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Polymeric Materials for Scale Inhibition in Cooling Water Systems

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Abstract

Calcium carbonate deposition is generally predominant in cooling water-circulating system. For the control of calcium carbonate, scale formation two types of polymeric scale inhibitors were used Polyamino polyether methylene phosphonate (PAPEMP) and polyacrylaminde (PAA).Model of cooling tower system have been built up in laboratory scale. Experiments were carried out using different inhibitor concentrations (0.5,1,1.5,2,3)ppm ,at water temperature of 40oC and flow rate of 150 l/hr. It was found that Polyamino polyether methylene phosphonate more effective than polyacryle amide' as scale inhibitor in all used concentrations and the best inhibition efficiency (95%) was at (2.5)ppm of Polyamino polyether methylene phosphonate and (85%) with poly acryle amide at concentrations of (3) ppm.

The performance of the polymeric scale inhibitors was compared with a method used to control heavy calcium carbonate scale forming by the deposition of sufficiently thin protective calcium carbonate scale using sulfuric acid and depending on Ryznar stability index controlling method.

Key words: Scale inhibitor, Cooling towers, Polymeric materials, Polyamino polyether methylene phosphonate, Polyacryle amide, Ryznar stability index, Calcium carbonate deposition.

استخدام المواد البولمرية لتثبيط تكون التكلسات في أنظمة التبريد

الخلاصة

تعتبر ترسبات كاربونات الكالسيوم المكون الغالب في انظمة التبريد.في هذا البحث تم تطوير طرق لتقليل ترسبات قشور كاربونات الكلسيوم في انظمة التبريد والتي تسبب مشاكل خطيرة في هذه الانظمة. تم استخدام نوعين من المركبات البولمرية هي البولي امينوبولي ايثرمثلين فوسفونيت والبولي اكريل امايد.

تم تصنيع برج تبريد مختبري ,واجريت التجارب باستخدامه عند معدل جريان 150 لتر/ساعة ودرجة حرارة40^oC وتراكيز مختلفة للمواد المثبطة (0.5,1,1.5,2,3) جزء بالمليون وقد وجد ان مادة البولي امينوبولي ايثرمثلين فوسفونيت هي الاكثر فعالية من مادة البولي اكريل امايد كمواد المثبطة لتكوين التكلسات.وان كفاءة تثبيط تصل (95%) عند تركيز(2.5) جزء بالمليون من بولي امينوبولي ايثرمثلين فوسفونيت و (85%) من مادة البولي اكريل امايد عند تركيز (3) جزء بالمليون.

ادائية المواد البولمرية قورنت مع استخدام طريقة اخرى للسيطرة على تكلسات كاربونات الكالسيوم السميكة بترسيب طبقة خفيفة واقية من هذه الكاربونات باستخدام حامض الكبريتيك وبالاعتماد على مؤشر رايزنر لتحديد القابلية على تكوين التكلسات.

Introduction

Water used as a coolant in several thermal systems, contains dissolved minerals which can precipitate and adhere on heat-transfer surfaces. It should be noted that minerals commonly uncounted in cooling water are inorganic salts, such as calcium carbonate, calcium sulfate, calcium phosphate, magnesium slats, silica and iron oxide, some of these salts, or their combination have inverse solubility characteristic, i.e. they are less soluble in the hot stream adjacent to the heat transfer surface. Thus hot stream of water can become supersaturated, which promotes precipitation and crystallization of the salts on the surface. The deposits thus formed are a major factor of reduced efficiency and capacity of many industrial heat exchangers and cooling systems. Furthermore, with an increases in energy and equipment cost [1].

Many cooling systems are operated at high cycles of concentration due to water conservation and waste water discharge regulations. However, these practices increase scaling tendency in re-circulating water and necessitate the use of high performance scale and deposit control additives to prevent the formation and deposition of unwanted materials on heat exchanger and other equipment surfaces [2] .

Calcium carbonate is the predominant component of scales deposited from natural water especially in cooling water systems, owing to its inverse temperature-solubility characteristics [3] .

The main reason for the mentioned precipitation is high carbonate hardness and excessive salinity of cooling water. Salts that are dissolved in the water get condensed as water evaporation proceeds and usually precipitate when the solubility product gets exceeded the process runs in heat exchanger (and in cooling installations) that make an advantageous environment for the beginning of solid phase crystallization scale deposits that form in cooling water systems are polycrystalline porous substances with amorphous inclusions.

Their physical – chemical and mechanical properties are variable depending on many factors such as [4]:

The kind and concentration of substances contained in the recycled water-both pollutants and substances purposefully added to enhance properties of the water, local heat load, kind of crystallization base, hydrodynamic conditions, contacts with polluted atmospheric air, Corrosive power of water against construction materials. Development of biological life in water.

The most common and effective scale control method is the use of scale inhibitor[3].Till recent times many inorganic metallic compounds such as chromates; molybdayes and zinc compounds as some non metallic ones like phosphates (polyphosphate), silicates, nitrites and azoles that effectively protect alloys have been applied as corrosion and scale inhibitors. Disadvantages of inorganic such as : toxicity (chromates), low stability (silicates) and (poly phosphates) or selective protective action (nitrites) as well as increasing rigid ecological standards, have turned the interest of researchers to the application of organic compounds as potential inhibitor of multifunctional properties [5] . A large number of synthetic polymers are used as scale inhibitors and as dispersants. Most of synthetic polymers have molecular weight below 50,000 and are polymers of acrylic acid, acrylamide, methacrylic acid, malic acid, etc. The effectiveness of the polymers decreases as the chain length increases. A length of about 10-15 repeating units is best. At this molecular weight, adsorption is maximized without causing bridging and dispersion is most efficient synthetic polymers such as polyacrylates are believed to inhibit scale deposition by adsorption on growing crystals. This is followed by both a charge repulsion mechanism of negative charges, which leads to destabilization of the crystallites [6] . Polymeric inhibitors function by an adsorption mechanism. As ion clusters in solution become oriented, metastable microcrystallites (highly oriented ion clusters) are formed. At the initial stage of precipitation, the microcrystallite can either continue to grow (forming larger crystal with a well defined lattice) or dissolve.

Scale inhibitors prevent precipitation by adsorbing on the newly emerging crystal, blocking active growth sites. This inhibits further growth and favors the dissolution reaction. The precipitate dissolves and releases the inhibitor, which is then free to repeat the process.

Inhibitors delay or retard the rate of precipitation. Crystals eventually form, depending on degree of super saturation and system retention time. After stable crystals appear, their continued growth is retarded by adsorption of inhibitor. The inhibitor blocks much of the crystal lattice as growth continues.

The distortions (defects in the crystal lattice) create internal stresses, making the crystal fragile. Tightly adherent scale deposits do not form, because crystals that form of surfaces in contact with flowing water can not withstand the mechanical force exerted by water. The adsorbed inhibitor also disperses particles, by virtue of its electrostatic, and prevents the formation of strongly bound agglomerates[7] .

The most commonly used scale inhibitors are law molecular weight acrylate polymers and organophosphorus compounds (phosphorates)[7] .

Poly amino polyethermethylene phosphonat (PAPEMP) is very effective in preventing calcium carbonate precipitation. The superior performance of PAPEMP has been attributed to its excellent ability to inhibit calcium carbonate crystal growth due to its affinity to the calcium carbonate surface and its excellent calcium tolerance.

In dynamic systems PAPEMP, especially when combined with other polymers, also acts as a dispersant as is evidenced by its ability to maintain clean heat transfer surface beyond inhibition[8,9] .

In 1996 Zahid Amjad ,et. al. [10] study the Polymer performance in cooling water, he investigated the influence of process variables such as temperature and concentration on the performance of calcium phosphate inhibiting polymers.

Zahid Amjad,et. al. [2] in 2004 performed a research for the use of polymers to improve control of calcium phosphonate and calcium carbonate in high stressed cooling water systems.In his study ,a sulfonic acid containing terpolymer was identified as an effective inhibitor for calcium phosphonates and calcium carbonate.

In (2009) Chen Wang, et. al.[3] studies the Calicum Carbonate inhibition by a phosphonate-terminated poly (maleic-co-sulfonate)polymeric inhibitor, they found that for the control of calcium carbonate scale and in response to environmental guidelines, a new low phosphonic copolymer was prepared. The anti-scale property of low phosphonic copolymer towards $CaCO_3$

in the artificial cooling water was studied through static scale inhibitor tests.

Another method to control heavy calcium carbonate scale forming by the deposition of sufficiently thin protective $CaCO_3$ scale using sulfuric acid (H_2SO_4).Protective coating in the form of $CaCO_3$ scale develops by regulating and adjusting the pH, Alkalinity. and Ca^{+2} ions maintain a slightly super saturated solution of $CaCO_3$(11).By such control, a thin in previous and adherent layer can be deposited on the surface requiring protection. Sulfuric acid is the most common acid used for this purpose due to its accessibility, low cost and minimal secondary problems.

$CaCO_3$ is a general inhibitor that covers both anodic and cathodic areas because its precipitation does not depend on the products of electrochemical reactions[11] .

Although an alkaline film on the cathodic surface is an added factor favoring precipitation of $CaCO_3$.

Powell and Bacon[12], investigated the use of $CaCO_3$ scale for corrosion prevention in cooling tower systems seving steel equipment, they found that rising temperatures cause the actual pH of the water to drop at the same rate as the $CaCO_3$ saturation pH, scale of uniform thickness, will be deposited.Extension of the use of $CaCO_3$ scale for prevention of corrosion and the control of excessive scale deposition has been encouraged by Langlier[13] . He advanced the idea of calculated saturation index as a mean of predicting scale behavior of a natural water.

Ryznar[14] developed Langlier method, he refined the Langlier index to allow for a distinction between two waters having the same Langlier index.

Many methods have been proposed to predict the tendency of calcium carbonate either to precipitate or to dissolve under varying condition. However, they all based upon the thermodynamic equilibrium of carbonic acid and alkalinity corrected for temperature and dissolved solids.

The more commonly used equation or index is Ryznar stability index (RSI) [14] .

Ryznar index is defined as :

$RSI = 2\,pH_s - pH_a$ ………………. (1)

Where pH_a is the actual pH measured value of water, and pH_s is the pH of saturation calculated from the expression :

$pH_s = A + B - \log[Ca] - \log[M - Alk.]$ …………. (2)

Where : A, B are constants related to the temperature and dissolved solids content of water respectively and their values are listed in table (1& 2) (14) in. The bracketed values are the ionic concentrations expressed in mg/L.

The predictive nature of Ryznar index is shown in table (3)[13,14].

This index indicated only the tendency for calcium carbonate to deposit, not the rate or capacity for deposition.

Calcium carbonate scale formation can be controlled by the addition of acids or specific chemicals tailored to inhibit its formation or modify the crystal lattice. Sulfuric acid which is inexpensive is most often used, its addition reduce the water alkalinity sufficiently to create non-scaling condition and reduces slats that are more soluble than $CaCO_3$.

These salts that can reach saturation and must be controlled to prevent precipitation on heat transfer surface [15] .

$Ca(HCO_3)_2 + H_2SO_4 \rightarrow CaSO_4 + 2(O_2 + 2H_2O)$ ……… (3)

$CaSO_4$ is calcium sulfate, which is more soluble than ($CaCO_3$) by at least a factor of 50. This phenomena provides the control $CaCO_3$ in circulating cooling water systems.

The normal upper limit for calcium and sulfate concentrations in the absence of inhibitor is expressed by [15]:

$[Ca^{+2}]\ [SO^{-4}] = 500{,}000$

Where the bracketed values are the ionic concentrations expressed in milligram per liter.

Referring to above upper limit, the sulfate ion concentration must be periodically determined to control the amount added of H_2SO_4, where excess of SO_4^{+2} concentration in cooling water show strong corrosively.

Blow down is the quantity of water bleed of the cooling tower to prevent concentration from becoming so high.

The main objective of this research work is to investigate the effect of addition of poly acryamid(PAA) and polyamino polyether methylene phosphonate(PAPEMP) at different concentrations as scale inhibitor on stainless steel in cooling water systems. Also it is aimed to compare the results of using polymeric material with the use of sulfuric acid to control heavy calcium carbonate scale forming by the deposition of sufficiently thin protective calcium carbonate scale and depending on Ryznar stability index controlling method.

Experimental Work

Experiments using the polymeric scale inhibitors

Cooling tower system was built up in laboratory scale so that it is possible to perform a simulation of processes that runs industrially.

Figure (1) presents diagram of the system. The cooling water system consist of tower contained within a basin which contains 40 L of water, the tower contained a series of slats positioned on a way to provide uniform cascade flow of water and water distributor positioned at the top of the tower, the system has a water pump used to circulate the water from the basin to the tower, the flow of water was controlled at 150 L/hr using rotameter. The temperature of the water in the tower was at 40°C and it was controlled using thermostat and thermocouple. Air was drawn out of the tower using air draft fan positioned at the top of the tower which withdrawn air from the bottom. The metal samples were positioned on the states of the tower. The sample used were stainless steel.

The stainless steel samples were of 20 x 10 x 2mm size. The samples were washed with distilled water and de-greased with acetone and accurately weight to 3 rd decimal fraction of a gram in an electrical balance type Satorius. To find the percent of scale inhibition it needs to know the weight of the scale formed in each experiment, so every sample weighted before each run. Then the sample positioned in the laboratory cooling tower for two weeks. After the test ,they were mildly rinsed with distilled water and acetone and weighted. The total scale formed is equal to the difference between the initial weight of the sample after the test and the weight of the sample before the test.

The first run was un-inhibited run. The other runs were received a one per week with dosage of (PAPEMP) and polyacrylamide(PAA) as scale inhibitors at different concentrations (0.5, 1, 1.5, 2, 3) ppm.

Experiments of sulfuric acid addition

1- Sample of used water was taken, its following characteristics were measured , pH_a values : Actual pH values were determined using electric pH meter model 744 (chemic company) calibrated by standard buffer solution.

M – Alkalinity : Was measured using standard titration method, with sulfuric acid [16] .

Ca^{+2} hardness (concentration as $CaCO_3$ in ppm) was measured using standard titration method, with (EDTA) solution[16].

T.D.S : Concentration of total dissolved solids were measured by T.D.S meter (Prestotek Corporation).

2- The second step included dosing of known concentrations of (H_2SO_4) into samples of 50 mL. then all characteristics of the water of (1) were re-determined and Ryznar stability index was calculated to predict the tendency of water in scale formation and the optimum condition of non or little scaling.

Results and Discussion

Effect of (H_2SO_4) addition

Referring to the characteristics of the used water in table (4) and Ryznar stability index tables, the value for the stability index (RSI) of the water can be calculated using equation 1 and 2 .

Table (5) represent the characteristics of the used water calculated using equations 1 and 2.

Referring to table (3) it would be expected that the used water would be heavy scale forming.

The scale formation could be controlled by the addition of sufficient acid to reduce alkalinity to obtain the desired saturation index (where ,alkalinity is the concentration of HCO_3^- ,CO_3^{-2} and OH^- present in the water, it can be reduced by acid Addition (eq.3). Figure (2 shows the relation between the actual pH_a and Methyl-orange Alkalinity in (ppm),it was clear that the acid addition causes M-Alk. to reduce. Many experiments were adopted to choose and determine the best concentration and dosing of H_2SO_4 acid. It was found that 5 wt% of H_2SO_4 and dosing amount shown in table (6) are the suitable values.

Table (7) show the values of pHa,M.Alk.,pHs,RSI of the tested water after H_2SO_4 addition.

Saturation pH(pH_s) can be calculated using equation 2 ,and it was clear that as M-Alk. increases the pH_s decreases ,that was shown in fig.3.

Figure (6) shows the variation of the stability index with M-Alk.,applying equation 3 to calculate the stability index(RSI).It was clear that (RSI) decreases as M-Alk. increases.

Figure (4) shows that the stability index of 5.85 – 6.84 in the tested water would be satisfied and could be obtained by reducing its methyl Alkalinity 205-170 ppm corresponding to a pH_a of 8.35-7.8 as shown in Figure (2) corresponding to pH_s of 7.1 – 7.32 shown in Figure(3).

Three tests of the data of table (6) were applied practically on the cooling tower built up in the labrotary scale.

Table (8) shows the resuls of practical application of the labrotary test table(6).

Labrotary cooling tower experiments shows that a thin scale layer was formed at the optimum amounts of sulfuric acid added(1.5-3.5) ppm on the stainless steel samples used within the tested period of two weeks.

Effect Of Polymeric Inhibitors Addition

In this study the efficiency of polymeric inhibitors used have been calculated using the equation :

$$\text{Inhibition eff.\%} = \frac{1 - \Delta W_{in}}{\Delta W_{unin}} \quad \ldots\ldots (4)$$

Where:

ΔW_{in}; weight change of metal samples in the inhibited solution.

ΔW_{unin}; weight change of metal samples in uninhibited solution.

Figure (5) shows the effect of using PAPEMP and PAA in cooling tower system, it is clear that PAPEMP is more effective than PAA as scale inhibitor in all concentrations. That is because the phosphnates exhibited singnificant reduction in calcium carbonate precipitation and the inhibitor molecules are preferentially adsorbed at active growth sites on the crystal surface[8] . The Maximum inhibition efficiency is 95% was at 2.5 ppm of PAPEMP and 85% with PAA of concentration 3ppm.

It was found that the polymeric materials is better than using sulfuric acid as the scale inhibitor, that was because inhibition by polymeric materials could reach to very high efficiency compared with the use of sulfuric acid which forming a thin layer of scale to protect metal surface from thick scale layer.

Conclusions

1- Polyamino polyether methylene phosphonate (PAPEMP) is more effective than polyacryle amide(PAA) as scale inhibitor in all used concentrations and the best inhibiting efficiency (95%) was at (2.5)ppm of (PAPEMP) and (85%) with (PAA) at concentrations of (3) ppm.

2- Sulfuric acid is the most proper acid used to control heavy calcium carbonate scale by producing a thin adherent layer of $CaCO_3$ on the surface requiring protection.

3- The use of polymeric scale inhibitors is more suitable for scale inhibition than the formation of a thin protective layer using H_2SO_4 acid, because the acid cause a thin $CaCO_3$ scale protective layer, but the use of scale inhibitor will protect the metal surface from scale formation without any layer of scale.

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Table(1) Constant (A) as a function of water temperature

Water Temp.(C^o)	Constant(A)
0	2.6
4	2.5
8	2.4
12	2.3
20	2.1
25	2
30	1.9
40	1.7
60	1.4
70	1.25
80	1.15

Table(2) Constant B as a function of T.D.S

T.D.S(ppm)	Constant(B)
0	9.7
100	9.77
200	9.83
400	9.86
800	9.89
1000	9.9

Table(3) Predictive nature of Ryznar stability index

Ryznar stability index	Tendency of water
4 – 5	Heavy scale
5 – 6	Light scale
6 – 7	Little scale Corrosion
7 – 7.5	Corrosion significantly
7.5 – 9	Heavy corrosion

Table (4)Chemical analysis of the tested water

Constituents, ppm (Ca^{+2}), Calcium hardness, as ($CaCO_3$)	475
Methyl-Orange(M–Alk) As ($CaCO_3$)(ppm)	267
Total solids (T.D.S)(ppm)	900
Actual pH(pHa)	8.74

Table (5) Characteristic of the used water

A	1.7
B	9.895
Log[Ca^{+2}]	2.67
log[M-Alk.]	2.42
pHs	6.73
RSI	4.72

Table (6) pH_a, M. Alk., Ca^{+2} and T.D.S values versus H_2SO_4 amount added

5Wt%, 0.02 N (H_2SO_4) ppm	pH_a	M.Alk.	Ca^{+2}	T.D.S
Without H_2SO_4	8.74	267	475	900
0.98	8.5	230	345	1000
1.5	8.35	205	250	1020
3	8	182	207	1200
3.5	7.8	170	180	1200
5	7.5	160	150	1300

Table (7) pHa ,M.Alk.,pHs,RSI of the tested water after H_2SO_4 addition

pH_a	M.Alk.	pH_s	RSI	Tendency
8.74	267	6.73	4.72	Heavy scale
8.5	230	6.9	5.3	Light scale
8.35	205	7.1	5.85	Tend to light scale
8	182	7.22	6.44	Little scale
7.8	170	7.32	6.84	Little scale (optimum condition)
7.5	160	7.42	7.34	Corrosion significant

Table (8) Application data on the laboratory cooling tower.

5%H_2SO_4(ppm)	Cooling water specifications				Ryzner variables		Tendency
Laboratory reading	MAlk.	pHa	Ca^{+2}	T.D.S	pHs	RSI	
0	267	8.79	490	1000	6.69	4.59	Heavy scale
1.5	205	8.349	255	1020	7.0883	5.82	Little scale
3	180	7.99	208	1200	7.227	6.46	Little scale
3.5	178	7.6	185	1200	7.31	6.96	Little scale

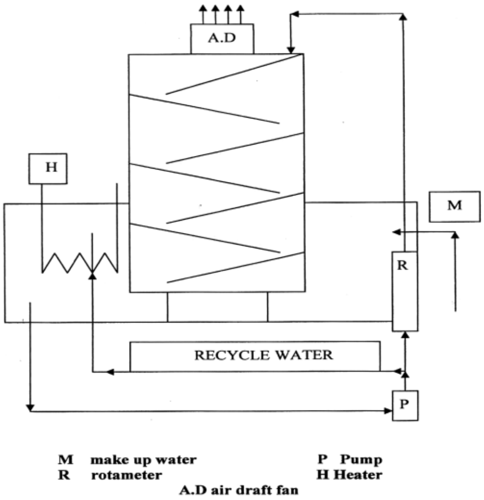
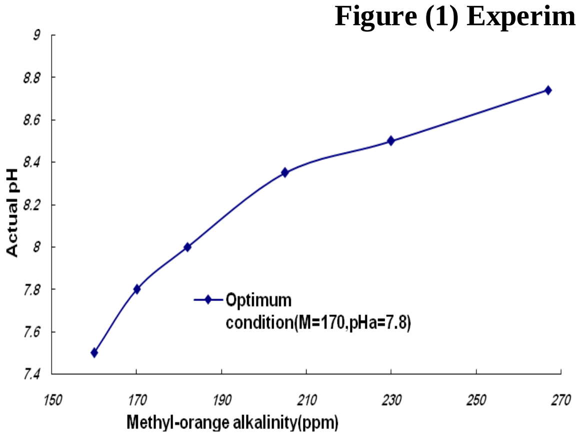


Figure (1) Experimental set up of cooling tower system



Figure(2)Methyl-orange Alkalinity versus Actual pH , at T=40°C

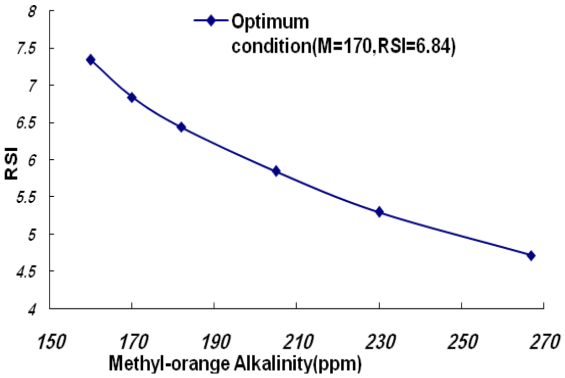


Figure (3) Methyl orange versus Actual pHs , at T=40°C

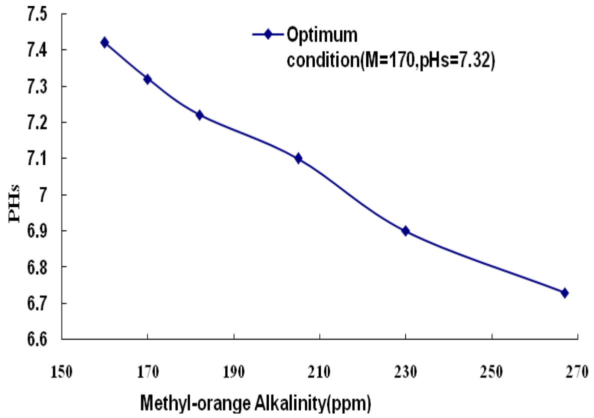


Figure (4)- Methyl orange versus RSI, at T=40°

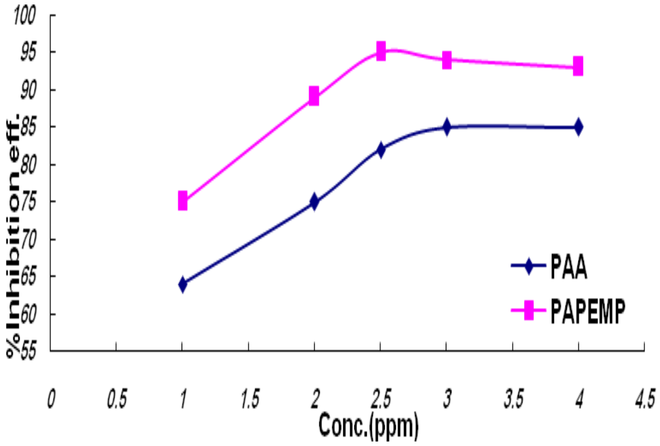


Figure (5) -Effect of concentration of (PAPEMP)and PAA on inhibition efficiency (Temperature=40°C, Flow rate=150l/h), where:(PAPEMP)is Polyamino polyether methylene phosphonate,(PPA) Poly acryamid