used
- Off-gas valve required at pump head for diaphragm and solenoid pumps
- Wetted materials
    - Passivated 304L stainless steel
    - PTFE / Teflon®
    - Santoprene® (peristaltic pumps)
- Secondary containment required
- Controller for flow-paced or compound-loop chemical addition control

Figure 6. PAA pump skid furnished PeroxyChem for LOTT Alliance in Olympia, WA

Pump control panel and 6,000-gal bulk storage tank in background

5.3 Piping

Considerations related to PAA piping include the following:

- No buried piping.
- Compatible wetted materials (304 stainless steel or PTFE)
- Vented ball valves
- Pressure relief valves to prevent overpressurization, which in extreme circumstances may lead to exothermic decomposition that can lead to combustion.
- Dilution water / flush line
- Flex connections for tanks, totes, and pumps

- Gasket materials
    - PTFE
    - GORE-TEX®
    - GarlockGylon® Style 3504
- Thread sealant
    - PTFE tape
    - Fluorolube®

6 Test plan general approach

This section addresses high-level design and monitoring considerations for the PAA trial. Certain issues are left open-ended for further discussion with Darigold staff and may be better informed by a future site visit focused on PAA systems planning and location.

6.1 PAA storage location

Anticipated PAA demand is such that drums or totes are expected to be sufficient for storage. These containers could be located indoors if adequate ventilation is provided. PeroxyChem recommends a minimum of 1 cfm/ft^2 for indoor PAA storage. Otherwise, PAA should be stored outdoors. Security of chemicals stored outdoors should be considered. Heat tracing is not required.

6.2 PAA dose

The basis for anticipated PAA dose was discussed in Section 3 and summarized in Table 3. The doses are in the range of 0.5 to 3 mg/L and under the anticipated discharge limit of 3.3 mg/L per the approach described in Section 4. As such, continuous PAA discharge monitoring should not be necessary. The maximum dose of 3 mg/L will not be exceeded unless supported by sampling showing significant PAA consumption along the COW water flow path and exhaustion of PAA near the river outfall.

6.3 PAA dose control

Flow rate at the effluent flume is monitored in a PLC. The effluent flow signal can be used to flow-pace PAA addition based on a PAA dose setpoint. Control wiring from the PLC to the PAA pump location may be required depending on the nature of Darigold's SCADA system.

6.4 PAA dose point

Several PAA dose points may be feasible. The preferred location may be affected by considerations including the following:

- Proximity to PAA storage or ability to co-locate PAA near the dose point
- Existing building systems (ventilation, etc.)
- Darigold operations and chemical contamination / cross-over considerations

Several potential PAA dose points are described below, from most upstream to downstream along the COW water flow path.

One potential dosing location is to the 4-inch stainless steel pipe at the SEP.PRE-HT.PHE "Sep Press" leading to the COW Buffer Tank. This location is the furthest practical upstream location for chemical addition. At this point, COW water is being directed to waste discharge and is not being reused. Being furthest upstream, this dosage point offers the maximum biofilm control potential and is the preferred location absent other considerations. The stainless steel pipe is likely compatible with PAA addition, but the specific material and compatibility needs to be confirmed. It is envisioned that an inline static mixer would be added to mix PAA with the COW flow stream.

The next potential dosing location is to the 6-inch PVC discharging to the COW Buffer Tank and approximately 15 feet above finished floor. A spool piece of PAA-compatible piping and inline mixer would be inserted into the existing pipe run.

PAA could be added directly to the COW Buffer Tank, but the tank would likely need supplemental mechanical or pumped mixing to achieve a relatively uniform PAA concentration. A similar approach could be to modify what appears to be an existing sample pump and small-diameter discharge pipe into a pumped recirculation system with PAA addition and in-line mixing on the recirculation line. The recirculation rate would be equal to or similar to the COW water flow rate to ensure uniform PAA concentration in the COW Buffer Tank and low risk of short-circuiting with high PAA concentrations.

Finally, PAA could be added to the manhole sump downstream of the COW Buffer Tank. This location appeared to be highly turbulent and well-mixed, thus not requiring additional mixing. One disadvantage of this location relates to potential tripping hazards of PAA piping leading to the manhole. Another disadvantage is that biofilm may grow in upstream piping and buffer tanks. Therefore the biofilm control potential within the Darigold facility is the lowest for this dose point.

6.5 PAA residual monitoring

Based on the PAA dosing strategy, occasional spot checks of residual PAA should be appropriate. Darigold may choose to purchase a wet chemistry "kit" for measuring PAA internally (see Figure 5) or send samples out for external laboratory analysis. An online PAA monitoring system may ultimately be preferred for process monitoring or driven by permit monitoring requirements, but this is not viewed as necessary for the full-scale demonstration based on intended PAA doses. PAA concentration at the effluent flume should be measured once per week. If possible, PAA concentration near the outfall can also be measured occasionally if access to a suitable sample location can be arranged. The PAA dose and residual concentration can be compared to provide and indicator of PAA demand.

6.6 Biofilm control efficacy monitoring

The effectiveness of PAA to control biofilm growth will be based on qualitative observations. More quantitative measures such as measuring the amount of biomass from a "scraping" of a defined surface area are challenging due to access limitations and the fact that the biofilm tends to break up when perturbed, thus making sample collection difficult. Operations staff should observe and report the extent of biofilm growth at particular location(s) on a weekly basis. Readily accessible locations include the COW Buffer Tank, sump manhole downstream of the buffer tank, and the effluent flume. Darigold can consider taking underwater photos of the biofilm at a defined location for record purposes.

6.7 Startup and sloughing monitoring

Initial startup at a low PAA dose of 0.5 mg/L is recommended to limit the risk of a dramatic instantaneous sloughing event. The dose may be gradually increased based on initial observations of biofilm control efficacy. Visual observations along the COW water conveyance system allow for qualitative evaluation biofilm control and extent of sloughing, if relevant. Effluent TSS data will also serve as an indicator of biofilm control and potential sloughing. Although the approach outlined above aims to avoid excessive sloughing and elevated effluent TSS concentrations, these may be unavoidable until the established biofilm fully responds to PAA addition at a steady-state dosing conditions.

6.8 Current biofilm conditions

Darigold has implemented plant improvements that have dramatically reduced the extent of biofilm growth in COW water lines since the excessive biofilm growth and sloughing events to the Nooksack River approximately four years ago. Chief among these were repairs to cracks in the evaporators. These repairs have resulted in consistently lower effluent BOD concentrations and lower biofilm growth. Recent observations by Darigold staff indicate that, although a perceptible biofilm remains in the COW water line within the Darigold facility and in a manhole near the current final discharge point, the current biofilm thickness is approximately 10% of prior levels during times of excessive growth. Darigold staff also report that the biofilm is slower to re-establish between COW water line cleaning events. The current low levels of biofilm growth equates to lower risk of a dramatic sloughing event during PAA testing.

6.9 pH control considerations

COW water is characterized by low ionic strength and pH buffering capacity meaning small doses of chemical may impact pH. COW water pH ranges from 6.3 to 8.5 standard units. 10^{th}, 50^{th}, and 90^{th} percentile pH values are 6.5, 7.1, and 8.0 standard units based on four years of operating data through 2018.

The peracetic acid and acetic acid components of PAA solutions are relatively weak acids but may impact COW water pH. Supplementary base addition may be required for pH adjustment to bring the discharged water within permit limits of 6.5 to 9.0 standard units for Sampling Point 1 and discharge to Outfall 001 or Future Outfall 002.

Darigold recently executed preliminary bench tests to evaluate the impact of different PAA doses on COW water pH. Increasing amounts of a dilute PAA solution were added to COW water while pH was monitored. The results are shown in Figure 7. At the low initial COW water pH between 6.4 and 6.7 standard units, even low doses of PAA less than the maximum 2 mg/L dose anticipated for biofilm control caused pH to fall below the minimum discharge limit of 6.5 standard units.

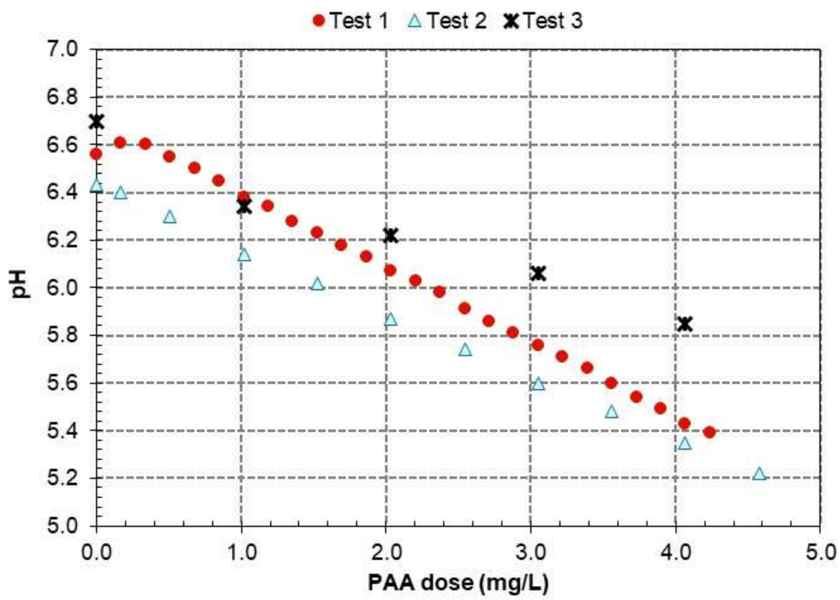

Figure 7. Curves for pH response with PAA addition to COW water

Test dates 9/11/19 (Test 1 and 2) and 9/24/19 (Test 3)

Another bench test evaluated the pH response with alkalinity addition following PAA addition to COW water. A sodium bicarbonate solution was added following PAA addition in Test 3 to evaluate pH recovery response. The initial PAA concentration at the start of bicarbonate addition was approximately 4 mg/L. The pH response with bicarbonate addition is shown in Figure 8. The results show that 10 mg/L alkalinity as $CaCO_3$ brought the pH above the minimum discharge limit of 6.5 standard units. Considering the relatively high starting PAA concentration of 4 mg/L, the results indicate that some alkalinity addition is required for pH control, but that the alkalinity dose is not anticipated to be extremely high. Other bases such as sodium hydroxide can also be used for pH control. An advantage of sodium bicarbonate is the buffered response as shown in Figure 8; extreme pH swings are less likely with use of sodium bicarbonate. Because PAA dissociates has lower efficacy under excessively alkaline conditions (pKa = 8.2), pH control should target pH near neutral conditions to maximize PAA efficacy and minimize chemical doses.

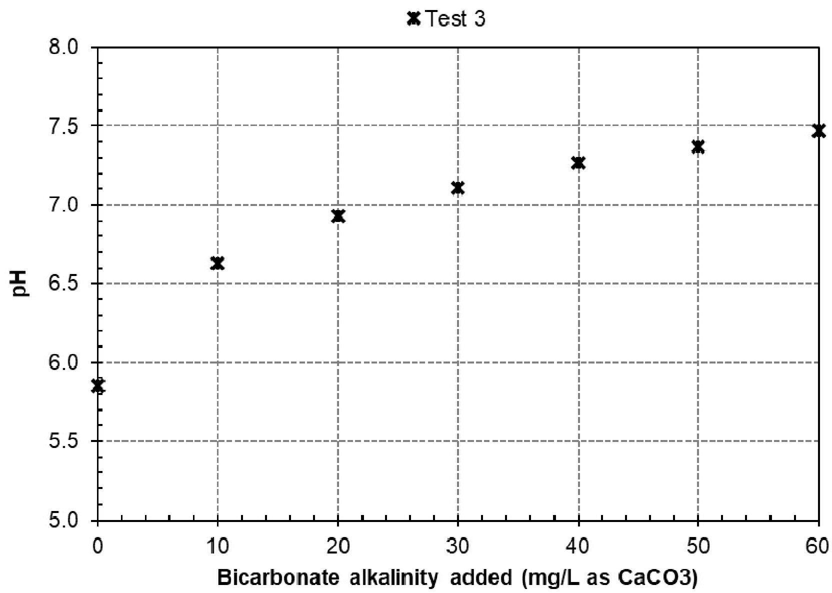

Figure 8. Curve for pH response with alkalinity addition to COW water with 4 mg/L PAA at start of alkalinity addition

Alkalinity added as sodium bicarbonate

Darigold's full-scale PAA addition trial will include provisions for pH control and base/alkalinity addition. The following framework is proposed for PAA addition and pH control:

- PAA addition upstream of the COW water tank in the 6" PVC line. This is the most practical upstream in-plant location for PAA addition to maximize its use for biofilm control.
- Addition of sodium bicarbonate as alkalinity/base for pH control at the COW water tank
- Feedback control of alkalinity/base addition based on pH measured at the COW water tank using the existing COW water tank recycle loop and pH probe. Alkalinity addition to the recycle loop for mixing and carrier water.
- Abandoned tanks near the COW water tank may be used for sodium bicarbonate solution makeup using dry chemical and City potable water.