Petroleum and Coal

WATER STABILIZATION IN CLOSED CIRCUITS BY PHOSPHATE COMPOUNDS

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Abstract

The stabilization of circulating water is meant to optimize water conditions to prevent the formation of deposits or corrosion. Calcium carbonate precipitation in pipes water decreases water carrying capacity and increase cost of transportation. Water should be stabilized to prevent these problems. Water stabilization is the adjustment of the pH, Ca^{+2}, and alkalinity to its $CaCO_3$ saturation equilibrium. Accordingly, stabilized water neither dissolves nor precipitates $CaCO_3$. In this study suitable chemicals for decreasing hardness, alkalinity and suspended solid from water are selected. Also the effects of some parameters such as pH, alkalinity, hardness, temperature, phosphate dosage and additive starch are studied on water stabilization.

Keywords: water stabilization; phosphate; starch; sediment.

1. Introduction

Suran was the first to use phosphates to remove calcium and magnesium salts from water [1]. Hall was first used sodium triphosphate to prevent the formation of calcium carbonate precipitation and control it in boiler water. He noted that sodium triphosphate is dissolved in water and reacts with calcium and magnesium salts, and converts to calcium phosphate and magnesium, which are in the form of sludge. He also suggested that use of triphosphate calcium, which has a low solubility and a stable solubility, is positive. He examined the problem by mathematical method and assumed that the phosphate would displace the remaining hardness, preventing corrosion, and displacing precipitated deposits which were previously formed [1-2].

Hall explained the mechanism of sediment formation in the walls of steam boilers. Sticky and hard sediments formed due to the direct crystallization of low soluble solids on heated walls that have reached saturation. These sediments can also contain water suspended matter. If the solubility of the soluble in solution is shown as S and the temperature as T, at dS/dT<0, the formation of the precipitate is certain and the resulting sediments are highly adhesive and very hard. At dS/dT>0, the formed sediments have little adhesion and are formed in cool parts and often remain suspended in sediment. Hall, used Graham salt $(NaPO_3)_6$ which is now called sodium hexametaphosphate, for the first time for boiler water treatment [1].

W.F. Langelier was related calcium carbonate solubility to several effective variables in dissolution. By defining the parameter of the saturation index, a tendency to precipitation or corrosion of water is obtained qualitatively. But this method is useful for water with low amount of soluble solids with pH=6.5-9.5. Langelier with the naming of pH water, which has neither a tendency to corrosion nor to precipitate to saturation pH (pH_s) and to compare it with real pH of water, could have gotten an idea of water instability [1]. This index is defined as LSI=pH-pH_s. pHs can be determine by analyzing water and by using the following formula:

$$pHs=11.017+0.197\log(TDS)-0.995\log(Ca)_t-1.041\log(Alk.)_t-0.016\log(Mg)_t+0.021\log(SO4)_t$$

whwre TDS is total dissolved solids that equal to total water soluble solids (total concentration of all the ions in the water).

If pH_s=pH then LSI=0, so, the solution is saturate and water does not have tendency to precipitate or corrosion. The positive LSI, shows pH>pH_s, under these conditions (temperature, alkalinity and soluble solids), the water is supersaturated from calcium carbonate and tends to precipitate. The negative LSI indicates that chemical equilibrium is not yet established, and if there is a precipitate in the system, it will dissolve in water and water may also attack to metal and cause corrosion.

This index is corrected for the water with high levels of soluble as follow:

$$LSI = pH-PCa-PAlk.-K \qquad PCa = -log[Ca] \qquad Palk. = -log[Alk.]$$

where K is a constant which relates to temperature and ion concentration of water.

Ryznar due to the work carried out by Langelier, presented a new method for the tendency of water sedimentation. He believed that the Langelier saturation index was qualitative and his suggested index represents a quantitative amount to determine the content of calcium carbonate that can precipitate up to 200°C. By Ryznar index can specified corrosive and sediment water [2]. Ryznar stability index = $2pH_s$-pH.

If the stability index is equal to 6 or less, the sedimentation property of the water will be high, and if this index is greater than 7, the precipitate will not be formed, and if this index is more than 7.5 or 8, the risk of corrosion will increase.

Feither investigateed the constraints of Langelier and Ryznar saturation indexes and stability of them. He introduced a new concept called critical pH, which was about 1.7 to 2 unit higher than the predicted value of the Langelier index [3].

Puckorius and Brooke were studied the formation of calcium carbonate precipitation in cooling water systems. According to their idea, the existing indexes for the formation of calcium carbonate deposition at pH above 7.5 in a cooling water tower are not accurate [4]. The percentage of water stabilization is calculated by using the following formula [4]:

$$Stabilization = \frac{(LSI)_{initial} - (LSI)_{final}}{(LSI)_{initial}} * 100$$

2. Water stabilization

The goal of water stabilization is provide adequate water for drinking, for boilers and coolants. Also in the industry, the aim is create a thin layer of protective calcium carbonate on the inner wall of the water distribution system. Due to the issues facing most industries today, water stabilization is one of the most important issues [5]. For this purpose, different materials such as chromate, silicate, sodium carbonate and phosphates can be used [6].

Phosphates are one of the most commonly used substances for stabilizing circulating water, which are used in a better and more effective manner than any other material mentioned above and there are different combinations in the market. Increasing their value depends on several factors such as sedimentation potential, reaction time, amount of phosphate added, pH and temperature [7].

The effect of the above parameters on the proper selection of suitable phosphate compounds, which will increase the efficiency and increase the time of unit operation, has always been a topic of interest in the industry [8].

The purpose of this paper is to investigate the effect of phosphate compounds on water stabilization in closed circuits. To achieve this goal, obtain of the best material for reducing hardness, suspended particles and alkalinity and determining the effective physical factors on increasing stabilization efficiency such as temperature, pH and reaction time are the objectives of the study. In this research, only water stabilization has been studied to optimize water conditions to prevent sediment formation, and the corrosion problem has not been discussed [9].

2.1. The effect of phosphates on hardness and water stabilization

Phosphates are one of the most common and effective materials for stabilizing circulating waters. Phosphates form complexes with dissolved calcium ions in the environment and reduces the equilibrium concentration of calcium ion prevent deposition of calcium carbonate in

the water pipes, boilers and coolants. In this way reduces water hardness and causes water stabilization [10].

2.2. Types of phosphates in stabilization of water

The major phosphates used in water stabilization are polyphosphates, glassy phosphates & metaphosphates. Also, the special phosphates are used in water stabilization, which are produced by heating of various types of orthophosphate salts which called dehydrated phosphates such as $Na_4P_2O_7$, $NaPO_3$, $Na_2H_2P_2O_7$, $(NaPO_3)_3$ & $(NaPO_3)_6$.

Effectively, the low amount of phosphate compounds prevents sedimentation. Excessive use of phosphates may result in the deposition of calcium phosphates or iron phosphates which is harmful [10]. Also, long contact time for some phosphates is harmful due to reversible reactions. To control sediment with phosphates, factors such as maximum temperature in the system, time dependence and precipitation potential are important [11].

2.3. Effect of different doses of phosphate on water stabilization at different times

According to the Figure 1, it can be seen that higher doses of phosphate increase the stabilization efficiency, the cause can be explained by the greater complexity factor (phosphates) and the greater involvement with hardness and calcium and magnesium ions in the environment.

According to the Figure 2, we find that over two hours, the efficiency goes up by about 30% while at 30 min, efficiency is 25%. This shows that over time, more complexes are formed.
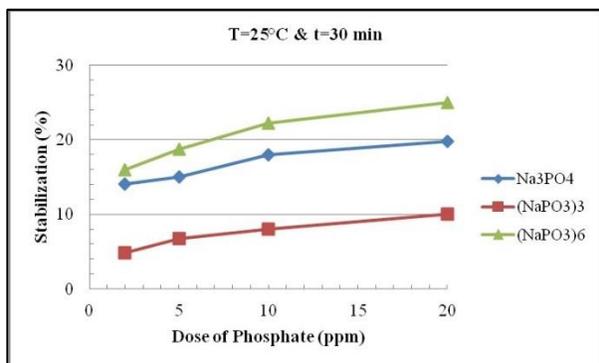

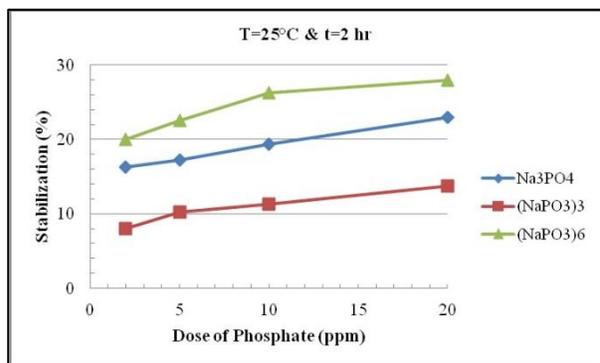Figure 1. Effect of different doses of phosphate on water stabilization percent at t= 30 min

Figure 2. Effect of different doses of phosphate on water stabilization percent at t= 2 hr

Also, according to the Figure 1 & 2, hexa methaphosphate is better than two other phosphates. Because polyphosphates have better efficiency than orthophosphates (Na_3PO_4). Unlike orthophosphates, which are deposited in calcium and magnesium phosphate, polyphosphates do not precipitate and keep calcium and magnesium ions in solution.

2.4. Effect of pH on the function of phosphates

According to the Figure 3, 4 & 5, we find that sodium hexametaphosphate has the best performance at pH=8. Sodium metaphosphate is an acidic phosphate that is better in alkaline medium. But it decomposes to orthophosphate at pH above 8 and decreases the efficiency. So, the efficiency at pH = 9 is lower than at pH=8. In pH= 6 because the environment is acidic, acidic sodium hexametaphosphate does not have good performance.

Figure 4 & 5, show the effect of the reaction time on the stabilization percentage at pH= 6 and 9, respectively. Due to its high alkalinity properties, this phosphate acts better at pH=6 and also has a better efficiency at 2 hours.
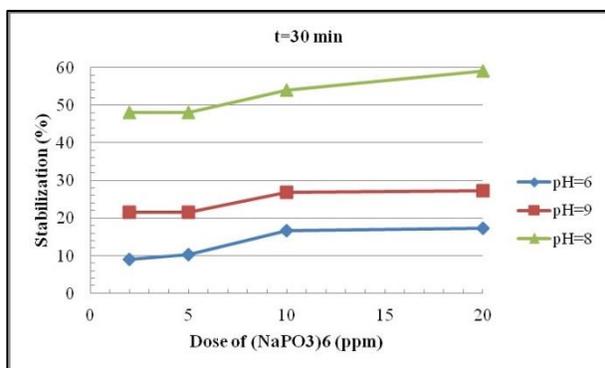
Figure 3. Effect of pH on water stabilization with $(NaPO_3)_6$ at t= 30 min
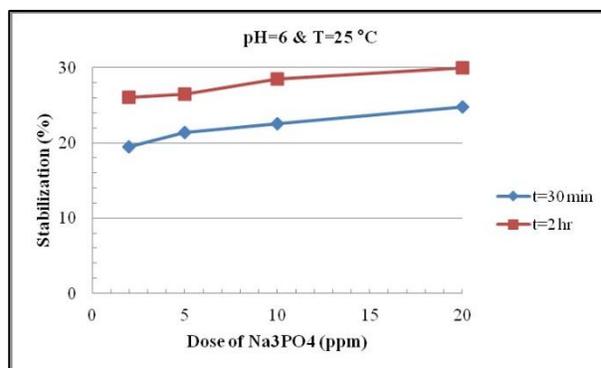

Figure 4. Effect of reaction time on water stabilization with Na_3PO_4 at pH=6 & T= 25°C
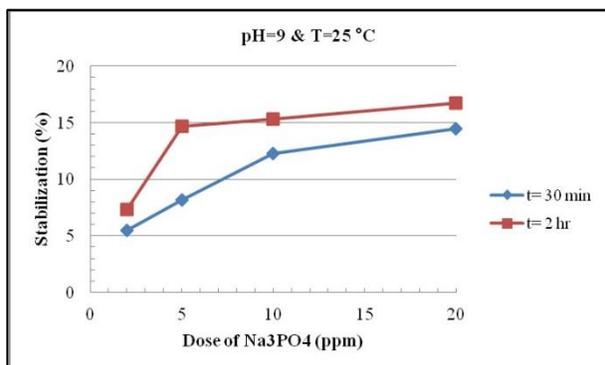

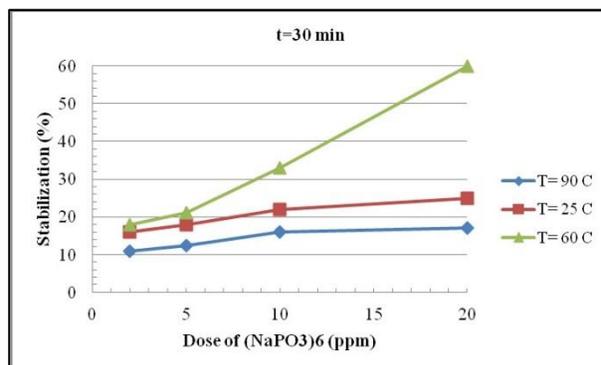Figure 5. Effect of reaction time on water stabilization with Na_3PO_4 at pH=9 & T= 25°C

Figure 6. Effect of reaction temperature on water stabilization with $(NaPO_3)_6$ at t= 30 min

The results for $(NaPO_3)_3$ is same as $(NaPO_3)_6$, but the efficiency is slightly lower, because it is a weaker polyphosphate than $(NaPO_3)_6$. In terms of economic, it is better that use of $(NaPO_3)_6$ in alkaline environments and Na_3PO_4 in acidic environments.

2.5. Effect of temperature on stabilization efficiency

According to the Figure 6 & 7, we find that an increase in the temperature up to 60°C, raises the efficiency, which may be due to carbonate decomposition into bicarbonate and CO_2 and increase alkalinity of environment, which results in better efficiency of the acidic $(NaPO_3)_6$.

But at 90°C, the polyphosphate is severely decomposed and converted to orthophosphate, the efficiency goes down even lower than 25°C.

According to Figure 7, by increasing the time reduces the stabilization efficiency, which can be explained by the decomposition of the polyphosphate and its conversion to orthophosphate. The result for $(NaPO_3)_3$ is as same as $(NaPO_3)_6$, only it has less efficiency.

The results for Na_3PO_4 indicate that the efficiency at T=90°C does not decrease too low (compared with $(NaPO_3)_6$), and the reason is that Na_3PO_4 is an orthophosphate, and the orthophosphate remains as the temperature rises. Only by increasing the temperature, carbonate decomposes and becomes bicarbonate and CO_2 which enters the environment and increases alkalinity, the efficiency decreases. Because Na_3PO_4 in a medium with high alkalinity, has less efficiency

2.6. Effect of starch with phosphate on stabilization efficiency

According to Figure 8, it is clear that add starch improves the stabilization efficiency and this due to the starch colloidal property which by creating a covering around sediments prevents them from sticking. This effect sees better at lower times and higher doses of starch.
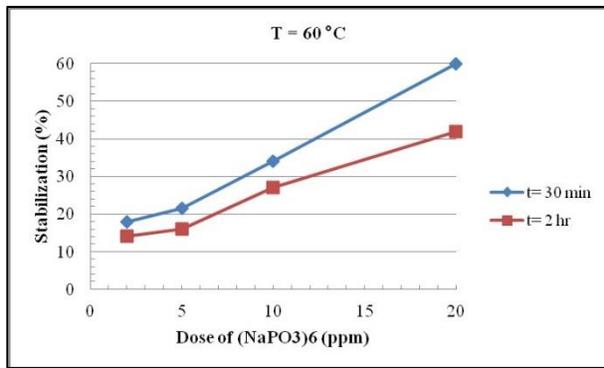
Figure 7. Effect of reaction time on water stabilization with $(NaPO_3)_6$ at T= 60°C
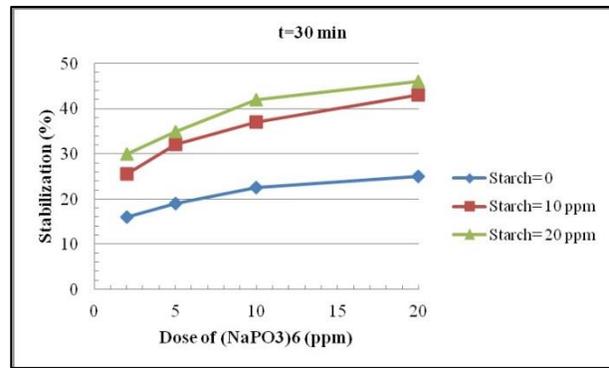
Figure 8. Effect of starch on water stabilization with $(NaPO_3)_6$ at t= 30 min

2.7. Hardness effect on the stabilization percentage

According to the Figure 9, the lower hardness has better stabilization efficiency. Because when the hardness is low, the phosphate can be more complex with them, but when calcium ions increase, phosphate can be less involved with them and can complex. As time passes, the efficiency becomes better because the phosphate has more time to form the complex

2.8. Alkalinity effect on the stabilization percentage

According to the Figure 10, we find that at the higher alkalinity, sodium hexameta-phosphate, has higher efficiency, which is due to its acidity. The result for two hours, shows that the efficiency is higher than 30 min, due to the surrounded more calcium ions.
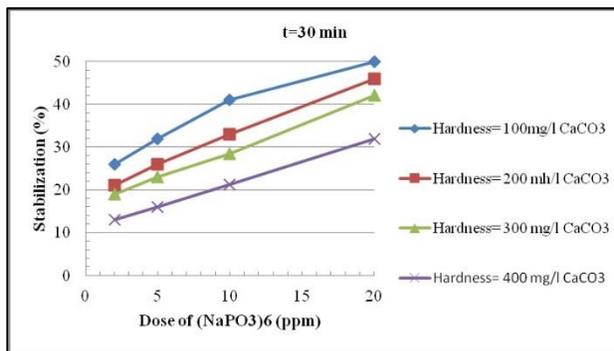

Figure 9. Effect of hardness on water stabilization with $(NaPO_3)_6$ at t= 30 min
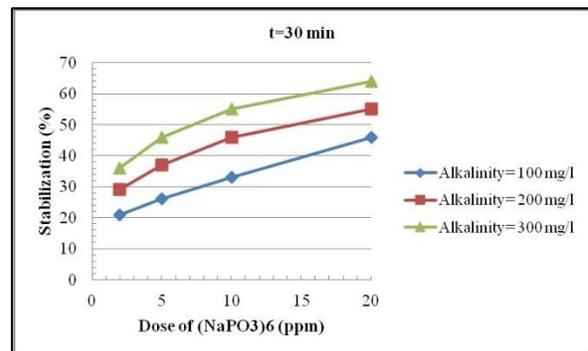
Figure 10. Effect of alkalinity on water stabilization with $(NaPO_3)_6$ at t= 30 min

3. Conclusion

Generally, the use of low phosphate dose (lower than 20 ppm), effectively prevents the formation of calcium carbonate precipitation. Also, for economic saving can be used less amount phosphate (10 ppm). Phosphates have different performance at different operating conditions, and the percentage of water stabilization at the same temperature and amount of phosphate, does not follow a given order for a different contact time. The stabilization efficiency with phosphate at different temperatures and times is between 20% and 80%.

The use of polyphosphates has better results than orthophosphates (about 3 times). At higher temperatures, the use of polyphosphates is not very suitable because it decomposes and converts to orthophosphate, and at higher temperatures it is better to use Glassy type polyphosphate.

In high alkaline environments, the use of sodium hexametaphosphate as an acidic property has better results in stabilizing efficiency, whiles the results in low alkalinity with Na_3PO_4 with

high alkaline properties, and is better. Usually, the time of 2 hours has the better stabilization efficiency

The use of useful additives such as starch increases the efficiency, and it is better to use lower doses (10-25 ppm) to make economically saving. In the environment with low hardness, the stabilization efficiency is improved, which is due to the effective function of phosphates in the formation of a complex with calcium ions

To prevent water corrosion, it is necessary to have a saturation index greater than zero to ensure that not only does corrosion not occur, but also a thin layer of sediment will be created. Depending on whether chemical inhibitors are used or not, LSI is chosen about 0.6-1. Today, in units where the water temperature is not high, they use the Langelier Saturation Index to control water quality, which is known as water stabilization.

It is emphasized that the Langelier Saturation Index or sediment index is merely a qualitative indication of the tendency to precipitate or corrosion, and does not determine the amount of sediment content is created or the amount of corrosion.

For example, water with high hardness and positive saturation index leads to a large amount of sediment, while the water with low hardness and the same amount of saturation index, may not produce considerable sedimentation.

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