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Confluence

Project: Distribution System Water Quality Evaluation

Cc:

Subject: Final – Silica White Paper

1 INTRODUCTION AND OBJECTIVES

Since switching sources of supply from the surface water treated at the Filter Plant on Fishers Lane to a ground water supply treated at the new Mint Farm Regional Water Treatment Plant (MFRWTP), the City of Longview has received complaints due to white spot formation. The spots seem to be formed upon evaporation of water drops on the exterior of cars, plumbing fixtures, and kitchenware. Investigations conducted to date have shown that the white spots consist largely of silica and to a lesser degree calcium carbonate and other minerals. Although the MFRWTP water has a higher hardness level compared to the Cowlitz River source, it is classified as Moderately Hard on most hardness scales. The nature and degree of white spotting is not consistent with other ground waters with a hardness of approximately 90-100 mg/L as CaCO₃ (calcium carbonate). Additional study has indicated that elevated silica levels in the ground-water supply (50 mg/L as SiO₂ (silicon dioxide)) is the primary cause of the white spotting.

The purpose of this white paper is to present background information on silica chemistry, to summarize information concerning silica treatment alternatives, and to discuss potential silica deposit modification alternatives. This document is not intended as an exhaustive review of the literature pertaining to silica, but rather as an overview of the key aspects of silica chemistry that may provide insights on the feasibility of removing silica from the water and methods customers of the City of Longview could use to reduce white spotting. Much of the available literature addresses silica precipitation and scale formation in industrial processes under conditions of higher temperatures and pressures than are applicable to the drinking water system at the City of Longview.

It is also important to note that the white spots from the water are associated with *evaporative*, not *precipitative*, processes per se. Neither silica nor any of the cations species such as calcium, magnesium, iron, or aluminum are present at or near their respective solubility limits, and at the current pH of 7.7, silica does not ionize and is not reactive with cations present in solution. The degree of similarity and differences between chemical and physical reactions due to evaporation versus precipitation of drinking water under standard conditions are not clear. However, as water is driven off due to evaporation, at some point, solubility limits are theoretically exceeded. In the absence of literature applicable to silica deposits formed

due to an evaporative process, discussion of precipitative processes as an analog for evaporative process is provided in this paper.

2 BACKGROUND AND SILICA CHEMISTRY

Silicon is the second most abundant element in the crust of the earth. Silica dissolves into ground water from naturally occurring minerals, such as feldspars, ferromagnesian and clay minerals, chert and opal (one type of opal is also known as amorphous silica), and micas (Chapman, 1996). In soils comprised of igneous rock, there are fewer opportunities for reactions to take place between water and solid minerals due to the physical shape of the pores, fissures, and cracks through which water flows through these types of soils (Chapman, 1996). Groundwater associated with igneous rock often therefore has a lower mineral content, although it may be characterized by higher silica content. Ground waters affected by volcanic activity and minerals such as basalt, typically have higher levels of silica. Silica generally occurs at concentrations between 1 and 30 mg/L as SiO₂ in ground waters, but can occur at concentrations up to 100 mg/L (Chapman, 1996). Silica levels are typically lower in surface waters, but some surface waters may contain elevated silica, depending on hydrogeologic conditions (Chapman 1996). All natural waters contain some dissolved silica (Meyers).

2.1 Forms of Silica in Water

Silica chemistry in water is very complex, with numerous forms and varying terminology and nomenclature reported in the literature. Dissolved silica is often described by the formula "SiO₂". The reason for this is that amorphous silica and solid silica deposits typically contain a ratio of two moles of oxygen per mole of silicon (Meyers). When silica is dissolved in water, it hydrolyzes to form silicic acid, and can be expressed as follows (Meyers):



Silicic acid is sometimes reported to have the formula H₂SiO₃ (referred to as metasilicate), however, it is more correct (and more useful) to use the formula Si(OH)₄, (which is equivalent to H₄SiO₄, and referred to as orthosilicate) with the structure as given in Figure 1 (Meyers).

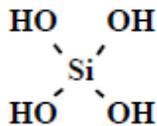


Figure 1: Molecular Structure of Silicic Acid

The molecule would also be surrounded by waters of hydration which are not part of the chemical structure but effectively increase the size of the molecule (Meyers). Silicic acid can be ionized to form silicate ions (Figure 2). The pK_a of this reaction is reported in the literature in the range of 9.7 (Meyers) to 9.9 (Handbook of Chemistry and Physics), so at the pH of most drinking waters silica exists in the silicic acid (non-ionized) form, which makes silica treatment/removal quite difficult. As pH is raised above a value of

10, silicate ions become increasingly more abundant (Meyers), and treatment techniques are more effective.

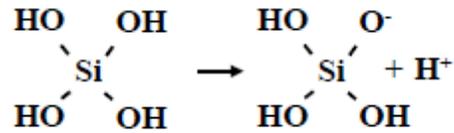


Figure 2: First Ionization of Silicic Acid to Form a Silicate Ion and a Hydrogen Ion

Subsequent pK_a values for the dissociation of the second and third hydrogen ions from the silicate molecule are 11.8 and 12 (Ning, 2002).

Silicate ions can be combined to form polymeric silica when covalent bonds are formed between oxygen atoms of adjacent silicate ions. The polymer is expressed as $(\text{H}_2\text{SiO}_3)_n$ and is as presented in Figure 3 (Meyers).

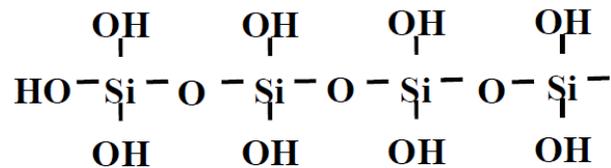


Figure 3: Polymerized Silicate of the Form $(\text{H}_2\text{SiO}_3)_n$ (Meyers)

Some longer chains of polymerized silica may not be properly accounted for when quantifying the silica concentration using the Molybdate analytical test, for which the results are usually expressed as "reactive silica" (Meyers). This terminology can be confusing, since the silica is still non-ionized, and therefore considerably "unreactive" with regard to treatability or modification. The term "reactive" silica refers to the portion that can be measured using the Molybdate analytical test.

Silica is generally found in natural waters in three different forms: dissolved silica; colloidal silica; and particulate silica. Reactive silica includes silicic acid, silicates, and polymerized forms with molecules smaller than the colloidal range (Sahachaiyunta et al., 2002). Colloidal silica is widely thought to be silica that has polymerized such that the molecular size is roughly in the range from 0.01 to less than 0.5 microns. Colloidal silica may be associated with organic compounds or with other complex inorganic compounds. Particulate silica is larger in size and mostly comprised of sand or suspended solids in water larger than 0.5 microns in size.

All of the silica measured from the MFRWTP supplies is in the form of silicic acid, and categorized as dissolved, reactive silica.

2.2 Silica Solubility

Silica solubility (i.e., the maximum amount that can be dissolved in water) is well known to be dependent on pH, temperature, trivalent metal ions, and total dissolved solids, and is generally accepted to be <150 mg/L. The potential for silica scaling occurs when the dissolved silica level in re-circulating water or an RO system reject stream exceeds the amorphous silica solubility limit, 100 mg/L at ambient temperature (Amjad and Zuhl, 2010). Silica concentrations as high as 300 mg/L in some volcanic waters and as high as 1,000 mg/L in a wastewater sample in Hawai'i have been reported in the literature (Meyers).

As shown in the Figure 4, silica occurs in the un-ionized form in the pH and oxidation reduction potential (ORP) range of natural waters, and silica solubility and speciation are largely independent of pH below pH 9.

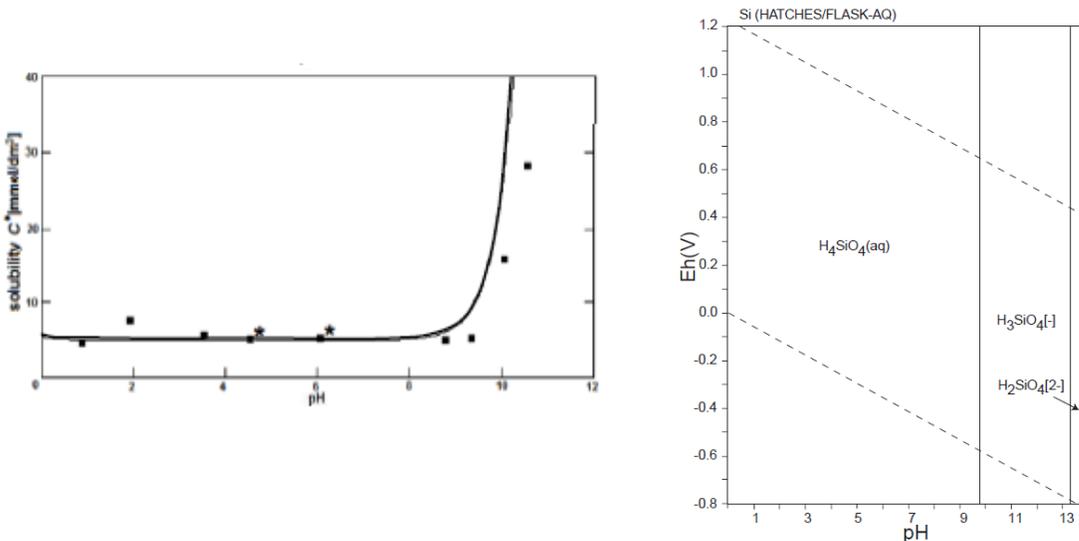


Figure 4. (above, Baldyga et al. and right, Takeno, 2005): Solubility and Eh-pH Diagrams for Silica

Below a pH of 9, silica is present mostly in the silicic acid form. As the pH of water exceeds 8, silicic acid (H_4SiO_4) increasingly dissociates into the bisilicate anions $H_3SiO_4^-$ and $H_2SiO_4^{2-}$. This will increase the solubility of the silica unless divalent and polyvalent cations are available at significant concentrations (Water Quality Association, 2000). Silica solubility increases with increasing temperature, pH, and sodium alkalinity (total alkalinity minus total hardness), and decreases with increasing concentration of divalent ions (such as calcium, magnesium) and increasing precipitation of salts (Meyers).

2.3 Formation of Silica-Based Solids

The processes responsible for the deposition of silica-based deposits include bulk precipitation which forms amorphous silica (via silica condensation and polymerization), precipitation of metal silicates, and co-precipitation of silica with metal salts. Most silica-based deposits consist of amorphous silica and/or magnesium silicate (Amjad and Zuhl, 2010). Although, the mechanisms of silica-silicate inhibition, deposition, dispersion, etc., have been studied in great depth, no unified understanding of various processes involved in silica-silicate deposition currently exists (Amjad and Zuhl, 2010).

One study was identified in the literature that assessed staining on surfaces associated with evaporation of tap water. Krongberg and Froberg (no date provided) studied the formation of insoluble stains on glass and glaze surfaces in the laboratory. The surface samples were dipped in acidic, alkaline and aqueous solutions and the analysis of the surfaces were carried out by scanning electron microscope (SEM) equipped with energy dispersive x-ray analysis (EDX) and atomic force microscope (AFM). All residual chemicals (calcium and sodium salts) could be cleaned away except silica which remained insoluble on the surface. The silica originated from the tap water and was not a result of a corrosion of the surface. The authors noted that if the samples were wiped with a cloth immediately after every dipping, no stain formation was observed. An EDX-analysis of several evaporated tap waters used in the study indicated residue consisting mainly of Ca, Mg, Na, S, Cl, and Si. The same elements were found in the stains on the examined surfaces after water exposure, thus indicating the origin of the stain formation. The average amount of Si in the residues of the evaporated tap waters was approximately 10%, but samples with up to 30% Si (calculated as oxide-%) were found. Si concentration was on average only 2.7 ppm in the tap water. The results showed that the more Si in the water, the more distinct was the insoluble deposit on the surface.

The literature cites many instances and problems associated with precipitation of amorphous silica and/or silica salts in boilers, steam turbines, geothermal applications, etc. The vast majority of technical papers found in the literature applied to industrial applications. For example, in evaporative cooling systems, it is recommended that silica be maintained at acceptable levels (usually < 180 mg/L in absence of silica/silicate control agents) to avoid the formation of silica-based deposits (Amjad and Zuhl, 2010). As stated by Demadis (2010), in a cooling tower operating at a pH level of less than 7.5, soluble silica generally should be maintained below 200 ppm (as SiO₂). For a pH level higher than 7.5, soluble silica should be maintained below 100 ppm (as SiO₂). Demadis (2010) also states that Mg²⁺ levels also should be taken into account at a pH level greater than 7.5. In this case, the product of (ppm Mg as CaCO₃) × (ppm SiO₂ as SiO₂) should be below 12,000. For comparative purposes, the average product of Mg as CaCO₃ (24 mg/L) × SiO₂ (50 mg/L) for MFRWTP finished water is approximately 1,200.

The magnesium silicate system is highly pH-dependent. Below pH 7, there is essentially no chance of precipitation, because the silica exists in an unreactive, non-ionized form. Above pH 9, magnesium silicate is very likely to form because silica forms reactive silicate ions. According to Demadis (2010), at pH < 8, magnesium is rarely observed in deposits. This does not imply the absence of Si-containing scale deposits, it merely means that magnesium is not incorporated in the deposit structure. Studies show that at pH >

8.5, analyses of several deposits showed that the Mg content increased with pH. Furthermore, temperature is extremely important. Precipitation begins at a lower pH if the temperature is sufficiently high (Demadis, 2010), such as in hot water heaters, boilers, and steam generating facilities.

According to the Water Quality Association (2000), cations of calcium, magnesium, iron, and aluminum, will likely cause precipitation of insoluble silicate salts, especially at higher pH levels. Below pH 8, dissolved silica in the silicic acid form (H_4SiO_4) precipitates to SiO_2 when the solubility of silicic acid is exceeded. Precipitated silica and silicates can be very difficult to re-dissolve. (Water Quality Association, 2000).

Several experiments performed by Demadis (2010) demonstrated that Mg^{2+} ions actually act as a catalyst in silicic acid condensation reaction for magnesium levels up to 100 mg/L, but not unless the pH is above 9. The author clearly states that at pH 8, Mg^{2+} up to 100 ppm has virtually no effect in the silicic acid condensation reaction. Considering that the Mg^{2+} level in MFRWTP finished water is approximately 6 mg/L, it does not appear that softening to further reduce Mg^{2+} will have a beneficial effect with regard to formation of magnesium silicate deposits.

The effect of cations on decreasing silica solubility follows the order $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{K}^+$ (Marshall et al., 1980). While calcium has a lesser impact compared to magnesium on silica solubility, according to Demadis (2010), CaCO_3 precipitates can provide a crystalline matrix in which silica can be entrapped and grown. In environments in which CaCO_3 or any other mineral precipitate is prevented completely, higher silica levels generally are tolerated in the process water as opposed to those environments in which other scales are controlled ineffectively. As stated previously, the MFRWTP finished water is not saturated with CaCO_3 , nor is the pH in the range to promote precipitation. While some degree of softening can be achieved through additional treatment, it is not advisable to deliver a water with zero hardness, or even hardness that is lower than the Cowlitz River supply, since the existing distribution system pipe scales would undergo significant destabilization.

2.4 Regulatory Considerations

In the United States silica is not regulated as a primary or secondary contaminant under the Safe Drinking Water Act. While often screened as part of source water characterization studies, monitoring of silica is required only for those utilities adding silicates to their water as a corrosion control strategy, as part of compliance with the Lead and Copper Rule. No other regulatory or monitoring requirements relating to silica in drinking water could be found, including the World Health Organization, the United Kingdom Drinking Water Inspectorate, the European Drinking Water Directive, or the Guidelines for Canadian Drinking Water Quality.

3 SILICA TREATMENT ALTERNATIVES

In the drinking water industry the application of treatment processes with the explicit goal of silica removal is extraordinarily rare. Colloidal and particulate silica can be removed in coagulation/filtration and membrane processes, however, as discussed above, the vast majority of silica is often present in the dissolved form which is more difficult to remove, so in most cases silica removal is very limited.

Treatment to remove silica is essentially only performed in industrial applications. Industries that may consider silica removal include cooling tower applications, boiler feed water or boiler blow down water, carwashes, semi-conductor manufacturers, and steam injection oil recovery wastewater treatment. In this section, treatment processes for silica removal are briefly discussed relative to the feasibility of application at the MFRWTP to reduce the tendency of the treated water to form white spots upon evaporation.

3.1 Chemical Precipitation

In a treatment process designed to chemically precipitate silica and remove it from water, a di- or tri-valent ion, such as calcium, magnesium, or aluminum may be added to the water (Meyers). As discussed above, magnesium silicate is the most likely metal silicate to form. Calcium silicate is highly insoluble, but this compound forms slowly and is not the predominant form of precipitated silica except at high temperature (Meyers). The type of silica precipitate may vary depending on how it is formed, and whether or not heat is applied. In cases where silica is intentionally precipitated in order to reduce its concentration in water, co-precipitation with magnesium is preferred. Magnesium silicate is generally of the form $(\text{MgO})_x(\text{SiO}_2)_y \cdot (\text{H}_2\text{O})_z$ (Meyers). The precipitation reaction occurs more quickly at higher temperature and requires a pH sufficiently high such that magnesium precipitation occurs. Similarly, co-precipitation with aluminum can be performed, although the residual aluminum remaining in the treated water is a concern. Precipitation with aluminum was evaluated at the bench-scale level for MFRWTP water. Specific examples of chemical precipitation processes include co-precipitation with magnesium during softening, co-precipitation with aluminum, and electro-coagulation.

3.2 Activated Alumina

Water flows over a bed of granular activated alumina and silica can be removed at high pH as it adsorbs to the available aluminum sites, although silica is not usually the target constituent for removal. Activated alumina is most commonly applied in home treatment units in developing countries for the removal of fluoride, phosphorus, and arsenic. Regeneration and reuse of the material may be possible, although it is often discarded upon reaching exhaustion and subsequently replaced with fresh material. Pilot-scale testing would be required to test the performance of activated alumina for silica removal and to determine its cost effectiveness for a large-scale municipal water treatment application.

3.3 Ion Exchange

Strong base anion (SBA) exchange resins can be used to remove silica. The process can be tricky to operate because silica may not exchange with an ion in the typical fashion as with other ion exchange applications. It appears that silica in the form of silicic acid dissociates and then the silicate ion attaches to the resin. This releases a hydroxide molecule from the resin which forms a water molecule with the hydrogen ion left behind by the silicate ion (Meyers). The process is operated at elevated pH (above 10.5), which would require softening as a pre-treatment to avoid precipitation of calcium and magnesium on the resin. A strong base is used to keep the resin in the hydroxide form to facilitate silica removal. The pH within the resin bed decreases as the run proceeds and silicate ions may begin to desorb from the resin, reform neutral silicic acid and begin passing through the column. Silica fouling of resin beds can occur, making

removal of the silica difficult. Pilot testing would be required to determine the operational conditions under which silica removal and subsequent regeneration can be successfully applied and to determine the effect of competing ions, such as sulfate and chloride.

The process would likely be implemented as a side-stream treatment system in which the ion exchange treated water is combined with a bypass stream to reach the silica treatment goal in the blended water. The fraction of water requiring treatment would be roughly equivalent to the removal required. Since 50 to 75% silica removal may be targeted in order to visibly reduce white spotting, the ion exchange system would be a substantial size, perhaps approaching 12 to 14 mgd for the current MFRWTP capacity.

3.4 Reverse Osmosis

Older reverse osmosis (R.O.) membranes exhibited poor rejection of silica, although some newer membranes perform better in this regard. The process produces a brine which in many cases controls the overall cost and complexity of R.O. project. Brines can be disposed using outfalls to existing waters with high salt content, such as oceans and seas, although the impact on such receiving bodies can be significant and environmental groups and concerned citizens have strongly opposed outfalls for some projects.

In instances where silica rejection is acceptable, membrane fouling can be problematic because silica tends to precipitate on the surface of the membranes when concentrated in the R.O. process. Antiscalants that limit precipitation of silica (and other constituents that tend to precipitate) are often applied to increase the recovery of the process.

To implement R.O., brine disposal methods must be identified and explored and pilot-scale testing of the process using selected anti-scalant chemicals would be required. As with ion exchange, an R.O. process would likely be implemented as a side-stream treatment system in which the R.O. treated water is combined with a bypass stream to reach the silica treatment goal in the blended water. Since 50 to 75% silica removal may be targeted in order to visibly reduce white spotting, the R.O. system would be a substantial size, perhaps approaching 12 to 14 mgd for the current MFRWTP capacity.

3.5 Anti-Scalant Chemicals

Controlling fouling in industrial water systems, especially those operating with elevated silica concentrations, is a challenge which has undergone significant study. In general, the degree of scaling due to low solubility salts can be controlled by acidifying the feedwater, which tends to provide conditions for which calcium carbonate scale is less likely to form. Alternatively, the water can be softened to remove calcium and magnesium, thus reducing the tendency for the precipitation of low soluble salts. With respect to silica, removing it upstream of the industrial process may not be feasible. As discussed above, treatment to remove silica is complex, difficult to operate, and it can be expensive.

Chemicals which specifically prevent silica deposition have been developed, although fewer products appear to be specifically marketed as silica fouling control agents compared to other sparingly soluble salts. The use of chemicals to control silica scale generally applies two approaches: inhibition or dispersion

(Demadis, 2010). A given silica scale control product may act to affect one or both of inhibition and dispersion and the actual mechanisms are complex and not fully understood (Amjad and Zuhl, 2010).

Inhibition is defined as the prevention of silicic acid oligomerization or polymerization. As a result, silicic acid remains soluble and, therefore, formation of colloidal silica is prevented (Demadis, 2010). Inhibition of silicic acid would follow the same principles as adding a phosphate sequestrant to reduce precipitation of iron, manganese, and calcium. Dispersion, on the other hand, is the prevention of particle agglomeration to form larger-size particles and the prevention of the adhesion of these particles onto surfaces (Demadis, 2010). Since Longview's customers are more concerned with white spots left behind after evaporation on surfaces, it seems plausible that the use of dispersants would be more effective than silicate inhibitors for reducing the accumulation and appearance of the evaporated residue.

The operating conditions for many of the industrial processes in which silica scale control is of interest can differ greatly from that of drinking water. High pressures of up to 1,200 psi and temperatures up to 350°C are often employed (Amjad and Zuhl, 2010). The stability of the scale control chemicals and their resistance to these high temperatures and pressures is of research interest (Amjad and Zuhl, 2010). These applications often have silica concentrations of 100 mg/L or higher, and the antiscalant products are intended to allow silica concentrations up to approximately twice the solubility limit while minimizing silica scale formation (Amjad and Zuhl, 2010). Amjad and Zuhl (2010) summarized various recent studies in which specific chemicals were used to prevent silica polymerization in cooling waters. Confusingly, these chemicals are polymers themselves. The performance of the chemicals for inhibition of polymerization of silica tended to vary depending on conditions and the industrial application.

Boric acid or its water soluble salts can be added to inhibit metal-silicate precipitation by forming borate-silicate complexes which are more soluble than silica and thus prevent formation of the less soluble metal-silicate precipitates.

Polymeric dispersants also exist which can be used to impart a negative charge by adsorption onto suspended silica particles and colloids, preventing agglomeration and deposition (Amjad and Zuhl, 2010).

There are a wide variety of products available in the marketplace. A brief internet search identified the following antiscalant products that are NSF 60 certified for use in potable water applications however NSF approval is for use in conjunction with membrane applications only, not for direct application to potable finished water:

- Avista Technologies Vitec 5000 (marketed as a reverse osmosis antiscalant for silica concentrations up to 120 mg/L as SiO₂)
- King Lee Technologies Pretreat Plus Silica (marketed as reverse osmosis silica scale inhibitor)
- Applied Membranes, Inc. Flocon 260 (reverse osmosis iron and silica antiscalant)

3.6 Silica Treatment Alternatives Summary

Considerations for silica treatment processes are summarized in Table 1.

Table 1: Summary of Silica Removal Treatment Processes

Treatment Process	Description	Applications	Feasibility for Implementation at MFRWTP
Co-Precipitation with Magnesium during Softening	<ul style="list-style-type: none"> Silica co-precipitates with magnesium hydroxides at elevated pH to form magnesium silicates 	<ul style="list-style-type: none"> Silica removal by this process can be achieved using lime softening, although silica is not usually the target compound for removal This process is being developed as an RO concentrate treatment method to reduce fouling in downstream stages The process is being modified as a pellet softener, as opposed to lime softening with gravity settling basins, so that the process produces a granular mineral by-product and not a sludge requiring dewatering 	<ul style="list-style-type: none"> The groundwater contains insufficient magnesium, so it must be added to facilitate silica removal Gravity settling is required for lime softening and a large amount of solids requiring dewatering and disposal is produced Traditional pellet softeners do not produce the required magnesium precipitates, so silica removal is questionable in this type of reactor Cost estimate of \$37 million for MFRWTP*
Co-Precipitation with Aluminum	<ul style="list-style-type: none"> Silica is removed by co-precipitation with aluminum at elevated pH 	<ul style="list-style-type: none"> No known full scale applications could be found Bench-scale studies on MFRWTP water show that the process can remove significant amount of silica 	<ul style="list-style-type: none"> Elevated residual aluminum in the treated water may precipitate in the distribution system Very high doses of aluminum coagulant are required, resulting in large amount of solids requiring dewatering and disposal Cost estimate of \$35 million for MFRWTP*
Electro-Coagulation	<ul style="list-style-type: none"> Direct current is applied to generate metals (aluminum or iron) ions which serve as a coagulant 	<ul style="list-style-type: none"> Applied for various applications in numerous industries 	<ul style="list-style-type: none"> Since high coagulant dosage is required electrical cost may be high

Treatment Process	Description	Applications	Feasibility for Implementation at MFRWTP
Activated Alumina	<ul style="list-style-type: none"> Water flows over bed of granular activated alumina and silica is removed at high pH by adsorption to aluminum sites Regeneration can be accomplished with caustic soda followed by an acid 	<ul style="list-style-type: none"> Mostly home treatment units in developing countries for fluoride, phosphorus, and arsenic removal No silica applications could be found 	<ul style="list-style-type: none"> Activated alumina regeneration may not be feasible and the material may require frequent replacement Unproven at large scale
Ion Exchange	<ul style="list-style-type: none"> Silicate ions can be removed using strong base anion resins pH above 10.5 is required to facilitate dissociation of silicic acid Sulfate and chloride are competing ions pH tends to drop as bed becomes exhausted and subsequent regeneration to remove silica can be challenging 	<ul style="list-style-type: none"> Used in some industrial applications, for example at Longview Fibre, for boiler make up water Requires heating water to 95 to 100 °F In industrial applications, often paired with other ion exchange and/or other treatment processes to demineralize water 	<ul style="list-style-type: none"> Pilot testing would be required to determine performance and regeneration procedure May require breaking hydraulic head and re-pumping Would require softening pre-treatment Ion exchange equipment is proprietary and process would likely be difficult to operate Maintenance costs may be high
Reverse Osmosis (R.O.)	<ul style="list-style-type: none"> Process uses feed pumps to overcome osmotic pressure and force water through membranes Dissolved solids remain in the concentrate and permeate water contains essentially no dissolved solids A brine is produced which requires disposal 	<ul style="list-style-type: none"> Silica rejection poor for older membranes, although newer membranes exhibit better performance Silica concentration in the brine often limits process recovery Current research is showing that R.O. may be applied at pH above 10, if low levels of divalent ions are present 	<ul style="list-style-type: none"> Likely prohibitively expensive due to high membrane feed pump pressures, potential need for additional upstream pre-treatment to reduce turbidity, and brine disposal costs Cost estimate of \$81 million for MFRWTP*

*Planning level cost estimates prepared by Kennedy/Jenks Consultants in February, 2014. Cost includes design, construction, permitting, construction management, and 30% contingency.

4 SILICA DEPOSIT MODIFICATION ALTERNATIVES

4.1 Feasibility of Modifying the Appearance of White Spots through Chemical Adjustment

Given the information found in the literature, there appears to be three broad approaches for modifying the behavior of silica, silica solubility, and precipitation of amorphous silica and silica salts. Again, it is important to point out that the literature focuses on silica precipitation and scaling, not necessarily evaporation and water spotting. Nonetheless, to the extent that precipitative reactions may be applicable, they are being considered here. The three approaches for modifying silica behavior under consideration include:

- Treatment to remove silica
- Removal of cations to reduce the formation potential of insoluble silicate salts
- Use of an inhibitor or dispersant chemical

Treatment to Remove Silica

Numerous treatment processes used in industrial applications were described above. While removal of silica is anticipated to be the most effective for reducing white spotting upon evaporation, treatment to remove silica has already been determined to be cost prohibitive.

Removal of Cations to Reduce the Formation Potential of Insoluble Silica Salts

- Based on the pH of the finished water (~7.7), the literature indicates the vast majority of silica would be deposited as amorphous silica. It is unlikely that magnesium silicate or calcium silicate are precipitating out of solution under current conditions.
- pH would need to be adjusted to >9 to begin to increase the solubility of silica, and its reactivity with cations in solution. Such a pH increase would result in precipitation of calcium carbonate, and would likely cause additional scaling and white spotting complaints within the distribution system. Calculations indicate that a pH increase to >8.2 could cause calcium carbonate precipitation in MFRWTP water at current hardness levels.
- Although precipitative reactions with cations may not be controlling white spot formation, the literature does indicate that the presence of magnesium and calcium can aggravate silica deposition, and that silica solids can become trapped in calcium carbonate matrices. It may be necessary to completely remove cations to avoid any interaction with silica, which is not possible for full-scale treatment and distribution. However, further evaluation of the impact of softening followed by pH increases seems warranted.

Use of an Anti-Scalant Chemical

- A number of products are available commercially for silica scale control in RO, geothermal, and evaporative cooling water applications. Such products may be appropriate for industrial use,

such as ammonium bifluoride (Demadis, 2005), but not for residential or homeowner use. Products added to the bulk water are primarily geared toward preventing polymerization and precipitation of silicates and metal-silicates on corroded metal surfaces and RO membranes.

- Some antiscalant products that are NSF 60 certified for use in potable water applications have been identified. As discussed previously, it is possible that dispersant-type chemicals may be more effective compared to inhibitor-type chemicals with regard to reduction of evaporative solids and solids accumulation on surfaces. However, NSF certification currently applies only to use of the product in the feed stream to the membranes, not for direct application to potable finished water.

Physical Water Conditioners

- Physical water conditioners include magnetic, electrolytic, electrostatic, electro-magnetic or electronic processes (British Water, 2004). Generally, the concept is that the crystalline structure of the minerals is altered, producing softer scales that either remain in the water or may be easier to remove from surfaces. There is considerable debate regarding the efficacy of these treatment processes, and they would not be applicable at the scale of the MFRWTP. However, homeowners may have success, assuming that the process actually works, and that it works on evaporative deposits as well as precipitative deposits.

4.2 Feasibility of Removing Accumulated Scale

Numerous cleaning products have been developed to remove scale after it has formed on household surfaces and appliances. The majority are geared toward control of hardness scale, not necessarily silica scale, but claims of success are made for a variety of scale-forming minerals. According to Peairs (no date provided), the two most effective solvents for the removal of “glassed-on” silica in a hot water system are hydrofluoric acid (HF) and hot caustic soda (NaOH). Both substances are hazardous materials and should be handled using appropriate safety precautions and with personal protective equipment, and are not appropriate for household use.

While the type of scale formed is likely different for evaporative versus precipitative processes, it seems reasonable that broad principles for cleaning product effectiveness might apply to MFRWTP water. Additional bench-scale testing that assesses deposit accumulation as a function of deposit surface material, rate of evaporation, and water chemistry would be needed to qualitatively assess the differences, if any, in accumulation rate and ease of removal with various commercially-available cleaning agents.

Acidic Products

Acidic products can be useful for dissolving hard water deposits formed primarily from calcium and magnesium. Acidic products may also remove metal stains. Given the increased hardness level of the MFRWTP, some fraction of the white spotting is like caused by evaporated calcium carbonate. As described by Lenntech:

“A carbonate deposit is usually granular and sometimes of a very porous nature. The crystals of calcium carbonate are large but usually are matted together with finely divided particles of other materials so that the scale looks dense and uniform. Dropping it in a solution of acid can easily identify a carbonate deposit. Bubbles of carbon dioxide will effervesce from the scale.”

Many areas of Washington State and across the U.S. deal with hard water spots, and there are numerous commercial products available for purchase. Acidic home cleaning products listed from mildest to strongest include vinegar (acetic acid) and lemon juice (citric acid), oxalic acid, and dilute solutions of hydrochloric and sulfuric acids (sometimes found in toilet bowl cleaners, etc.) (Maintex Chemical Manufacturer <http://www.maintex.com/page/usage>).

Calcium has been identified as a component of the evaporated residue in the MFRWTP water (ALS Laboratory Report K1310585) and the report states that the recovered residue from each sample exhibited effervescence with the addition of acid. Additionally, calcium carbonate crystals were identified using x-ray diffraction (XRD) on samples provided to USEPA for analysis. Given the mineral content of the MFRWTP water, it is not surprising that calcium would be present in evaporated residue. However, the ALS laboratory also stated that each sample contained material insoluble in a nitric/hydrochloric acid digestion. Additionally, Longview customers have reported more stubborn scales that are not easily removed using conventional cleaning products. While softening would not reduce silica levels, and did not change the visual appearance of the white spots formed during evaporative tile testing, it is possible that softened water deposits might be more easily removed, or might accumulate at a slower rate. This could be explored further using bench-scale testing.

Basic Products

Basic or alkali products are usually recommended for removal of heavy dirt and grease. Since basic or alkali products will raise the pH, they may be more effective for removal of existing silica scale, given silica solubility properties discussed in detail previously. As stated by Demadis (2005), enhancement of silica dissolution is directly proportional to pH. However, metallic corrosion of critical system components (heat exchanger tube bundles, piping, etc.) becomes an issue when silica deposit cleaning requires prolonged times and high concentration of hydroxide ions (OH^-). As described by Lenntech:

“A high silica deposit is very hard, resembling porcelain. The crystal of silica are extremely small, forming a very dense and impervious scale. This scale is extremely brittle and very difficult to pulverize. It is not soluble in hydrochloric acid and is usually very light coloured.”

Basic home cleaning products, listed from mildest to strongest include baking soda, ammonia, Borax, TSP, washing soda (sodium carbonate), and lye (sodium hydroxide). (Maintex Chemical Manufacturer <http://www.maintex.com/page/usage>).

A comparison of scale removal from softened and unsoftened water, using acidic versus basic cleaning products, could be evaluated using bench-scale testing. The results of such testing could be used to pro-

vide guidance to Longview customers regarding the safest and most effective products to use. Such testing would provide further input to the City regarding what, if any, benefits might be realized from installation of a full-scale softening process.

5 SUMMARY AND CONCLUSIONS

- The white spots forming from MFRWTP finished water are predominately silica deposits associated with *evaporative*, not *precipitative*, processes per se.
- The vast majority of literature related to silica solubility, precipitation, scaling, and fouling applies to industrial applications which operate at much higher temperatures and pressures compared to drinking water systems.
- Silica solubility and speciation are largely independent of pH below pH 9.
- Silica is present as silicic acid (H_4SiO_4) at pH 7.7, and the silica in MFRWTP water has been determined to be dissolved, “reactive” silica (meaning all of it was measurable using the Molybdate reaction test).
- Silica is not regulated as a primary or secondary contaminant in the U.S. or Canada, or by the European Union or World Health Organization. There are no requirements to monitor for silica in drinking water unless it is added purposefully for corrosion control under the Lead and Copper Rule.
- Treatment to remove dissolved silica from drinking water is very complex and extremely rare, and is essentially performed only in industrial applications.
- Industry guidelines for avoiding silica-based deposits in cooling towers when pH is >7.5 suggest the product of $(\text{ppm Mg as CaCO}_3) \times (\text{ppm SiO}_2 \text{ as SiO}_2)$ should be below 12,000. For comparative purposes, the average product of Mg as CaCO_3 (24 mg/L) \times SiO_2 (50 mg/L) for MFRWTP finished water is approximately 1,200.
- Cations of calcium and magnesium, iron, and aluminum will likely cause precipitation of insoluble silica salts, especially at higher pH levels. The degree to which silica salts may be forming upon evaporation from MFRWTP is currently unknown.

6 SUGGESTED ADDITIONAL TESTING

Bench-scale tests that could be conducted to provide more specific information on silica-containing spots from Longview drinking water include:

- Calcium is present in the evaporated solids from the MFRWTP, as would be expected. Removal of calcium to either reduce the potential formation of insoluble silica salts, or to reduce the rate at which evaporative solids accumulate, or to increase ease of cleaning, etc., may warrant further study. Bench-scale tile testing indicated that softening did not improve the visual appearance of the white spots, but did not address these other issues.

- Contact additional vendors to further research the use of NSF 60 certified silica dispersant products and application directly to finished water.
- Both acidic and basic (alkali) cleaning products are commercially available for homeowner use. Longview customers have reported difficulty removing accumulated scale using conventional cleaning products, suggesting the deposits are not simply calcium carbonate. A comparison of the effectiveness of cleaning product types, with and without additional treatment (calcium removal) may warrant further study.

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