

CHALMERS



Silica Scale Inhibition in Mechanical Pulping

With Focus on Refinery Process

Bachelor of Science Thesis

EMINE TEMIZ

NADIEH SOOKHTANLOO

Department of Chemical and Biological Engineering
Forest Products and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden, 2014

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Emine Temiz

Nadieh Sookhtanloo

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Department of Chemical and Biological Engineering
Forest Products and Chemical Engineering
Chalmers University of Technology

SE-412 96 Gothenburg

Sweden

Phone +46(0)31-772 1000

Department of Chemical and Biological Engineering
Gothenburg, Sweden 2014

Acknowledgment

This study has been carried out in the BIM KEMI AB in Stenkullen in spring 2014 with supervising of Johan Berglund, supporting Peter Wållberg and examining of Hans Theliander. This study comprises 15 credits and is a part of Bachelor of Science in Chemical Engineering program at Chalmers University of Technology.

We would like to thank Johan who helped us a lot with beneficial instructions and supports during the time we have been on the BIM KEMI. Special thanks to Peter for his willingness to give us supportive and helpful directions. We would also like to thank all staff for a friendly welcoming.

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Emine Temiz and Nadiéh Sookhtanloo

Department of chemical and biological engineering

Chalmers University of Technology

Abstract

Silicate precipitation often occur in Kraft pulp mills, and cause problems in different types of equipment that is difficult to handle , therefore this types of deposits are prevented by using various additives . Silica tends to react with alkaline ions such as magnesium and calcium to form the magnesium-and calcium silicates deposits which can anticipate in pulp and paper industry.

There are two different processing options that are used to produce a paper pulp; Mechanical- or Chemical pulping. Mechanical pulping is simpler compared with chemical pulping due to no requirement for chemical recycle system.

This study is focused on the silicate precipitation in the refinery process, which is a part of mechanical pulping process and treatment a silicate deposits by different types of inhibitors.

Different methods have been used to reach some settlement for silicate problems. Methods based on testing various inhibitors at different conditions(pH and temperature), and compared them with the reference solution by using different analytical instrument such as Ultraviolet visible spectroscopy (UV-VIS) and BIM pressure grid measurement (BPG) to find the most effective inhibitor against calcium-and magnesium silicate. UV-VIS results indicated the amount of solids that can be formed at different pH values and at ambient temperature. The purpose of using BPG was to simulate primarily deposits building in similar environments in the production of pulp in terms of temperature, pH and ionic content and also confirm the UV-VIS results. The inhibitors (about 15 products) which had been selected contain different types of polymers: copolymers, terpolymers etc., and these polymers have different functional groups providing different properties; anti-scaling control, chelating agents and so on. Two of inhibitors (P5 and P6) have been showed an impressive result against calcium silicate deposition.

Magnesium silicate deposits do not stick to stainless steel even at high temperature and therefore they require no inhibitors.

Key words: Silicate, Inhibitor, Magnesium silicate, Calcium silicate, Mechanical pulping, Refinery

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1. Aim

The purpose of this project is to find a method for controlling and preventing the formation of silica precipitation such as magnesium- and calcium silicate and try to find effective inhibitors to inhibit the formation of silica deposits in pulp and paper making system.

2. Introduction and background

Silica precipitation is a very complex process and leads to major deposits where water is used in large quantities [24]. Preventing silica scaling on equipment surfaces is one of the most difficult challenges, thus it has become extremely difficult to remove and often require the use of mechanical and/ or chemical methods. Silicate deposits results not only in reducing equipment life and system operations in paper mill, but also reduces quality in the paper products. Preventing and controlling the formation of precipitation is very difficult to achieve because it often required some additives which have an inhibition effect. Inhibitors have the tendency to reduce the rate of chemicals reactions i.e. deposit formation rate is decreased.

2.1. Mechanical Pulping

In the pulp and paper industry two different methods are used, chemical and mechanical pulping. Additionally it is not needed any recycling system for chemicals which are used in the process. Mechanical pulp is made mainly of spruce and used for newsprint and pasteboard and the papers which produced in mechanical way have good printing properties but poor strength [15]. Woods decompose in thermo mechanical - and chemi thermo mechanical way (CTMP).The fibers in mechanical processes change their structure and being more damaged compare with fibers that obtained from chemical process. They even have a tendency to being yellow; hence lignin in wood is not separated from the pulps [15]. The main advantage of mechanical pulping is that it provides a higher yield (over 90%) but it becomes more difficult to bleach the pulp in comparison with chemical pulping, because it contains a higher lignin [18].

2.1.1. Thermo Mechanical Pulping (TMP)

Thermo mechanical pulping is a common process, however energy demanding system in pulp and paper industry. TMP-process require high temperature and pressure which makes the lignin soft and therefore fiber removal becomes easier [21].The processes for mechanical pulp manufacturing is divided in two stages and each stage conducted in three or four parts. In TMP, the barks and wood chips are removed in the first stage, then the stocks are heated by water steam before they supplied into refiner which consist of either single –or two disk. A short illustration of the process is shown in figure 2.1. Furthermore, approximately 60% of electrical energy is recycled to form of stream in low pressure and used to drying paper [21].

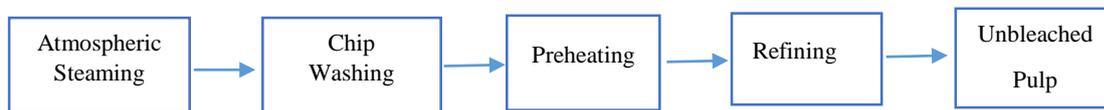


Figure 2.1: Schematic of TMP process [13]

2.1.2. Chemi-Thermo Mechanical Pulping (CTMP)

In CTMP process (see figure 2.2), the wood chips are pretreated with water steam and impregnated with chemicals such as sodium sulfite (Na_2SO_3) [14].However in CTMP process, papers get a higher brightness and higher strength materials than TMP process [14]. CTMP has a disadvantageous which is more expensive due to its high consumption of chemicals during process and lower yield [14].



Figure 2.2: Schematic of CTMP process [13]

2.1.3. Bleaching Chemi-Thermo Mechanical Pulping (BCTMP)

Another process called bleaching chemi-thermo mechanical pulping (BCTMP), which resembles CTMP, but there is an extra stage where fibers are bleaching with different chemicals and provides a more brightness in paper. The two different bleaching processes are used: Reductive and oxidative bleaching. Sodium peroxide (Na_2O_2) or Hydrogen peroxide (H_2O_2) is used in oxidative bleaching and the pH range is 10-10.5 with 50-60°C in temperature. Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) is used in reductive bleaching process to provide brightness increase up to 12%. The pH is varying between 5.6 and 6.5 and temperature is up to 70 °C [13].

2.2. Refinery Process

Refining is very complex processes which refine wood chips into fine fibers. The refiner has two disks and between these two disks the chips and water are fed, the makes softens- and protects the wood against high temperature. One of the disks rotates all the time while the other can be stationary or rotating [17]. Temperature in first stage refinery is between 120-130°C and pressure keeps around atmospheric pressure in both first and secondary refiner [14].

The refiner consist of three zones: breaking zone (I), inner refining zone (II) and outer refining zone (III). Wood chips are cutting roughly into coarse strips in the breaking zone of the refiner. The circulation of coarse pulp is very significantly in breaking zone and about 70 - 80% of disk area is covered with pulp. A high coverage of pulp between coarse and fine structure in the transition area in the inner refining zone is presents. In the last zone that called outer refining zone, there are fine bars where the fiber surface and strength properties are developed [17].

High hemicellulos and low lignin content in wood make it easier to refine it and develop strength properties .The energy needed in the refiner can be reduced at increase temperature and pH, and also increases the hydration rate due to fiber swelling but in lower pH in the refiner make fibers harder [16].

2.3. General Wood using in mechanical pulping

In Sweden, spruce, pine, birch and aspen wood are usually used in pulp production. Depending on the type of wood that have been used in the refining process, different final pulp properties is obtained. Different types of wood also affect the energy demand of the process. When birch and aspen used in the manufacture of pulp, the chips must be pretreated with chemicals, therefore it is preferred to use in a Chemi-mechanical pulping process. Spruce is the best raw material to thermo-mechanical pulping process, although pine can be used, but pine avoids because it requires a higher energy and the produced pulp have less quality because it has a higher content of extractives [15] [17].

2.4. Silica

Silicate is a chemical compound that contains silicon (Si) and oxygen which presents naturally as minerals such as quartz and cristobalite, but can also be synthesized. Silicates are characterized by containing silicate ions SiO_4^{4-} as the smallest building block. Additionally, the most silicates are hard, insoluble in water and acid and also thermally stable which means that it is very useful in various areas [10]. Moreover, silicate compounds exist in form of amorphous which is soluble in alkali solutions and crystalline form that is none stable. [13]. Silicates could react with hydrofluoric acid and form the volatile gas SiF_4 that is toxic and corrosive [11].

2.5. Silica amount in wood

The amount of silicon in wood is about 25 mg/kg but it can vary between different wood types and it depends on geographical area and the time of the year. Soil acidity has an influence on the silica concentration which means that the Si concentration increases in lower pH. The Si concentration in different needles of the same coniferous trees depends on how much water transpired [2].

2.6. Scaling

Scaling is a phenomenon that implies that a surface is covered with a solid material in form of crystals of solid salt, precipitating from an aqueous solution. Scaling is a problem on surfaces of tanks, pipes, evaporators and heat exchangers and destroys equipment and reduces flow rate through the tube, and also decreases heat transfer rate in heat exchanger. Removing of these scales is one of the most difficult challenges in industries; therefore it often requires the use of mechanical and / or chemical methods [19].

2.7. Inhibitors

The prevention and controlling the precipitation is very difficult and it often requires additives that have an inhibition effect. Inhibitors have the tendency to reduce the rate of chemical reactions; it means that the deposit formation rate can decrease. It is desirable that inhibitors have some functions such as:

1. Reduce the rate of crystal growth
2. Ability to dissolve the crystals
3. Work against deposits building
4. Serve as chelating agent
5. Withstand the high temperature and pH state in solution
6. Be degradable in wastewater treatment plant [19].

2.8. Silicate scaling and Inhibition

Silica in water can be found such as reactive silica, colloidal silica and particulate silica. The monosilicic acid (H_4SiO_4) is obtained from dissolving of reactive silica (SiO_2) in water [12]. Colloidal silica are polymerized and form large molecules (see figure 2.3) in appropriate pH, thus this phenomenon forming silicate scales which can stick on metal surfaces and therefore damage the system e.g. in heat exchanger [23] [1]. Silica deposition occurs in processes where water is used, it leads to an undesirable silicate formation and scaling in paper machines which requires a lot of work to remove. The amount of silicate present in water is undesirable and the polymerization takes place only in supersaturated waters with respect to silica.

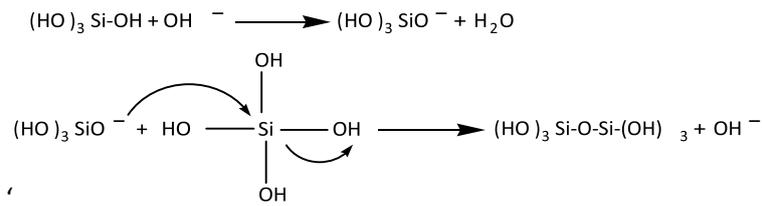


Figure 2.3: Silica Polymerization Process [5]

Silicate precipitation is a very complex process and this phenomenon is based on different chemical reactions in aqueous solutions. Metal ions such as magnesium and calcium in the water must be taken into account, because at alkaline conditions silica combine with magnesium or calcium ions and form a calcium- or magnesium silicate deposits [23]. Besides, silicates prefer to react with magnesium when both calcium and magnesium ions are present. Magnesium silicates are soft compared to calcium silicates ($\text{Ca}_2\text{O}_4\text{Si}$) which are hard; therefore it is easier to remove magnesium silicates from the equipment surface. Furthermore magnesium silicate do not bind to the metal surface and do not destroy stainless steel, while calcium silicate, which form hard scaling on the surface, damage the equipment. High magnesium concentrations may lead to elimination or minimized calcium scaling in the process equipment [5].

Silicate scaling results not only to reducing quality in the paper products, but also reduces equipment life and system operations in paper mills. Preventing silica scaling on equipment surfaces is one of the most difficult challenges, and often requires the using of mechanical and / or chemical methods [5].

Magnesium silicate system is pH dependent. When pH is below 7, it is no great risk for precipitation of silica, because silica is non-reactive and in non-ionized form. Above pH 9, there is a good chance for magnesium reacts with reactive silicate ions and forms a magnesium silicate which is relative soft. This compound acts as an effective flocculating agent and is easier to handle, finally resulting in higher proportion of silicon is removed [1]. Temperature is also an important factor that must be taken into account, when the temperature of the solution decrease, it leads to that the solubility of amorphous silica reduced [20].

Magnesium silicates has inverse solubility; this means that the solubility decreases as temperature increases, but the solubility of other silicates increases as the temperature increases [5]. Calcium- and magnesium silicate scales can be dissolved in acids and it leads to that crystal structures of scales can be changed or destroyed [25]

Silicate precipitation can be controlled in alkaline conditions in pulp process [1] by using different kind of inhibitors or dispersants. Inhibitors are used to prevent polymerization or oligomerization of colloidal silica. Dispersing agent is used to prevent formation of large particles and that these particles do not adhere to the surface [5]. The different types of additives are used depending on systems and processes.

Another method to control magnesium silicate deposit is using the addition of EDTA, this inhibit magnesium from catalyzing the polymerization of silicic acid [5]. When the pH value is high ($\text{pH} > 9.5$), EDTA is effective and it is dose-dependent. The dosage has an inverse relationship; this means that high EDTA dose has little effect on silica solubility while low doses provide effective solubility of silica, but still the reason is investigating [5].

2.8.1 Polyacrylates

One of the inhibitors which can be used to avoid polymerization of silicate are polyacrylates which are multi-functional and soluble in water. These type of polymers exist in form of homo, co- and ter-polymers and used as a chelating agent, anti-scaling agent and as an ingredient for detergents. These polyacrylates can be used to inhibit the precipitation of silicates, carbonates and phosphates. The amount of inhibitor dosage should be properly determined to obtain a maximal effect. Inhibitors performance rises from poor to excellent with a dosage up to 35 ppm and increases progressively [12].

2.8.2 Boric acid

Boric acid is combined with other chemical treatment and inhibit the silica scaling effectively. This sort of treatment with boric acid could even contain nonionic, anionic or cationic surface active agents, or polymers that have low molecular weight as threshold agent. When boric acid dissolved, it form the orthoborate ions (BO_3^{3-}). Silica ions react with orthoborate and form a water soluble component as borosilicate which inhibit silica scales [3].

2.8.3 Dendrimers

There is different kind of silica inhibitors which have dendrimeric structures. Dendrimers are macro branched molecules with an atom that is located in a center [5]. The word 'dendrimer' was invented by D.A. Tomalia and adopted from two Greek words: *dendros* (tree) and *meros* (part) [7]. Poly amino amide (PAMAM) is the one of the dendrimers that has either COOH-terminated or NH_2 -terminated with several generation each. PAMAM- 1 and PAMAM- 2 have most inhibition effect on silica polymerization. These inhibitors are expensive, therefore other inhibitors should be used that have lower cost and be as effective as PAMAM [8]. The structure of PAMAM has been shown in figure 4.

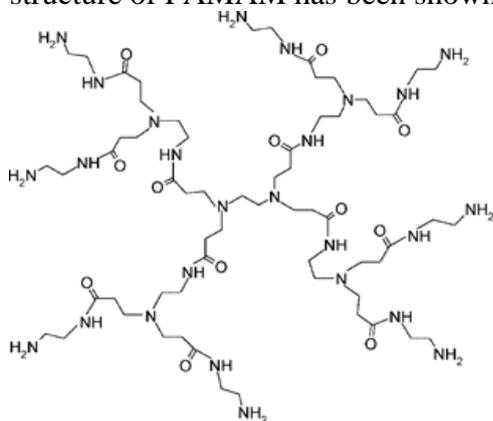


Figure 2.4: PAMAM structure with NH_2 -ended [6]

Polyethylenimine (PEI) polymer is another type of dendrimers (see figure 2.5) which has a high positive charge density but it has a poor effect on silica inhibition and according to one study, PEI at 10 ppm dosage offers 55 % silica inhibition at 24 h [8].

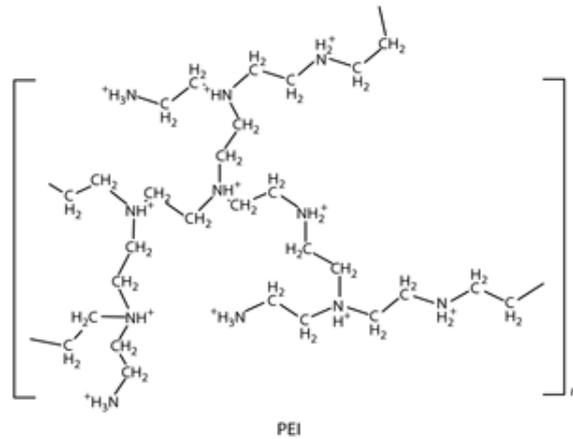


Figure 2.5: Schematic structure of Polyethylenimine (PEI) [5]

2.8.4. Quartz

Another type of inhibitors is a ‘cationic organic fixing agent’ [17] polymer and known as a quartz [1] that is a colorless and has a pH value between 3 and 5 and even is available in different types. A study that had been performed [1] describes how pH and dosage of different types of this inhibitor have an influence on the silica removal; e.g. according to one study at a low dosage (0.1 g / L) perform a great influence on Si removal and also at pH 10.5 eliminate 90% of the silicon [1].

3. Experimental

This methodology explains the comparison between two different groups of solutions; reference solution containing silicate and alkaline ion (no inhibitor) and the sample solution (with inhibitor presence) and optimizes silica scaling with some analytical methods.

3.1. Instruments

Different analytical instrument had been used during laboratory; inductively coupled plasma-mass spectroscopy, ultra violet visible spectroscopy and BIM pressure grid.

3.1.1. Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS)

ICP-MS (inductively coupled plasma-mass spectroscopy) is an analytical technique to determine the elemental content of the samples. ICP-MS has the capability to detect metals and several non-metals and give a quick identification and detection of trace metal content in aqueous solvent. The majority of samples which analyzed with this method are liquid. Solid samples can be analyzed with this method but they must first be vaporized by laser, heat cells or dissolve in acid. Gas samples can also be measured by ICP-MS, there samples inject directly into instrument [22].



Figure 3.1: ICP-MS instrument

3.1.2 Ultra Violet-Visible Spectroscopy (UV-VIS)

UV-VIS (Ultraviolet-Visible) spectroscopy is an analytical method to measure absorbance, transmittance and determine the concentration of the substance in sample [22]. Absorbance show that how much light that absorbs in a gas - liquid or solid samples and with transmittance means permeability of light for a specific substance in a particular wavelength. UV-VIS is used for quick and easy measurements in water, quality control, clinical facilities, in teaching laboratories and for quantitative analysis of elements and compounds [22].



Figure 3.2: Schematic of UV-VIS apparatus

3.1.3 BIM Pressure Grid Measurement (BPG)

BPG (see figure 3.3) is an instrument that is produced and modified just for BIM KEMI where the process of building inorganic deposits (scales) in the paper and pulp industry has been simulated. BPG apparatus consists of an oven with stainless steel capillaries containing anions and cations from two different test solutions inside it. Brines are flowing through the small capillary where the pressure is measured. The pressure in the system will increase when the scales decreasing the diameter of the capillary. The instrument need to be cleaned between each run and depending on solutions, the different washing procedures and detergents are used.

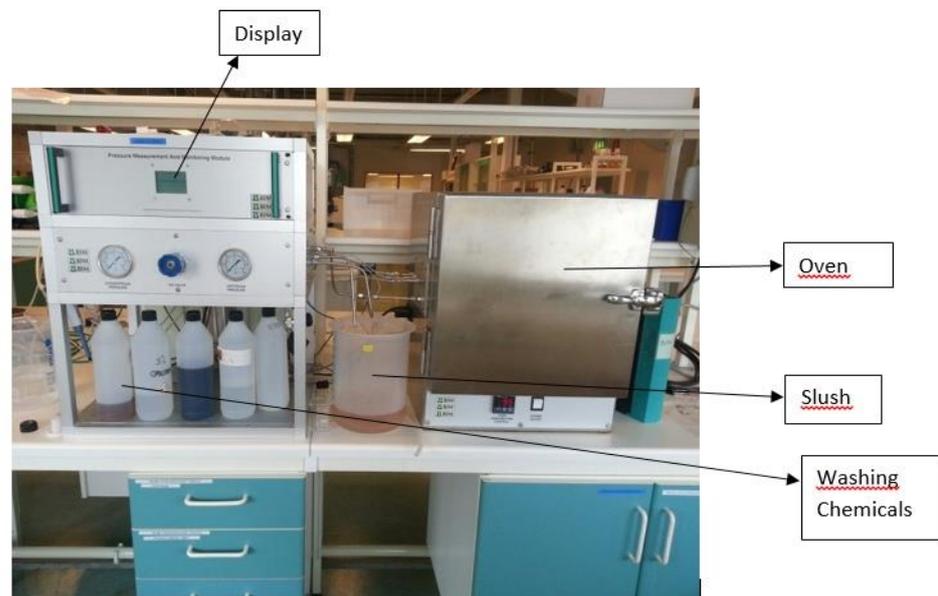


Figure 3.3: Schematic of BPG apparatus

3.2. Solution preparation and precipitation of silica with calcium and magnesium

The first stage of experiment was to prepare three different salts solutions containing Ca^{2+} , Mg^{2+} and silica ions which were diluted with deionized water and concentration of these ions in solutions have been chosen to 500 ppm. The salts were $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The pH of the silicate solution was adjusted between 12.3 and 11.8 with 10% HCl, but pH of cations containing solution had not been adjusted. Silicate solution was mixed with calcium in a flask named flask A and with magnesium in a flask B under stirring at room temperature.

3.3. Temperature and pH influence to control silica scaling

Next stage was to increase temperature to 90 °C and adjust pH of silicate solution to 8 with 10% HCl and then mix silicate with magnesium-and calcium with 500 ppm concentration under stirring. Different pH values have been investigated on both type of silicate containing solutions at room temperature to find out the critical pH.

3.4. The effect of different inhibitors on calcium- and magnesium silicate

Various inhibitors are prepared by weighing different products and then dilute them with distilled water. These inhibitors are commercial products and therefore, this report does not include their trade name. The solids content was chosen to 0.4% and dry content calculated by $C_1 \cdot V_1 = C_2 \cdot V_2$ formula, since all the inhibitors have different solids contents (see Table 3.1).

Table 3.1: A list of inhibitors with different dry content

Acronym	A	B	C	D	E	F	G	P1	P2	P3	P4	P5	P6	P7	P8
Dry Content (%)	40	40	40	29	45	50,64	50	25	50	35	50	36	50	51	47,27

One of the products (Inhibitor B) was added to silicate containing solution to visually investigate how this inhibitor affects silicate precipitation in ambient temperature. The temperature of the both magnesium silicate solution (with inhibitor and without inhibitor) was increased to 90°C to find out inhibition effect at high temperature.

Each of these inhibitors was added to magnesium-and calcium silicate solution at room temperature and high pH (pH=11.78). All solutions which were mixed with inhibitor, was analyzed using the UV-VIS apparatus to find the most effective inhibitor against magnesium- and calcium precipitation.

3.5. Evaluation and confirmation by BPG

BPG has been used to simulate more real conditions that is similar to refiner, e.g. under high temperature compared to previous tests that carried out with UV-VIS. By measuring the pressure drop, formation of precipitates can be determined and confirm that if the precipitations stick to thus capillary walls.

Three different products that showed good performance in the UV-VIS, has chosen in order to confirm that these inhibitors are still effective, additionally investigated at what dosage of inhibitors have a maximum effect.

Different solution consisting of Mg^{2+} , Ca^{2+} and silicate ions with various concentrations have been chosen to investigate whether magnesium ions prohibit calcium silicate deposits on the basis of literature study that found the silicate ions have a tendency to react with magnesium when both Mg^{2+} and Ca^{2+} are presented.

4. Result and Discussion

In an initial experiment it was shown that calcium silicate form larger and crystal shaped particles compared with magnesium silicates which are sufficiently smaller (See figure 4.1). Consequently, calcium silicate deposits provide a major problem in the refiner in pulp and paper making system.

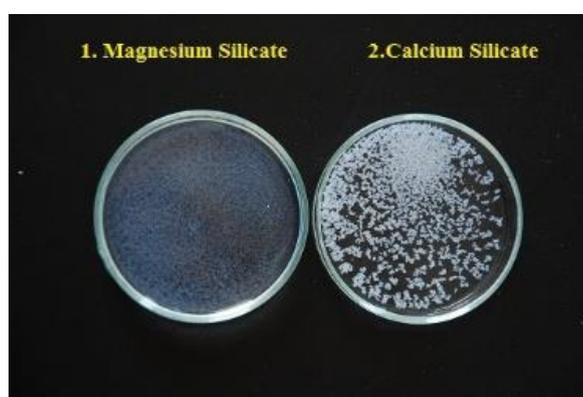


Figure 4.1: A picture illustrates a difference between MgSiO_3 and CaSiO_3 particles in room temperature and alkaline pH.

Temperature dependence on silica deposits has been tested and based on laboratory results, shown in figure 4.2; it was observed that calcium silicate does not precipitate at high temperature while the magnesium silicate deposits were obtained at 90°C . Moreover, literature studies have verified that the magnesium silicate's solubility decreases as temperature increases, but other silicate compound such as calcium silicate's solubility increases as the temperature increases. Since the refiner process takes place at high temperature, it is more probable that the magnesium silicate deposition occurs which is beneficial. Magnesium silicate is more manageable and will not adhere to the equipment's surface.



Figure 4.2: Flask to the left is calcium silicate and flask to the right is magnesium silicate at 90°C (pH=8.0)

The UV-VIS results are shown in figure 4.3 and 4.4. The pH has been adjusted for silicate solution but not measured in final mixing solutions. When calcium or magnesium was added in silicate solution the transmittance of light is reduced to 20 respective 50 percent after about 10 minutes. This indicated that the precipitation is dramatically in high pH, but there is no precipitation at the low pH values. Consequently, the pH in refiner must be high to develop silicate problems. More precipitation of calcium silicate than magnesium silicate obtained in high pH and ambient temperature, which may depend on optical properties.

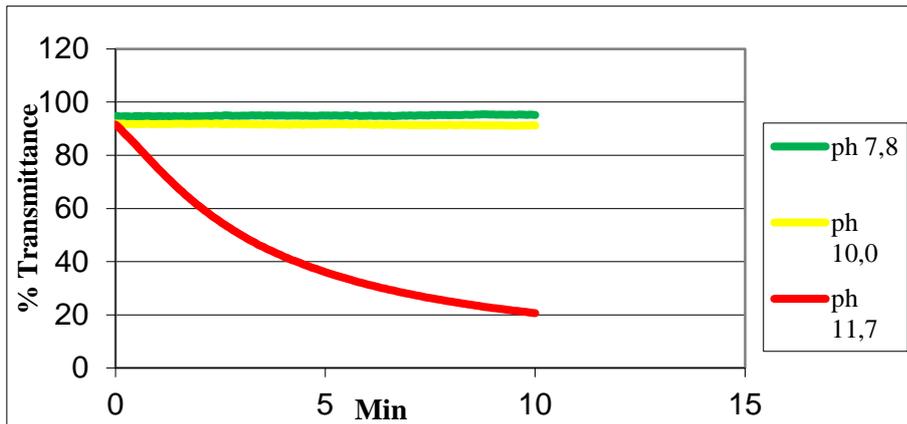


Figure 4.3: The pH effect on calcium silicate precipitation

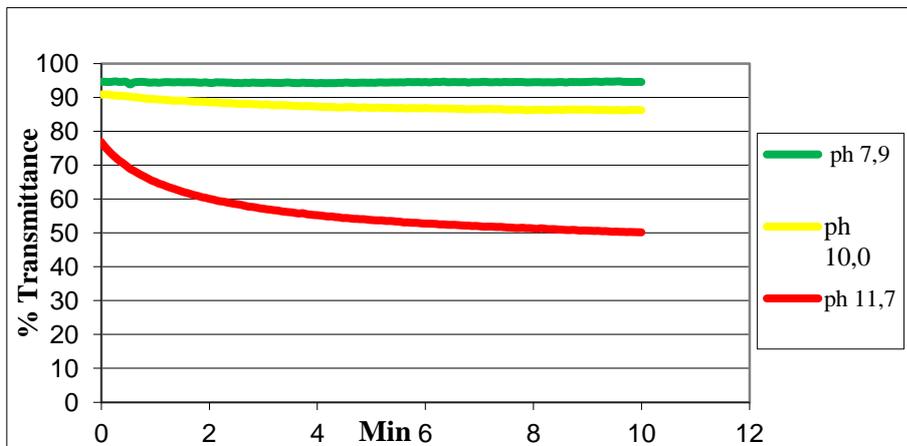


Figure 4.4: The pH effect on magnesium silicate precipitation

The calcium silicate solution without inhibitor was compared to calcium silicate solution with inhibitor (see figure 4.5), and there was a clear difference. In the solution without inhibitor precipitation occurred immediately and the particles were large and formed in a crystal form but the particles in the solution with inhibitor the particles were smaller.

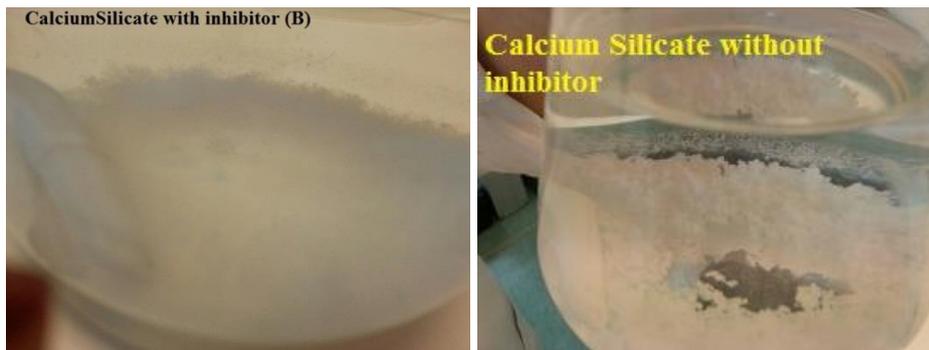


Figure 4.5: The picture to left shows calcium silicate with inhibitor B and the picture to right shows calcium silicate without inhibitor B (T=20 ° C)

Magnesium silicate solution without inhibitor at high temperature (90°) and pH=7, 8 was compared to magnesium silicate solution with inhibitor P5. In the solution without inhibitor precipitation occurred but in solution with inhibitor, there was no precipitation (see figure 4.6).



Figure 4.6 a) The picture to the left shows magnesium silicate with inhibitor P5, b) The picture to the right shows magnesium silicate without inhibitor.

All selected inhibitors are tested in both magnesium-and calcium silicate and based on Figure 4.7 and 4.8, some inhibitors can exclude because these inhibitors are not effective to inhibit magnesium- and calcium silicate. The most effective inhibitors at 40 ppm for calcium silicate are P5 and P6 and for magnesium silicate are P3, G and E. Inhibitor A, P7 and E had the worst influence on calcium silicate precipitation P4 and P8 had the worst effect in magnesium silicate precipitation.

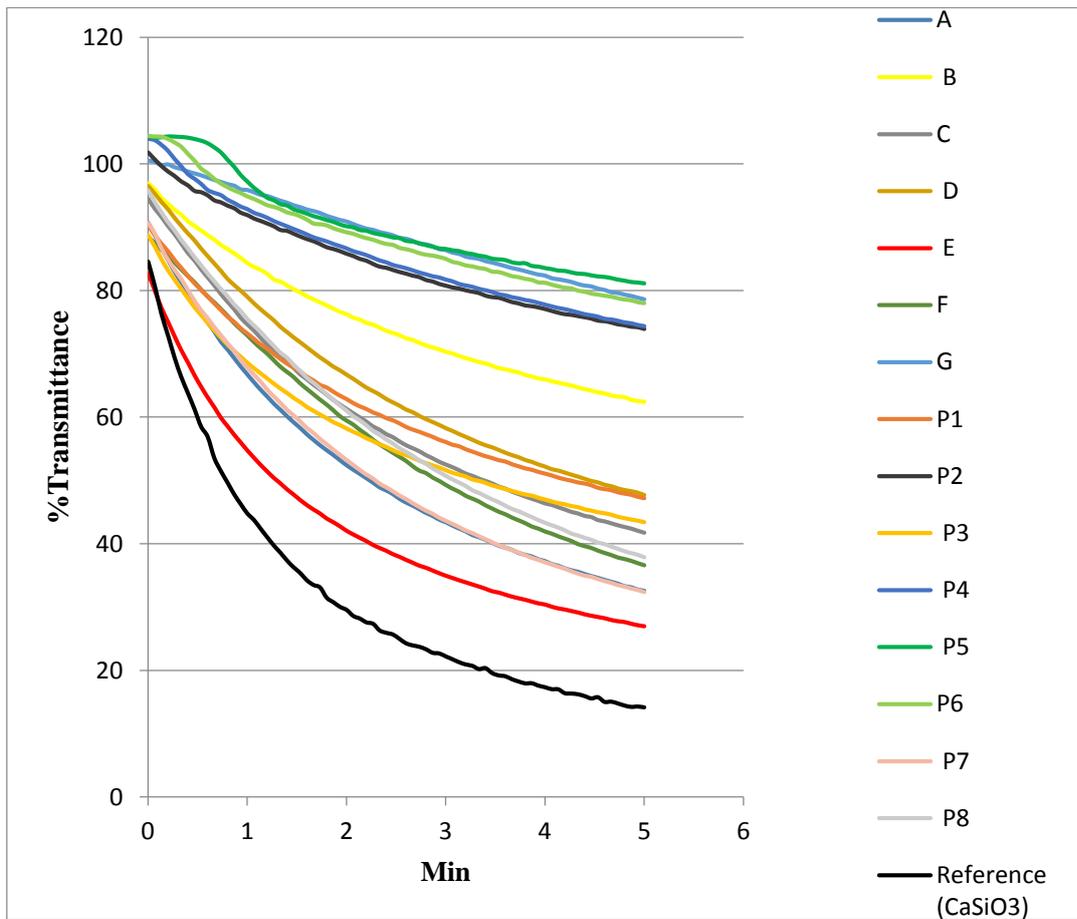


Figure 4.7: Different inhibitors influence on calcium silicate scaling, pH=11.78 and Temperature=20

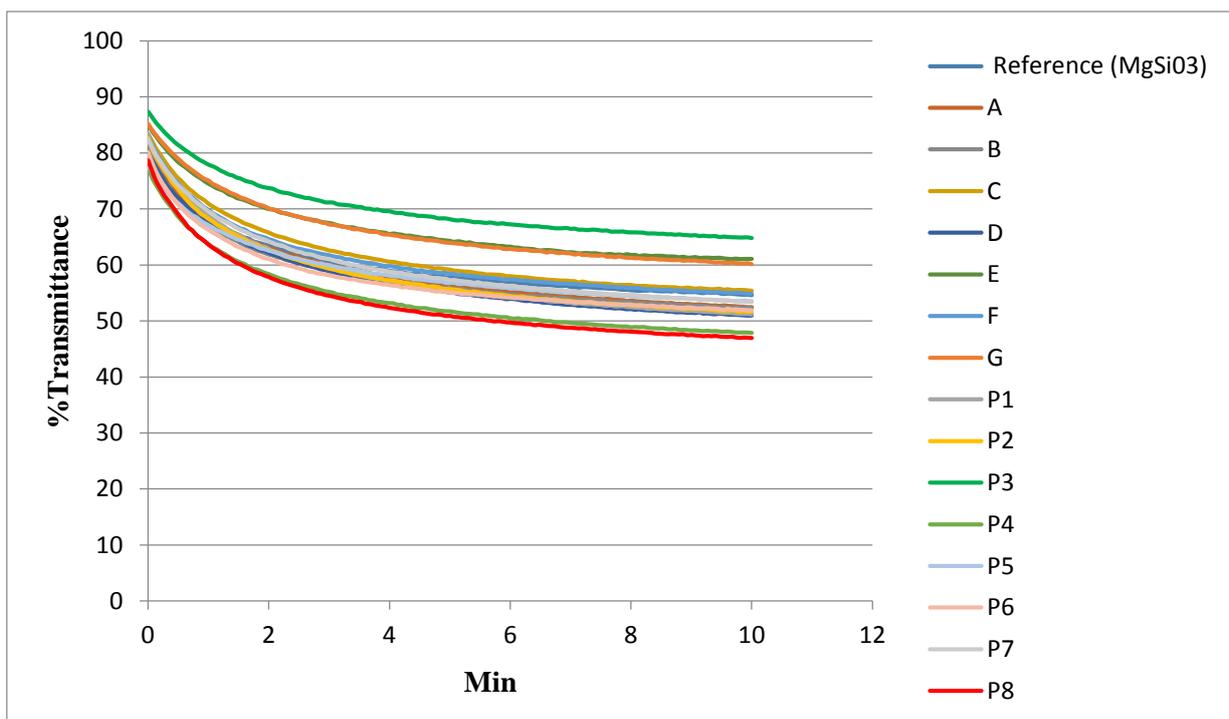


Figure 4.8: Different inhibitors influence on magnesium silicate scaling, pH=11.78 and Temperature=20

Table 3.1: The effect of different inhibitors against silicate precipitation

	Magnesium Silicate	Calcium Silicate
Effective inhibitor	P3, G and E	P5, P6 and G
Less effective inhibitor	C	B
Worst inhibitor	P4 and P8	E, A and P7

In the literature it was found [12] that the high dosage of polyacrylates inhibitors may increase the inhibition effect. P5 which showed good effect at 40 ppm and P8 which showed lower effect in the same concentration have been selected. A high dosage (70 ppm) has been tested to verify this claim and the result has been shown in figure 4.9. According to figure 4.9 is P5 very efficient at 70 ppm, and it keeps the calcium silicate solution stable for two minutes before precipitation begins, but at 40 ppm it keeps the solution stable for about 1 minute.

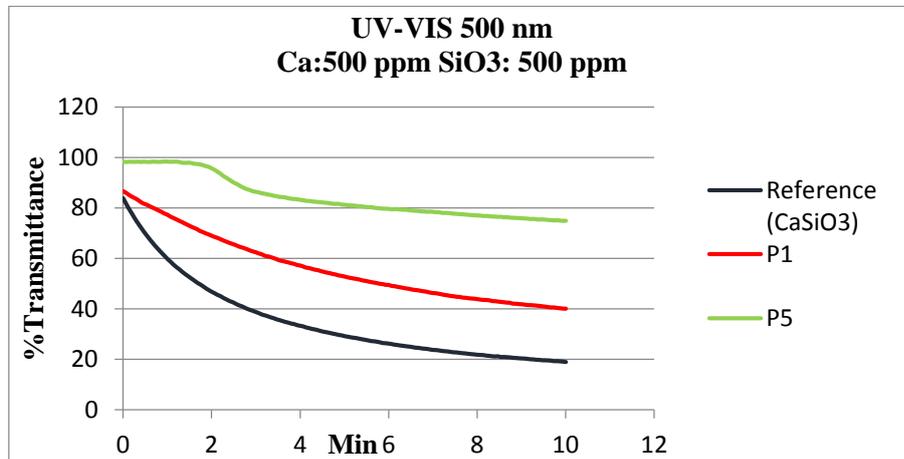


Figure 4.9: High dosage of inhibitors effect on silica scaling

As mentioned previously, are P5 and P6 the most effective inhibitors for inhibition for calcium silicate. The inhibitors were mixed together to examine if the effect will be better. Inhibitor mixture (P5 and P6) has a good influence on the inhibition of calcium silicate, but when P5 is used alone, it shows better effect (see figure 4.10). Inhibitor G mixed with P5 showed no great result for inhibition of calcium silicate as shown in figure 4.10. Based on laboratory results, it is better to use P5 and inhibitor G alone for the inhibition of calcium silicate.

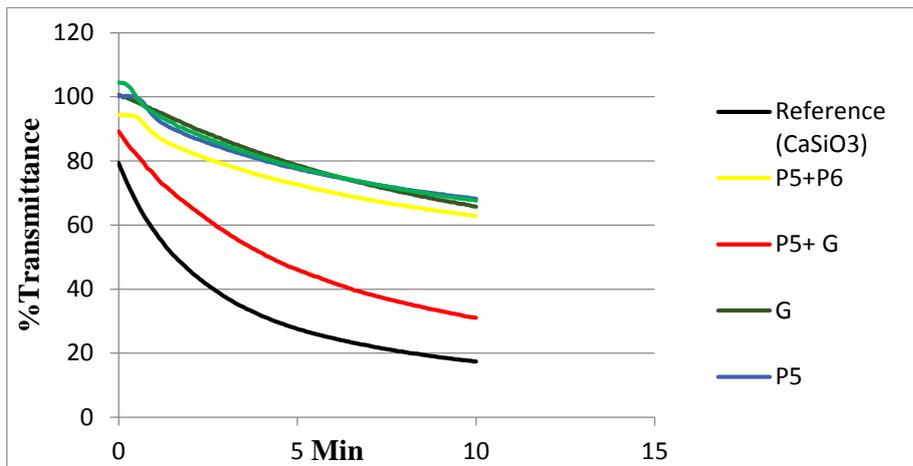


Figure 4.10: Effect of mixing inhibitors on calcium silicate precipitation

250 ppm Mg and 250 ppm Ca were added in a flask and then added 500 ppm silicate in the same flask, and this was done to investigate whether silicates react with magnesium or calcium. ICP instrument was used to determine which ion had been consumed most. It was found that the concentration of Mg was reduced to 165 ppm and Ca to 240 ppm, which means that nearly all Ca ions remains, 34% of Mg ions consumed while Ca ions had only 4% consumed. The result implies that if you have equal concentrations of both Mg and Ca in the silicate solution, the silicate ions reacts with magnesium ions rather than calcium ions. This is an advantage, as mentioned previously; magnesium silicates do not stick to the equipment compared with the calcium silicates. Silicate scaling can be significantly eliminated or reduced since silicate ions build a compound with magnesium rather than calcium.

BPG results have been compiled and as seen in the diagram below (Figure 4.11), the inhibitor G is not an effective inhibitor for calcium silicate scales in different dosage. Therefore, this inhibitor completely excluded and is not recommended to use.

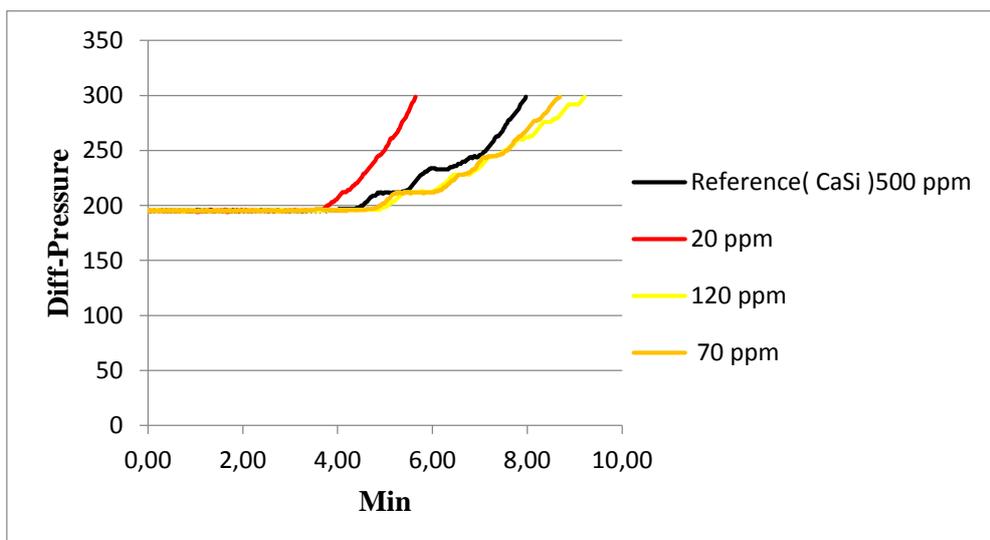


Figure 4.11: Evaluation of G inhibitor on Calcium Silicate, Temperature=95°C

Figure 4.12 shows that the inhibitor P6 is effective to prevent calcium silicate at high dosage, which has also been confirmed in the UV-VIS results. Calcium silicate solution keeps pressure stable if P6 dosage is increased to 50 ppm and consequently no deposit received.

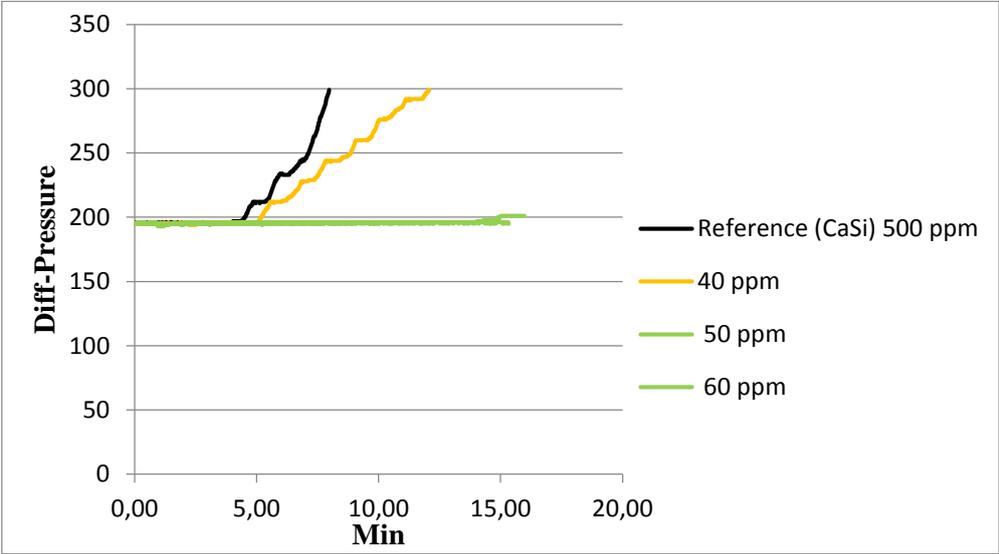


Figure 4.12: Evaluation of P6 inhibitor on Calcium Silicate, Temperature=95°C

According to the graph below, it was found that the P5 is also dependent on the dose and has a positive effect on calcium silicate scales (see figure 4.13). The only difference is that P5 is not as effective as P6 at 50ppm. The maximum inhibition effect can be achieved, if dosage of both P5 and P6 increased to 60 ppm instead.

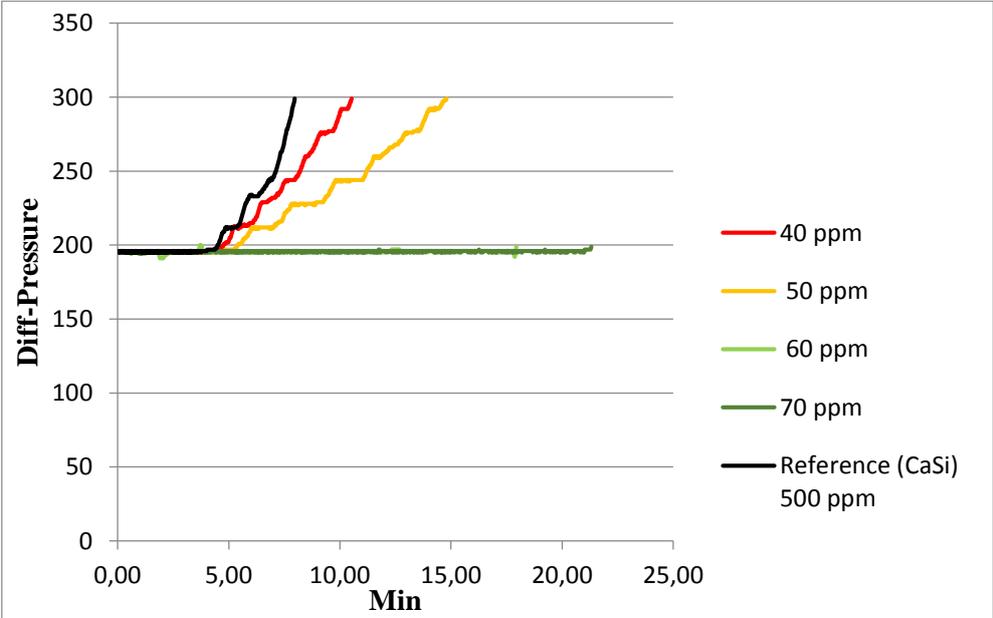


Figure 4.13: Evaluation of P5 inhibitor on Calcium Silicate, Temperature=95°C

The last BPG test was done to investigate if magnesium ions can have any effect on reaction between calcium and silicates. It means that in order to ICP and literature study, silicates should react with magnesium when both calcium and magnesium ions are provided in solvent and consequently, magnesium silicate deposits do not settle in stainless steel capillaries and finally no increasing in pressure should get. The results of BPG (see figure 4.14) is not feasible. The diagram below illustrate that the silicate scales settle down on capillaries and the pressure increase pretty quick irrespective magnesium present in solvent together with calcium and this is not desirable. When only magnesium containing solution mixed with silicate containing solution, there was no increasing or alteration in pressure and it indicated that no deposit stick in capillaries.

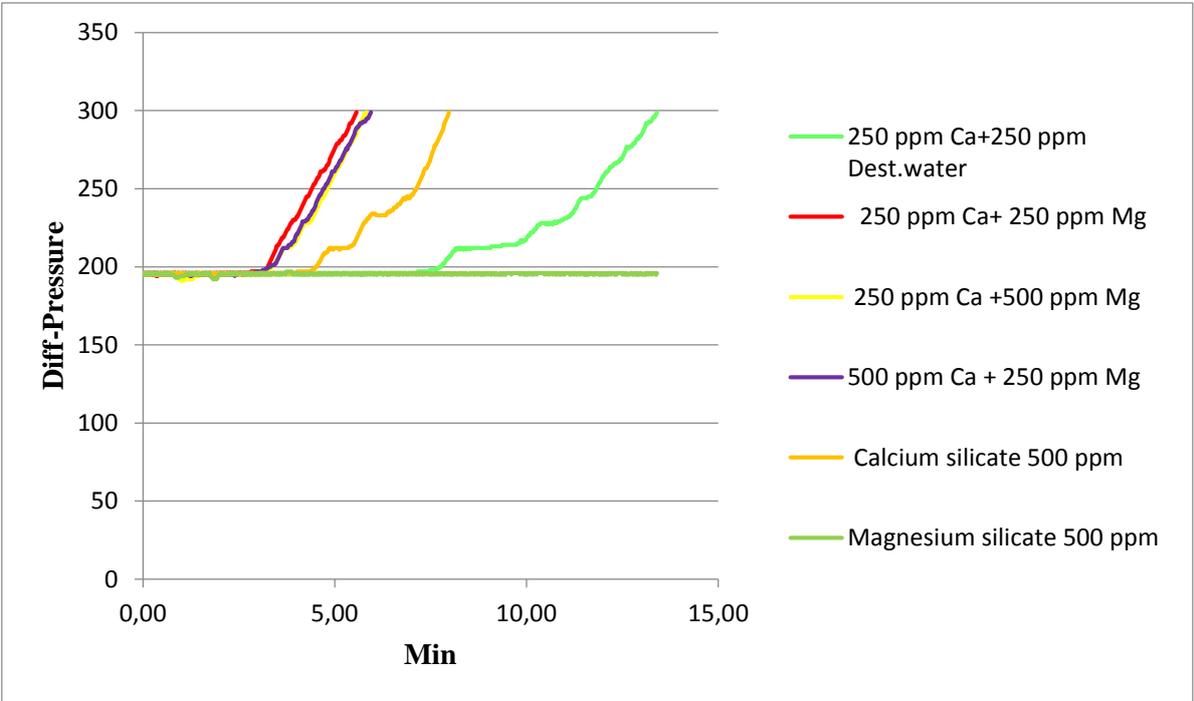


Figure 4.14: Evaluation of magnesium ions effect on the formation of calcium silicate deposits

The pH measurements (see table4 &5) was performed to find out reasonable argument about magnesium impact on silicate precipitation and Mg^{2+} render solution to buffer and consequently pH value of solvents decrease.

Table 4.1: pH values on different concentration of magnesium, calcium and silicate containing solutions

Solution	pH value
Ca¹ +Si²	11, 31
Mg¹ +Si	9, 58
Mg¹ +Ca³ +Si	9, 86
Mg³ + Ca¹ + Si	10, 17
Mg¹ + Ca¹ + Si	9, 71
Mg¹ + Ca³ + Si	8, 46
Mg³ + dest.water +Si	10, 22
Ca³ + dest.water + Si	11, 57

¹ Concentration= 500 ppm

² Silicate ions concentration is 500 ppm in all solutions

³ Concentration= 250 ppm

5. Conclusion

- Temperature and pH have a great influence on silicate scale formation in aqueous alkaline solvent; at low pH and temperature have not been received any precipitation of either magnesium or calcium silicate. In contrast, at high pH and low temperature precipitation of both magnesium and calcium silicates have been obtained.
- Preferably, silicate form a complex with magnesium when both magnesium and calcium are exists in solvent and render stainless steel devices easy to handle, thus magnesium silicate deposits do no stick to this type of metal.
- In further, more focus on calcium silicate inhibition was attempted, due to that particles are relatively larger and precipitated more compared with magnesium silicate in the same conditions based on UV-VIS results and evaluation by BPG instrument as an analytical techniques.
- Several products that contain large molecules of polymers have been selected and proved to find the most effective inhibitor against silica scaling. High dosage (> 60 ppm) of inhibitor P6 and P5 are recommended and beneficial to use for elimination and inhibition of silica precipitations.

6. Future Works

Further research and development studies still needs in order to minimize silicate scales. For further study, the pH adjustment of all mixed solutions to the same value is recommended, e.g. $\text{pH} \approx 11$ and accomplish under the same circumstances and this might give more adequate results. Sources of errors can be minimized if the inhibitors analyzed in a longer period of time and even test the repeatability of inhibitors influence in several times. A more detailed research of the different ions such as silicate, magnesium and calcium is required to investigate how they will perform in aqueous solvent at different conditions. Other types of inhibitors which have been discussed in this report can also be an alternative to research more on them and finally try to simulate more closely conditions in refinery process.

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