Assessment of Sodium Silicofluoride as a Fluoride Source in Drinking Water Systems

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ABSTRACT: *Fluoridation is a process of adding fluoride to the treated water source as the fluoride present in the drinking water is beneficial in preventing dental and bone caries, especially for children. The range for fluoride dosage concentration in drinking water systems is different from one country to another. In Malaysia, the allowable range of fluoride has been gazetted at around 0.4 to 0.6 mg/L. The source of fluoride from sodium silicofluoride (SSF) has been reportedly used due to its advantages compared to the other sources. In this work, the solubility of SSF as the fluoride source dosed at a dedicated Water Treatment Plant (WTP) was analyzed and different fluoride dosage range was evaluated from the WTP. This evaluation was done to ensure its single distribution system contains sufficient fluoride levels as recommended by the national drinking water standard. The solubility of SSF from different sources namely SSF1, SSF2, and SSF3 were studied at a different range of concentration using the gang jar test. Fluoride levels in the drinking water system were evaluated by taking the water sample from 7 sampling points, where fluoride dosages were grouped at three different ranges of fluoride concentration at the fluoridation dosing tank; (i) low (4.6 g/L), (ii) medium (7.1 g/L), (iii) high (11.8 g/L). Results show that at a high range of fluoride dosage, 10.4% of insoluble substance was recovered from the dilution of SSF3, which amount was found much lower than from SSF1 and SSF2. This finding indicates that SS3 is considered the best quality fluoridating agent compared to the other two sources to be applied in the fluoridation system. Spectroscopic analysis performed for the fluoride water samples shows that a high concentration of fluoride is required to obtain the concentration of fluoride at the allowable limit. Meanwhile, the fluoride preparation*

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at the dosing tank of medium range of fluoride concentration shows an average fluoride concentration level of 0.60 mg/L at all the seven (7) sampling points specified along the studied distribution system. Although the fluoride level is supposed to remain the same along the distribution system, the presence of various minerals and metals in the treated water may have caused fluoride concentration to reduce due to their reactions of them to form metal precipitates and/or complexes. Therefore, the dosage of SSF for fluoridation at WTP is recommended at the medium of-range fluoride concentration in order to obtain desired concentration at the distribution system within the allowable limit.

KEYWORDS*: Drinking Water System; Dosing System; Fluoridation; Fluoride Concentration; Sodium Silicofluoride; Water Treatment.*

INTRODUCTION

Over the last century, water scarcity has intensified as worldwide freshwater consumption has risen up to sixfold due to the rapid growth of the global population and economy [1, 2]. Along with the impact of climate change and the increase in water usage per capita, water scarcity is estimated to worsen which could affect around 6.6 billion people by the year 2050 [3-5]. More than 783 million people around the world have lacked access to clean water [6]. As water scarcity arises, the lack of access to sufficient fluoride also has affected around 2.3 billion people to suffer from caries of permanent teeth, while 530 million children suffer caries of primary teeth [7]. To combat this major crisis, the fluoridation of public water supply is marked as one of the greatest advances of Public Health interventions in the 20th century as it plays a vital role in caries prevention [1, 8]. Through decades of research and more than 70 years of practical experience, fluoridation of public water supplies has been responsible for dramatically improving the public's oral health. At present, around 437.2 million people worldwide have access to fluoridated water, either *via* naturally or artificially [9-11]. However, this number only accounts for about 6% of the total global population representing around 370 million people to consume artificially fluoridated water [11].

Fluoride is essential for developing resistance to caries and it could be beneficial for a long time. Fluoride reduces the susceptibility of teeth to caries by stabilizing the apatite crystal of the dental enamel, making it more acid-resistant and results in remineralization of the enamel [12]. It has been proven that moderate levels of fluoride help to prevent dental caries. Conversely, exposure to high fluoride concentrations can cause hard tissue deformities, namely dental and skeletal fluorosis, and cause damage to the soft tissues like liver, kidney, lung, and others [13-15]. High fluoride concentrations also could possibly induce skeletal cancer and neurotoxicological effects [16, 17] as well as hypertension [18]. For safe use, a daily fluoride limit of 1.5 mg/L has been recommended by the World Health Organization (WHO) as an international guidelines for fluoride concentration in drinking water. However, WHO also recommended that this set limit should be adapted to local conditions such as climate, water consumption, and diet [19-23].

In Malaysia, in upholding the public health initiative to combat dental caries, the public water supplies have been artificially fluoridated treated water at a rate of 0.7 mg/L since early 1972 [24]. However, considering the consumption of other sources of fluoride such as fluoridated toothpaste and also the concern over the higher water intake due to warmer climate condition in Malaysia, the optimum level of fluoride standard was reviewed from 0.7 mg/L to 0.5 mg/L by the National Drinking Water Quality Committee. Meanwhile the recent standard that has been revised and accepted in the National Guidelines for Drinking Water Quality is between 0.4 mg/L to 0.6 mg/L, effective in 2005 [24, 25].

Water fluoridation is the most economical and effective way of delivering fluoride to the community. Fluoridation process is believed to improve the mineral composition of water and does not in any way change the smell, taste or appearance of drinking water [26]. It is one of the final measures in water treatment systems. Unlike the other stage of water treatment processes, fluoridation does not treat the water. It only involves the addition of fluoride into the municipal water supply at the recommended level, to benefit the consumers through the water consumption. To date, several types of fluoride sources have been used worldwide as the fluoridating agent for the fluoridation process including fluorosilicic acid, sodium fluoride, and SSF [21]. Among these, fluorosilicic acid is the most common fluoridating agent used [27]. This acid has varied strengths, typically between 23% to 25%, which may adversely affect the shipping costs due to the significant amount of water in its composition [21]. Sodium fluoride in contrast is an inorganic salt of fluoride and was the first fluoride compound used as the reference standard for the water fluoridation process. Even though sodium fluoride is more expensive than the other available fluoride compounds, it is easily operated and has usually been used by a smaller-scale WTP [28]. Meanwhile, SSF is a powder or a very fine crystal that is easier to ship than fluorosilicic acid. The SSF compound is widely used as it is readily available, relatively inexpensive, and safe. SSF contains a high percentage of available fluoride ions around 60.7% compared to sodium fluoride which has only 45.3% fluoride. It also has a high percentage of commercial purity of around 98 to 99% compared to fluorosilicic acid the lowest around 22 to 30% and sodium fluoride slightly lower at 95 to 98% [21]. Based on this information, SSF seems to own more advantages compared to the other two types of fluoridating agents sodium fluoride and fluorosilicic acid, and thus has been widely used to date.

Next, fluoride reactivity regardless of its sources is considered as high where it will actively react to inorganic elements such as minerals and heavy metals available in the water to form a metal-fluoride complex. This reaction could result in the variation of the fluoride concentration reading along the water distribution system. *Reshetnyak et al.* [29] have studied the difference between free fluoride and total fluoride concentration in oral hygiene products and they have concluded that free fluoride concentration value may be difficult to measure under certain measuring conditions. Due to that, the total fluoride value has been used to represent the fluoride content as it is a relatively more reliable measurement method. Meanwhile, the ratio between free fluoride to total fluoride is usually different because of the binding of fluoride ions with other components in water or the ability of the fluoride source itself to form its complexes. This could lead to a much lower concentration of free fluoride measured in the water in comparison with the total one that has been supplied, which this issue could contribute to a decrease in the caries-preventive effect as targeted in the national fluoridation program. It is also affirmed that to the best of our knowledge, there is still a lack of recent studies reported on the fluoride concentration measured in the water distribution system, either in Malaysia or at the international level. One of the most recently published works found in open literature has discussed the fluoride concentration in public water supply in the city of Araçatuba, São Paulo, Brazil [30]. The city has been found to be able to control the fluoride levels in the public water supply based on their obtained results, as they have observed a minimal variation in the fluoride concentrations in water from the study. On the contrary, the other two similar studies have reported on large variations in the fluoride concentration in the public water supply in Brazil [31, 32].

Based on the presented issues that have been scarcely published in the literature on fluoridation at the WTP from other countries, especially in Malaysia, this work is believed to be worth conducting. Thus, this study aimed to assess the adequacy of the SSF that was dosed in a specified drinking WTP with a connected single distribution system. The utilization of the SSF as the fluoridating agent for fluoridation was clearly justified based on its advantages, and it has also been used in the investigated WTP located at one of the smallest states in Malaysia for years. Initially, a comparison of using a different source of SSF supplied from different manufacturers was conducted where the concentration of the SSF was identified at the same dosing quantity. In an ideal fluoridation condition, the same amount of the SSF of the same specification used for fluoridation could give the same concentration value, even if they are from different manufacturers, provided that all solutes were well mixed during the dosing process. However, this case could be invalid upon utilizing different SSF products and quantities if there is a slight change in the SSF properties as well as if there is a presence of the undissolved SSF in the system. Therefore, a solubility test was also performed to identify the best SSF fluoridating agent that can be used in lab/plant scale dosing, based on the lowest insoluble percentage found from the study. Furthermore, in a WTP and its distribution system, constant monitoring of fluoridation equipment as well as maintenance of fluoride concentration within the recommended values is necessary, but difficult to achieve due to the chemical characteristic of the fluoride itself that could form complexes and/or precipitates in existence of various minerals and metals in the treated water. Next, fluoride dosage at the dosing tank in WTP was grouped at three different ranges of fluoride concentration (low, medium, and high doses) and the fluoride level at every sampling point in the drinking water system were evaluated whether it abides the limit recommended by the national drinking water standard, Ministry of Health, Malaysia.

EXPERIMENTAL SECTION

Materials

SSF from different suppliers were used in this study as received. SSF1 was supplied by the 1st company while SSF2 and SSF3 of different specification were from the 2nd company. The name of the companies is undisclosed due to business confidentiality. These fluorides were all originated from China. Other materials namely SPADNS 2 (Arsenic-Free) Fluoride Reagent, Fluoride Standard Solution (1.00 mg/L) and deionized water were also used.

Analytical tests conducted on SSF

SSF Solubility Test

Solubility of each SSF in the fluoride dosing system was investigated where a series of solubility test at a lab scale was conducted using a gang jar tester apparatus (PHIPPS & BIRD, Richmond, Virginia) in order to see its solubility profile in water. This solubility test was conducted in a lab scale to imitate the fluoridation process in the fluoride dosing system for the specified WTP, in order to determine the exact amount of fluoride required for dosing. The results obtained from this test is targeted to be used to improve the plant scale's dosing performance. The amount of SSF used in the test was based on the possibility of having 3 different concentrations of SSF (low/ medium/ high) prepared in the dosing system at a plant scale having a total water volume of 10,600 L (representing the real working volume of the fluoride mixing/dosing tank in the WTP). Solution of SSF at different concentration ranges of low (2.4 g/L), medium (4.7 g/L) and high (7.1 g/L) were prepared by dissolving the SSF at different weights into 0.8 L deionized water in 3 different beakers (possessing equal ratio between the plant and lab scale) respectively, for obtaining the set concentration range. The fluoride concentration at each beaker was expected to be equal to the fluoride concentration in the mixing/dosing tank in the plant, as per values tabulated in Table 1. In the lab scale, the solutions were stirred at 60 rpm for about 8 hours at room temperature, similar to the practice done in WTP scale. After the mixing, the SSF solution was filtered using commercial filter paper (ADVANTEC, grade no. 131, 125mm, Japan) that reported could allow the separation of precipitates usually below 5 μm. The dried filter paper was weighed using an electronic balance (SARTORIUS, Goettingen, Germany) for initial weight, (Wi) prior to filtration. The used filter paper was kept at room temperature in the fume hood for more than 24 hours for drying before weighing for its final weight, (Wf). The undissolved SSF in percentage can be obtained by measuring the insolubility percentage using Eq. (1).

$$\text{Insolubility } (\%) = \frac{\text{Initial Weight } (W_i) - \text{ Final Weight } (W_f)}{\text{Initial Weight } (W_i)} \times 100\% \quad (1)$$

SSF Particle Size Analysis

SSF was also tested for the other tests namely chemical requirement, impurity, physical requirement and toxic substance, following the Standard of MS 1724:2004, (guidelines for SSF usage in potable water supply) as summarized in Table 4. These values are then compared with the values reported in the Certificate of Analysis (CoA) that was given by the suppliers.

Fluoride dosing and sampling method

SSF is commonly used in WTP in Malaysia for water fluoridation. It has been the main additive used because of its cost effectiveness. In this study, Melaka WTP was chosen as the studied area because this state is one of the smallest in Malaysia, so it will be easier to find a dedicated WTP and its individual distribution system to perform the study. In this work, the investigated WTP has an established treatment and fluoridation system with only one dedicated distribution system that does not mix with other water network. High purity SSF was used for the fluoridation in this WTP. Based on the schematic diagram of a feeder of the fluoride chemical

Table 1: Different fluoride ranges and its concentration prepared in the mixing tank of the fluoride dosing system.

Fluoride Range	Fluoride Bag	Fluoride Dosing Quantity in Plant (kg)	Equivalent Fluoride Dosing Quantity in Lab* (g / 0.8 L)	Fluoride Concentration in Mixing/Dosing Tank in plant* (g/L)
Low	1	25	1.887	2.4
Medium	2	50	3.774	4.7
High	3	75	5.660	7.1

**Both concentrations in lab and plant scale was based on 10,600 L volume of water filled up in dosing tank in the WTP*

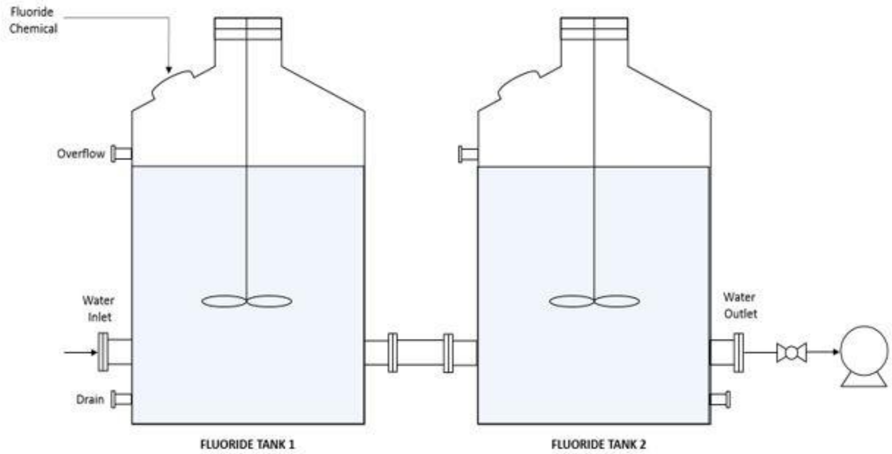

Fig. 1: Schematic diagram of a feeder of a fluoride chemical solution consisting of two fluoride tanks in series used in the fluoridation system at the specified WTP

solution illustrated in Fig. 1, the fluoride solution was prepared by adding 75 kg of SSF into the mixing tank that contains three different volumes of water at different measured times that are: i) 16,260 L, ii) 10,600 L, and iii) 6,360 L of water. Three different volumes of added water have given three different ranges of fluoride concentration in the mixing tank of 4.6, 7.1, and 11.8 g/L, as shown in Table 2. This solution was stirred at a controlled rate of 60 rpm for about 8 hours. It was then withdrawn through a mechanical diaphragm dosing pump and injected into the main treated water stream prior to ground storage and further distributed through the dedicated distribution system. The diaphragm pump used for dosing was designed to ensure that the dosing flowrate variation was maintained at below ± 1.5% and the linearity deviation was kept at below 4% at all times. In a plant scale, this practice allows a very precise dosing of fluoride chemicals – as much as necessary, as little as possible. Note that the fluoride concentration in Table 2 is based on the calculation of the amount of dry SSF dissolved in the water that was prepared at different volumes, and these values were obtained theoretically.

Upon using Equation 2, in order to obtain the calculated dosage or the fluoride concentration of range between 0.4 mg/L and 0.6 mg/L (recommended fluoride concentration based on the guidelines) at the distribution system, the fluoride solution’s flowrate at the dosing pump from the mixing tank was set at 540 L/h and fluoride solution concentration of 0.7% (fluoride dilution) was supplied for 24 hours (continuously) from the fluoridation system to the treated water produced from the specified WTP daily with constant production capacity of around 114 Million Liter per Day (MLD). Note that MLD is a common SI unit used for a WTP production.

$$\text{Calculated dosage}\left(\frac{\text{mg}}{\text{L}}\right) = \frac{\text{flowrate}\left(\frac{\text{L}}{\text{h}}\right)\text{x Fluoride dilution}\left(\frac{\text{mg}}{\text{L}}\right)}{\text{Water treated each day (MLD)x }100\%} \times 24 \quad (2)$$

Sampling areas

Purposive sampling was conducted to investigate the concentration of fluoride delivered from WTP to the set distribution points/sites located in Melaka State, Malaysia

Table 2: Measured concentration of SSF solution prepared under the same fluoride weight in different water volume in the fluoridation system at the specified WTP.

Fluoride Range	Volume of Water (L)	*Fluoride Concentration (g/L)
Low	16,260	4.6
Medium	10,600	7.1
High	6,360	11.8

**75 kg of SSF mixed in different volumes of water in a mixing tank to produce different fluoride concentrations to be dosed at WTP with treated water production.*

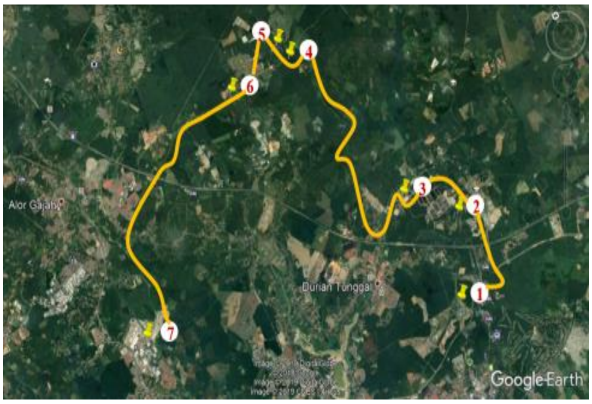

Fig. 2: Location of the seven (7) sampling areas starting from the WTP (Point 1) to the final distribution system (Point 7) of individual distribution line specified for the water sampling purposes.

as shown in Fig. 2. There were 7 sampling points selected as the sampling areas where these sampling points have a standardized design and sampling protocol that complies with ISO/IEC 17025:2017 certification. The sampling was conducted from WTP (point 1) to its distribution system (point 2 to 7), which involved 24.9 km pipeline system that does not mix with other water source. The real exact location and its satellite image of the sampling point can be found in Table 3. Further details on the sampling point can be found in our recent publication in [33]. This WTP operates using a water source taken from the main river in the state. The fluoride level in this source was identified using a spectrophotometer (USEPA SPADNS 2) with method no. 10225.

Sampling protocol

Water samples were collected weekly between March and April 2019 from the 7 sampling points as listed in Fig. 2 and Table 3. A total of 56 water samples were taken from the fluoride dosing tank (point 1) till sampling points at site (point 2 - 7). The volume of the water collected each time was at 60 mL per sample. Polyethylene bottles were used for the collection of water samples which had been thoroughly washed and rinsed by using deionized water to avoid any concealed pollutants. At the sampling point location, the sampling pipe was flushed for about 3 to 5 min at maximum flow prior to sample collection. This was done to allow fresh distributed water to be collected in the sampling bottle instead of the water that was trapped in the sampling pipe. The flow rate was reduced before the sample was taken. In-situ test was done for pH, turbidity, and chlorine residue. Water samples were then kept in a Coolman box, filled with a cool ice pack with a temperature range between 2ºC to 8ºC for storage before testing. Ex-situ testing inclusive of the fluoride test was conducted following the specific spectrophotometry technique. The method of testing is presented in the Water Sample Characterization section below.

Water sample characterization

Fluoride concentration was identified using the spectrophotometry technique. Two types of samples were tested for fluoride. The first type of sample was from fluoride solution prepared in the lab and underwent certain tests such as insolubility, concentration, etc. The second type of samples came from the collected samples from the sampling point at the WTP distribution system. These collected samples were analyzed within 24 h from the sampling dates using SPADNS 2 method 10225 on a direct reading DR3900 spectrophotometer (HACH, Colorado, United States). This method involved the reaction of fluoride with red zirconium-dye solution, where fluoride combined with part of the zirconium to form a colorless complex that bleached the red color in an amount proportional to the fluoride concentration. This method is equivalent to the EPA method for NPDES and NPDWR reporting purposes when the samples have been distilled. The measurement wavelength was at 580 nm for the spectrophotometer (HACH Method 10225).

RESULTS AND DISCUSSIONS

Fluoride solubility in water

Solubility study on SSF from different supplier was conducted in order to identify the best SSF as the main

Table 3: Exact sampling area coordinates based on the longitudinal and latitudinal extent of Melaka State in Malaysia.

Sampling Area	Longitude	Latitude
Point 1	102.3015	2.2956
Point 2	102.3121	2.3142
Point 3	102.3005	2.3270
Point 4	102.2905	2.3765
Point 5	102.2891	2.3814
Point 6	102.2700	2.3781
Point 7	102.2149	2.3378

fluoride source dosed in the drinking water system. Solubility is the capacity of two or more substances to form spontaneously, one with the other, without chemical reaction, a homogeneous molecular or colloidal dispersion [34, 35]. It is one of the most important parameters to be achieved in order to obtain desired concentration of fluoride at the WTP. Initially, fluoridation process in the real plant scale was simulated in the laboratory scale to measure the undissolved SSF. This test was performed in order to measure the solubility of different SSF used as the fluoride source at the WTP. The obtained result in this lab scale study has become the basis in the dosing of the SSF at the plant scale later on. In this study, three different range of fluoride concentrations were investigated: (2.4 g/L), medium (4.7 g/L) and high (7.1 g/L) as presented in Fig. 3.

Based on the initial finding, it was found that the SSF3 dosing at a high range of fluoride concentration has contributed around 10.4% of the undissolved fluoride. This value is equivalent to around 7.8 kg of SSF precipitates at every 8 h, or similar to 23.4 kg per day. Surprisingly, the SSF2 dosing at a high range of fluoride concentration contribute to the highest undissolved SSF substance of 23.3%, which was equivalent to 52.4 kg of SSF precipitates per day, while SSF1 contributed to around 15.0% of the undissolved SSF substance or similar to 33.8 kg of SSF precipitates per day. This finding shows that SSF3 has the highest solubility in water compared to SSF1 and SSF2 even though it was measured at the highest fluoride concentration range. It is known that the high amount of the SSF used can result in a high concentration of fluoride in the treated water. However, the result revealed otherwise, which there was a large amount of insoluble SSF observed in the fluoridation system. In a WTP scenario, this can contribute to the formation of slurries in the dosing system. It was reported that slurries must not be tolerated in the feeding of the fluoride solution since the undissolved fluoride compound can go into the solution subsequently, causing a higher-than-optimum situation, or if the fluoride compound remains undissolved, a lower-than-optimum situation will be obtained in the distribution [36]. This explains the need for these WTPs to use a secondary fluoride mixing tank to effectively eliminates the chance of carrying over the SSF solids/precipitates from the first mixing tank into the dosing pump.

The presence of the undissolved substance in the dilution of SSF may be due to the formation of the fluoro-complexes. When SSF is dissolved in water, virtually, 100% of dissociation occurs within several minutes. During the solubilization process, SSF dissociates to form sodium ions and silicofluoride ions. This silicofluoride ion then reacts in two ways, either through hydrolysis to form free fluoride ion and silica or it dissociates very slowly to form silicon tetrafluoride which then reacts with water to form silicic acid or silicon dioxide [21].

$$\mathrm{Na_2SiF_6} \leftrightarrow 2\mathrm{Na^-} + \mathrm{SiF_6^{2-}} \tag{3}$$

$$\mathrm{SiF_6^{2-}} + 2\mathrm{H_2O} \leftrightarrow 4\mathrm{H^+} + 6\mathrm{F^-} + \mathrm{SiO_2} \tag{4}$$

$$\mathrm{SiF_6^{2-}} \leftrightarrow 2\mathrm{F^-} + \mathrm{SiF_4} \tag{5}$$

$$\mathrm{SiF_4} + 3\mathrm{H_2O} \leftrightarrow 4\mathrm{HF} + \mathrm{H_2SiO_3} \tag{6}$$

$$\mathrm{SiF_4} + 2\mathrm{H_2O} \leftrightarrow 4\mathrm{HF} + \mathrm{SiO_2} \tag{7}$$

The free fluoride ion can react with the inorganic element present in the water to form soluble fluoro-complexes. Fluoride, as a strong ligand in water, may form complexes with polyvalent cations, such as Mg^{2+}, Fe^{3+}, Al^{3+}, and Ca^{2+} depending upon the water pH (favourable to happen at below 6) as well as with trace elements present in water, such as Boron, Beryllium, Silica, Uranium, Vanadium, and rare earth elements [37]. Past studies mentioned the presence of various mineral and heavy metal in Malaysian tap water namely sodium, magnesium, potassium, calcium, chromium, manganese, iron, nickel, copper, zinc, arsenic, cadmium and lead while the non-metal elements were fluoride, chloride, nitrate and sulphate [38-40]. Fluoride ion complexes readily with Al^{3+} [41]. Hence, the present of Al^{3+} in the treated water either due to the addition of chemical additive such as aluminum sulphate as coagulant in the water treatment process or naturally occurring Al^{3+} may results in the formation of fluoroaluminum complexes. Previous study also reports on occurrence of encrustation due to the presence of calcium and magnesium in water [42]. The reaction of free fluoride ion and silicofluoride ion with the inorganic element may results in precipitation which may lead to encrustation that normally happens in solution tank or feeder of a fluoridation system at a WTP. In lab scale, these reactions may contribute to the occurrence of precipitation, thus results in the presence of insoluble substance. Equations 8 to 12 show the possible reaction of fluoride ion and silicofluoride ion with various potential inorganic elements:

$$Al^{3+} + 3F^- \leftrightarrow AlF_3 \quad (8)$$

$$Ca^{2+} + 2F^- \leftrightarrow CaF_2 \quad (9)$$

$$Ca^{2+} + SiF_6^{2-} \leftrightarrow CaSiF_6 \quad (10)$$

$$Mg^{2+} + 2F^- \leftrightarrow MgF_2 \quad (11)$$

$$Mg^{2+} + SiF_6^{2-} \leftrightarrow MgSiF_6 \quad (12)$$

Other than that, the impurities present in the fluoride additive used for the water fluoridation process also contributes to the insoluble substance available in the SSF solution. It is known that the production of fluoride additive involves phosphate rock which contains cadmium (Cd), arsenic (As), lead (Pb), chromium (Cr), mercury (Hg), nickel (Ni), vanadium (V), uranium (U), and other radionuclides and metals at levels that vary by geographical origin. Metal contaminants in the fluoride additives are a potential contamination source of the water supply [43].

Another factor that could affect the rate of solubility is the surface area of a solid. Solubility depends on the physical size of the crystal of a solute or on the specific surface area or the molar surface area of the solute [44]. According to the SSF specification standard (MS 1724: 2004), the requirement for particle size is that the passing sieve of 250 µm, % (w/w) must be at a minimum of 90%. A typical sieve analysis of the regular grade allows more than 99% of particle to be sieved through a 200-mesh sieve and more than 10% of the particle is to be sieved through a 325-mesh sieve. Depending on the feeding characteristics, the other size specifications can also be selected. Previous study has shown that a relatively narrow size distribution plus a low moisture content have resulted in a material that has been handled better by dry feeders than the solution feeders [21]. Next, Table 4 presents the properties

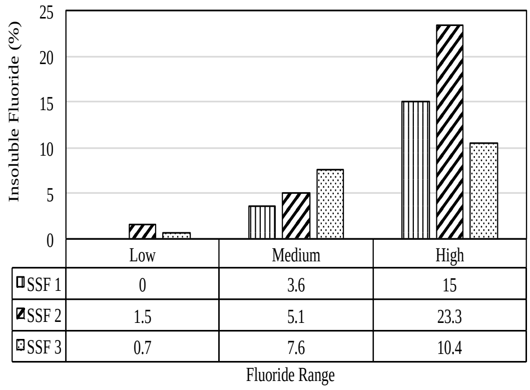

Fig. 3: Insoluble fluoride percentage of SSF type obtained from different fluoride sources (named as SSF1, SSF2, SSF3) measured upon mixing the SSF in fixed water volume at different fluoride weight (SSF unit presented is in g/L).

of different type of the SSF that have been investigated in this study. These properties were obtained from various tests that have been conducted to confirm the specification of the fluoridating agent used in the WTP. Apart from the fluoride solubility property, the information of these properties is essentially required in order to understand the behavior of the fluoride source upon dosing in the treated water. Based on the properties of the SSF3 presented in Table 4, the analysis shows that the particle size of the passing sieve of 250 µm was at 90.5% (90% min) and the moisture content was at 0.45 (0.5 max). Thus, these properties are found suitable for solution type fluoride feeders instead of dry-feed system to solution-feed system as described in Fig. 1.

Correction of the fluoride dosing at WTP to the distribution system

Next, Fig. 4 shows fluoride concentration of SSF3 measured using spectrophotometer versus its theoretical concentration obtained from the real mass of fluoride mixed in a specified volume of water. From the result, the relationship between the theoretical and the measured fluoride concentration was established in a linear plot (Y=0.555x+0.0926) with a very good R^2 value of 0.9159. Based on the relationship obtained, the measured concentration of fluoride was found to be lower than the theoretical value at all times. Thus, the fluoride dosing conducted in the WTP must be revised or corrected to get the desired concentration of fluoride along the water supply system.

Table 4: Certificate of Analysis (CoA) of the properties of three different SSF obtained from different fluoride sources originated from China.

Description	Limit, mg/kg of product, max	SSF1	SSF2	SSF3
Supplier / Origin		Product A/China	Product B/China	Product C/China
SSF as Na_2SiF_6	98.0 Min	99.0	99.6	98.6
Moisture	0.5 max	0.37	0.5	0.45
Insoluble Matter	0.5 max	0.39	ND (<0.005)	ND (<0.005)
Particle Size, Passing sieve 250μm	90% min	99.2	99.8	90.5

ND- Not detected

Meanwhile, according to the results reported in the fluoride solubility, the required dilution of SSF3 at the solution tank must be set at 0.7% in order to ensure that all fluoride particles is completely dissolved prior to dosing it to the treated water. This is because, any undissolved particles entering the treated water will result in unacceptable variations in the fluoride reading. The formula presented in Equation 2 was again used to calculate the optimum dosage of fluoride (set at 0.5 mg/L as this concentration is intermediate between 0.4 to 0.6 mg/L, the allowable fluoride concentration standard) at the WTP and the distribution system. The fluoride solution was prepared by adding of 75 kg dry SSF3 into the mixing tank that contains 10,600 L of water in the dosing system for the specified WTP having 113.4 MLD of production. Detail information on the methodology can be found in the fluoride dosing methodology section. Since the SSF3 measured concentration has been found to be lower than its theoretical value (based on the results presented in Fig. 4), the mixing of a higher amount of SSF3 was crucially needed to make sure that sufficient fluoride concentration was obtained at the distribution site. In addition, a complete mixing of SSF3 was compulsory in a way to avoid the chance of transferring any carryover of SSF3 solids from the first solution tank into the fluoride dosing pump. This design has been clearly illustrated in the feeder diagram in Fig. 1 whereby a chemical pump was used to draw a known flow rate of fluoride solution from the fluoride mixing tank and further discharging the fluoride concentrated solution into the treated water stream for dosing purpose. The best practice identified for the fluoride dosing system in the specified WTP was by using a secondary fluoride mixing tank to prevent the built-up of undissolved SSF. This practice eventually eliminates the chance of bringing the carryover of the SSF solids from the mixing tank into the chemical dosing pump, hence making it possible to maintain accurate fluoride feed rates.

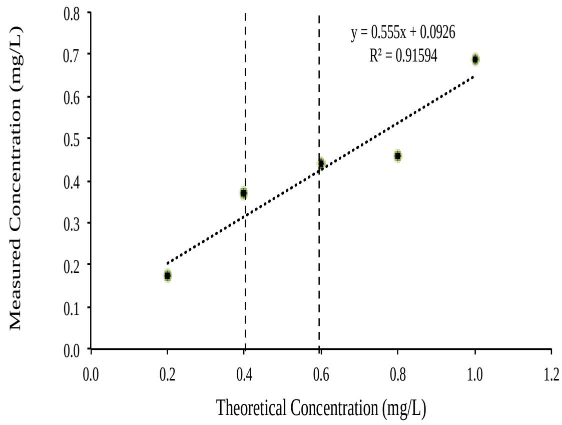

Fig. 4: Measured concentration of fluoride in relation to its theoretical concentration of fluoride identified from the respective fluoride testing using spectrophotometer and real mass of fluoride mixed in a specified volume of water.

Using the obtained equation of $y=0.555x + 0.0926$ plotted in Fig. 4, in order to get 0.5 mg/L of the measured fluoride using spectrophotometer (at y-axis), the theoretical dosage of fluoride must be obtained at 0.8mg/L (at x-axis). To achieve this, an adjustment to the set flowrate of the dosing pump was re-set at 540.0 L/h instead of 337.5 L/h that has been used previously, just to be sure that the desired concentration of fluoride (between 0.4 mg/L to 0.6 mg/L) was obtained at the distribution areas. This adjustment was applied in Equation 2 for accurate calculation of fluoride dosing at the WTP.

Identification of fluoride concentration from WTP to distribution system

Next, extensive fluoride data collection from the studied WTP to the distribution system was performed where a total of 56 samples were collected and analyzed for identifying the fluoride concentration at all the selected sampling areas. All data of the fluoride concentration was calculated based on its respective sampling areas and the mean values of the results were tabulated in Table 5. Meanwhile Fig. 5 shows the level of fluoride concentration in the sampling areas and the limit recommended by the national drinking water standard set by the Ministry of Health, Malaysia. The concentration of fluoride that fell between the two dotted lines indicated the measured concentration values were at the recommended allowable concentration of fluoride (between 0.4 to 0.6 mg/L). Three ranges of fluoride concentration were investigated in this plant scale study namely low (4.6 g/L), medium (7.1 g/L), and high (11.8 g/L).

Based on the results presented in Table 5, the mean fluoride level for the medium-range fluoride concentration in all the 7 studied distribution/sampling sites was within the national drinking water standard recommended by the Ministry of Health, Malaysia, which was at 0.60 mg/L. Minimal variation in the fluoride concentration values was observed in Fig. 5, which showed that the mean fluoride concentration along the water distribution system was considered stable. According to the obtained result, at a high range of fluoride concentration (11.8g/L) presence in the dosing system, all samples collected from the water distribution system have a high mean fluoride concentration of 0.81 mg/L, with the highest concentration observed at the sampling point no. 3 (0.91 mg/L). Meanwhile, for the low-range fluoride concentration (4.6 g/L), almost all of the water samples collected from the water distribution system showed a very low mean fluoride concentration of 0.36 mg/L, with the lowest obtained at sampling point no. 2 (0.22 mg/L). Both two ranges (low at 4.6g/L and high at 11.8 g/L) were found to have in compliance with fluoride concentration in the distributed water.

A number of studies on the fluoride concentration in drinking water distribution systems have been done and reported by several researchers. A previous study on the fluoride concentration in the public water supply at the local area supplied by the Water Treatment Station of Bauru, São Paulo, Brazil have shown a large variation in the fluoride concentration of 0.31 mg/L to 2.01 mg/L [32]. This large variation indicated an instability in the fluoride concentration with only 56% of the samples collected considered acceptable according to the range classified by this study [32]. Another study in Bauru, São Paulo, Brazil also reported 89% of the samples collected from the public water supply system have a mean fluoride concentration of less than the optimum level (0.8 mg/L) [31]. Based on the results from this study, more rigorous surveillance and monitoring of water fluoridation in Bauru, São Paulo, Brazil has been recommended to make sure that the fluoride concentration in water to comply with the local standard. Meanwhile, a different study on the fluoride concentration of the public water supply system in Araçatuba, São Paulo, Brazil, showed that most of the samples' fluoride levels were within the recommended parameters (0.55 to 0.84 mg/L) [30]. Minimal variation was observed among the analyzed collection locations, showing that the city has been able to control the fluoride levels in the public water supply and reinforcing the importance of surveillance and constant monitoring to assure the quality of the water delivered to the population. In Malaysia scenario, a previous study has reported on a low fluoride concentration in the drinking water retrieved from several states in Malaysia, which resulted in the possible susceptibility to fluoride related diseases [45]. In achieving fluoride levels within the recommended limit set by the health authorities is foreseen as a crucial target since studies have reported that the prolong exposure to high fluoride concentrations could strongly contribute to an increase in the prevalence of fluorosis over time, whereas inadequate fluoride supply may result in caries [46].

Overall, the amount of fluoride in all samples measured in the selected water distribution system after the fluoride dosing correction have complied with the limit stipulated by WHO, which is between 0.7 mg/L and 1.2 mg/L [20]. However, given other factors, such as the consumption of other sources of fluoride and the climate in Malaysia, the limits recommended by national drinking water standard, the Ministry of Health, Malaysia must be strictly followed that is between 0.4 and 0.6 mg/L only. Therefore, the dosage of SSF for fluoridation at WTP is recommended to be always at the medium range in order to obtain the desired concentration of fluoride at the distribution system within the national recommended limit.

CONCLUSIONS

In conclusion, the solubility of using three different SSF of SSF1, SSF2 and SSF3 in the treated water as the

Table 5: The concentration of fluoride measured via spectroscopic analysis at different range of fluoride level at the specified distribution system.

No.	Range	No. of samples	Range of Fluoride level (mg/L)	Mean of Fluoride level (mg/L)
1	Low	28	0.01 - 1.08	0.36 ± 0.24
2	Medium	14	0.43 - 0.70	0.60 ± 0.08
3	High	14	0.74 - 0.97	0.81 ± 0.06

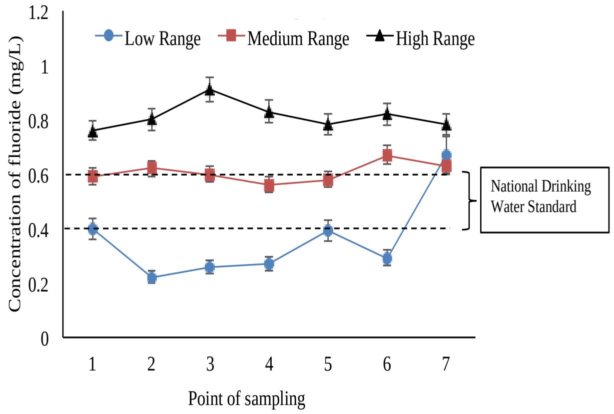

Fig. 4: Different range of fluoride concentration of water samples taken from sampling point 1 to 7 in comparison to the national drinking water standard of fluoride at 0.4 to 0.6 mg/L.

fluoride source was successfully analyzed. The solubility study shows that SSF3 was found as the best fluoride source that can be used in the specified WTP as it has the highest solubility in water, even at the highest range of fluoride concentration investigated. Thus, this contributed to the minimum carryover of fluoride solids in the fluoride solution tank than the other SSF investigated. Based on the spectroscopy analytical test, a higher amount of SSF was required for dosing in order to obtain the desired concentration of fluoride at the allowable limit. SSF dosing study at the specified WTP for different concentration range of fluoride in the mixing tank was performed to evaluate the sufficiency of fluoride concentration at the distribution system following the recommendation by the national drinking water standard. The SSF dosing of the medium range in the WTP resulted in the fluoride level of the treated water either at the WTP or at any point in the distribution system to match the set level of between 0.4 mg/L and 0.6 mg/L. These obtained values are also found below the international guidelines by WHO of which is between 0.7 to 1.2 mg/L. Hence, this finding has proven that an accurate dosage of SSF added at the WTP is necessary to ensure the water distribution system manages to get fluoride concentration as per standard. In the next study, drinking water quality is to be monitored continuously using relevant modelling software in order to ensure that the water does not pose any harm to the public health. Simulation and modelling study of the hydraulic and water quality analysis in a water distribution network from a specified WTP is essentially needed for identifying sufficient amount of fluoride in the water that can be beneficial for consumers health.

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