

## Zinc Element Traces to Inhibit Scale Formation on Cooling Tower and Air Cooler Systems

**Shaymaa Abdul Rahman Ahmed Reshan**

Chemical Engineering Department – College of Engineering – University of Baghdad –Iraq

### Abstract

Calcium carbonate is predominantly present in aqueous systems, which is commonly used in industrial processes. It has inverse solubility characteristics resulting in the deposition of scale on heat transfer surface. This paper focuses on developing methods for inhibition of calcium carbonate scale formation in cooling tower and air cooler system where scaling can cause serious problems,  $ZnCl_2$  and  $ZnI_2$  has been investigated as scale inhibitor on AISI 316 and 304.  $ZnCl_2$  were more effective than  $ZnI_2$  in both systems, and AISI 316 show more receptivity to the chlorides salt compared to AISI 304. The inhibitors were more effective in cooling tower than air cooler system. AISI 316 show more constant inhibition efficiency in cooling tower with maximum of 95% with  $ZnCl_2$  and 83% with  $ZnI_2$ .

**Key Words:** scale .cooling tower, air cooler, zinc compounds, AISI 316 and 304.

### Introduction

It is known that aqueous systems such as cooling tower, boilers, heat exchangers, heating/cooling system, paper mills, fire service water, reactors, and the like are subjected to the formation of deposition on the internal surfaces which are in contact with the circulating water .In the operation of systems unitizing cooling tower and like so, quantities of water, as required, are introduced and utilized at a rate depending upon the service requirements of the installation. Make-up water universally contains a quantity of impurities and the contaminants which, unless treated, contribute to a constant build up of deposits on the working surfaces of the system [1, 14]. Normal operation of these systems results in the

consumption of reasonably large quantities of water, and as water is lost from the system, normally through evaporation, levels of concentration of these contaminants and impurities increase. These contaminants and impurities are normally the same elements or compounds which commonly contribute to water hardness, specifically certain calcium salts along with certain quantities of iron oxides.

The precipitation of these compounds known to be scaling, which is serious problem in units because the scale layer acts as a thermal insulator, because the thermal conductivity of scale material is such greater than that of copper and steel [2], as given in table (1).

Table 1, thermal conductivity of some used metals

Compound	K (W/m.K)
Calcium carbonate	0.8
Silica	0.08
Copper	343
Steel	75

Scale precipitation (precipitation fouling) occurs when ever process condition lead to creation of super-saturation with respect to one or more of the sparingly soluble salts, which is the most important factor determining the intensity of scaling [3].

Super- saturation condition is achieved when a solution is concentrated beyond the solubility limits of one or more of its constituents by evaporation. Super-saturation condition can also be achieved by change in temperature.

Most of the frequently encountered scaling salts  $\text{CaCO}_3$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{CaSO}_4$ , and  $\text{Ca}_3(\text{PO}_4)_2$ - exhibits inverse solubility characteristics, i.e., solubility decrease with increasing temperature. The dependence of salt solubility on temperature or presence of evaporation will often be the deriving force for scaling. The important distinction is between salts with normal or retrograde dependence of solubility on temperature. The salts with natural solubility increase their solubility with increasing temperature and thus will foul the cooling surfaces. The salts with inverse solubility will foul the heating surface. [4] Super-saturation solution is at unstable equilibrium and relieves its super-saturation by precipitating of solid phase. Attainment of super-saturation alone is not sufficient for a system to be precipitated. At relatively moderate super-saturation, the solution can remain stable without precipitation for a certain time, which is termed the delay or induction period. Only at sufficient high super-saturation level, the induction period is virtually absent

and precipitation will be instantaneous. The induction period phenomenon is of utmost particular importance in scale control efforts. The widely used technique discussed below, of scale control by dosage of anti-scaling, is based on the increase of induction period induced by the presence of the anti-scaling. [5, 13]

Once the initial scale layer is formed, subsequent deposition is facilitating. Growth of crystal layer on a flow surface involves several consecutive processes:

- Diffusional transport of the crystal – forming ions towards the crystallizing layer;
- Incorporation of the ions on growth sites of the crystal lattice;
- Adhesion and removal processes.

Scale build up on heat transfer surfaces causes ongoing expense to the owner and an increase in thermal impedance and thus decreases the rate of heat transfer through the surface. This contributes to an overall loss of efficiency of the system.

It would be very desirable to be able to quickly remove scale deposits from metal surface under safe conditions without the use of strong acid. It would also be desirable to be able to remove scale deposits from metal surfaces without the risk of perforating the metal wall of the system. Further, it would be desirable to be able to remove scale from metal surfaces while leaving a stable protective coating. [6]

The removal of scale and iron oxide deposits is necessary to prevent corrosion beneath the scale area since corrosion control agents are unable to effectively contact the metal surface. If the deposits are not removed, under deposits corrosion can penetrate through the metal, breaching the containment. Once this occurs, fluid starts leaking from system and system must be taken off line and this portion

of the system must be repaired or replaced. Thus, clean scale –free heat transfer surface represent a desirable condition in cooling water system. [7]

The main scale control strategies are:

- removal or reduction of scale forming species;
- inhibition of deposition by dosage of anti-scalant;
- Controlled scale deposition with periodic cleaning schedules.

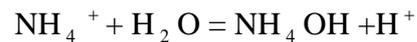
A number of approaches have been attempted to create an effective scale cleaner. Cleaning can be done either mechanically or with the use of chemicals. Mechanical cleaning obviously takes a great deal of down time and dose not always gets all scale out. The most widely used chemical technique for scale control is by dosage of anti-scaling. This technique is cost effective because in many cases scaling can be suppressed with only few ppm of anti-scaling, typically less than 10 ppm. The system is simple in that, it may be controlled by adding the product directly from the container to cooling water and the system is capable of maintaining a reasonable amount of control over scale.[8]

The inhibition mechanisms is done by the adsorption of the inhibitor on the crystallization surface acts to delay nucleation , reduce the precipitation rate, and distorts the crystal structure such that the deposit tenacity to the flow surface is weakened.

Commonly used anti-scaling are derived from three chemical families: condensed poly phosphate, organo phosphates, and poly phosphates. Numerous studies have shown that all inhibitor polymers are effective only within a relatively narrow range of molecular weights, typically around (1000-5000 Da). It is presumed that the size of the inhibiting molecule should be sufficiently large so that when adsorbed on the scaling ,it occupies a sufficient area for exerting its effect,

but it should not be so large that it lacks sufficient mobility and that its adsorption rate is too slow. A low molecular weight fraction of a given inhibitor is adsorbed on the scaling species more rapidly than a high molecular weight fraction, but the adsorbed quantity is larger with the high molecular weight fraction. [9]

Some researchers found that the combination of 15 ppm of maleic acid and 6 ppm of phosphorus acid and 20 ppm of hydrogen peroxide gave consistently high level of inhibition [11]. It has been suggested by other researches to use weak base (ammonium) and strong acid (hydrochloric, sulfuric) salts instead of using acids alone. The salts hydrolyze and safely acidify the environment. [1]



However these anti-scaling are expensive and sometimes will result in environmental problems.

There is ample evidence in the literature that small amount of metal impurities, such as Fe, Mg, Cu, and Zn which are commonly encountered in water ,can affect the nucleation and crystallization rate of precipitation  $\text{CaCO}_3$ . Coetzee et al. reporte that  $\text{Cu}^{+2}$  was found to be only half as effective as  $\text{Zn}^{+2}$ , while  $\text{Mg}^{+2}$  required concentration levels 1000 times larger to produce comparable effects [11]. Pernot et al. indicated that  $\text{Fe}^{+2}$  was quarter as effect as  $\text{Zn}^{+2}$  for  $\text{CaCO}_3$  scale inhibition [12]. Also Yang founds that 2 to 5 mg/L of zinc ions is very effective in membrane permeability in reverse osmosis. But the full potential of  $\text{Zn}^{+2}$  for scale suppression has been very scantily explored so far [15].

This paper presents an investigation the addition of  $\text{ZnCl}_2$  and  $\text{ZnI}_2$  at

different concentration (1,2,3,and 4 ppm) to scale precipitation on AISI 304 and 316 stainless steel ( because of their wide use and important application ) in cooling tower and air cooler system for two weeks of working for each and the results were compared to the optimum condition of that of ammonium sulfate (50 ppm) [1], and to the optimum composition of (15+6+20) ppm of maleic acid and phosphorous acid and hydrogen peroxide respectively at the same conditions[9].

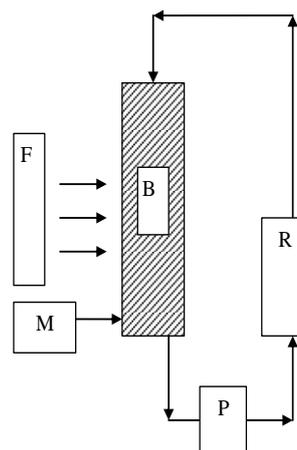
### Experimental Work

Models of air cooler system and cooling tower system have been built up in laboratory and it make as possible to perform a simulation of processes that runs industrially. Figures (1) and (2) presents diagrams of the models.

The air cooler system consists of hot air supply (which consists of fan blow air through the heating coil to the air cooler windows). The hot air suppliers used to pour out hot air at 45°C through sheets of wetted metal samples (AISI 304 and 316) that are fixed in air cooler windows. Water pump has been used to circulate the water at about 30°C from air cooler box up to the windows through down the metal samples. The flow of the circulating water has been controlled by rotameter and fixed at 160 L/hr.

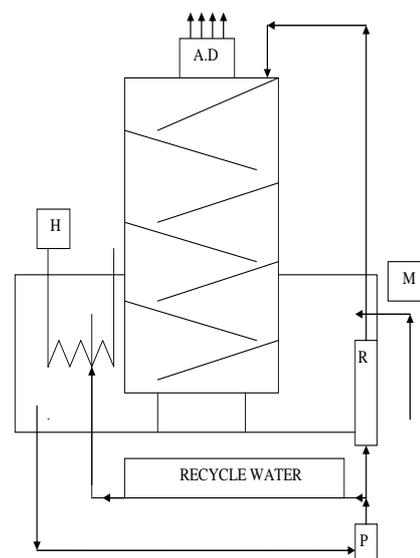
The cooling water system consist of tower contained within a basin which contains 40L of water, the tower contained a series of slats positioned in a way to provide uniform cascade flow of water and water distributor position at the top of the tower, the system has a water pump used to circulate the water from the basin to the tower, the flow of water was controlled at 160 L/hr using rotameter. The temperature of the water to the tower was at 45°C and it was controlled using thermostat and

thermocouple and leaves the tower at 38°C. Air was draw out of tower at 35°C using air draft fan positioned at the top of the tower which is with drawn air from the bottom of the tower through holes in the bottom at about 25°C. The metal samples were positioned on the slates of the tower.



R water rotameter                      M make up water  
 F hot air fan                            B air cooler box  
 P water pump

Fig. 1, Schematic diagram for air cooler system



M make up water                            P Pump  
 R rotameter                                H Heater  
 A.D air draft fan

Fig. 2, Laboratory cooling tower system

The samples used in both systems were stainless steel 304 and 316; the compositions for both of them are shown in table (2). The metal samples were of 20x10x2 mm size. The samples were progressively wet polished to grit silicon carbide paper, after polishing, the samples were washed with distilled water and degreased with acetone and weighed. The samples then positioned in each system for two weeks for each run. After the test, they were mildly rinsed with distilled water and acetone and weighted.

The first run of the two systems was un-inhibited runs. The other runs in each system receive a one per week dosage of zinc chloride and zinc iodide in several concentrations (1ppm, 2ppm, 3ppm, and 4ppm) for each compound. Also two other experiments were made ,one using ammonium sulfate (50ppm) [12], and the other by using 1.5 gm/L of mixture of inhibition solution consist of (15ppm maleic acid, 6ppm phosphorous acid, and 20ppm hydrogen peroxide) [9].

Table 2, Composition of AISI 304 and 316 Stainless steel

AISI	Cr	Ni	C	Mn	Si	P	S	N	Mo
304	18.6	9.4	0.08	1.9	0.73	0.045	0.028	0.09	
316	17.2	11.5	0.08	2	0.75	0.045	0.3	0.1	2.4

### Result and Discussion

In this study the efficiency of the inhibitors used have been calculated, according to the equation

$$\text{Inhibition eff. \%} = 1 - \Delta W_{in} / \Delta W_{unin}$$

Where

$\Delta W_{in}$  Is the weight change of metal samples in the inhibited solution.

$\Delta W_{unin}$  is the weight change of metal samples in uninhibited solution.

In cooling tower system , figures 3 and 4, zinc chloride was more effective than zinc iodide on the AISI 316 than 304 ,with stability in all concentration (316 is more stable to the environment effect than 304 because of its structure) and we get the better inhibition efficiency (95%) at 2-3 ppm of zinc chloride with AISI 316. AISI 304 shows decrease in inhibition efficiency after increasing the concentration beyond 2 ppm (this may be imputing to the increase of acidity and less stability of 304 comparing to that of 316).

Zinc iodide shows the same behavior as zinc chloride with both SS 403 and 316, but with less inhibition efficiency. We get maximum inhibition at 2 ppm (83%) for both metal samples, but with 316, increasing the concentration beyond 2 ppm gave us the same efficiency to that of 1 ppm (79%).

In the air cooler system zinc chloride gives the same efficiency as increasing the concentration increased beyond 2 ppm and it was the same for both AISI 304 and 316 (about 70%). Inhibition activity of zinc iodide slightly decrease after increasing the concentration beyond 2 ppm , the maximum was at 2ppm and it was 67% for 316 (figure 6) and 60% for 304 (figure 5) .

In air cooler system the efficiency was less than that in cooling tower at the same concentration for both compounds ,this my be attributed to the hot air effect on drying the metal samples.

In both metal samples and in both systems zinc chloride was more effective than zinc iodide, this attributed that the aqueous solution of

zinc chloride are acidic, and the acids works as scale removal. The acidity aqueous zinc chloride solution relative to solution of other zinc ions salts is due to the formation of tetrahedral chloro aqua complexes, where the reduction of in coordination number from 6 to 4 further reduces the strength of O-H bonds in the solvent water molecules. [16]

Metal ions present in water can acts as the deriving force. Zinc compound influence the reaction in two ways, the first being in the solution were they can form complexes with the reaction ions altering both activity coefficient and the rate out which transformation reaction occur. Secondly, zinc ions can be adsorbed on to the surface of the reaction solids, adsorption of these foreign ions is preferred at high energy sites that are also favored for

dissolution and crystal growth. The inhibition of calcite growth can cause the formation of aragonite, it is believed that this is how existing carbonate scale in a system is removed.

When using ammonium sulfate at concentration of 50 ppm, the inhibition efficiency was 93% for both metal samples in cooling tower system while zinc compounds shows 95%. In air cooler system the efficiency was 70%.

The composition of (15ppm maleic acid and 6ppm phosphorous acid and 20ppm hydrogen peroxide) shows very high efficiency, it was about 98% for AISI 316 and 95% for AISI 304 in cooling tower system, and 82% for AISI 316 and 80% for AISI 304 in air cooler system.

Both of the last inhibitors have environmental problem and corrosive action on the metals.

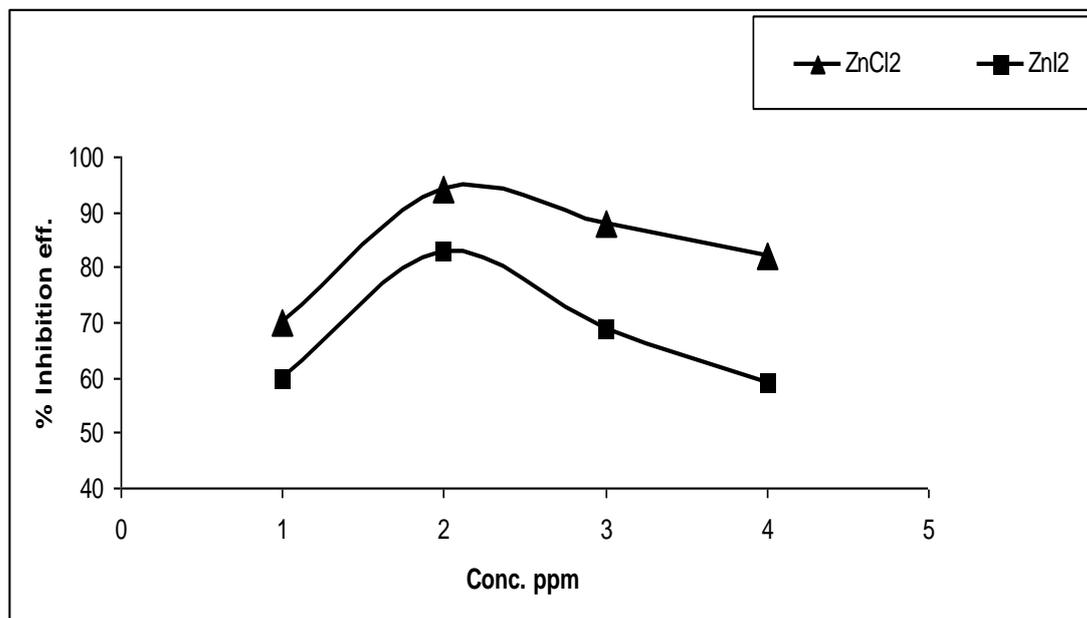


Fig. 3, Effect of concentration of  $ZnCl_2$  and  $ZnI_2$  on 304 SS in cooling tower system for two weeks operation

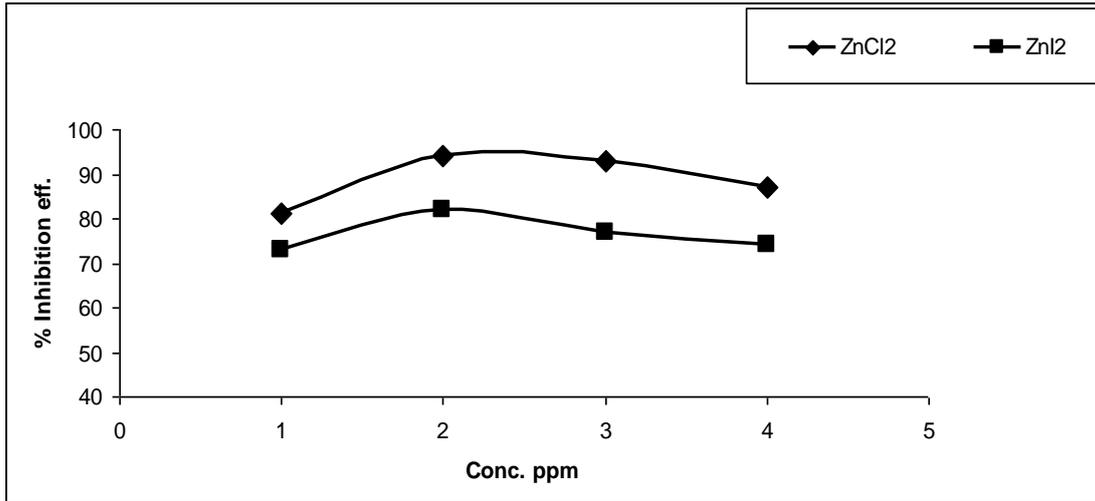


Fig. 4, Effect of different concentration of ZnCl<sub>2</sub> and ZnI<sub>2</sub> on 316 SS in cooling tower system for two weeks operation

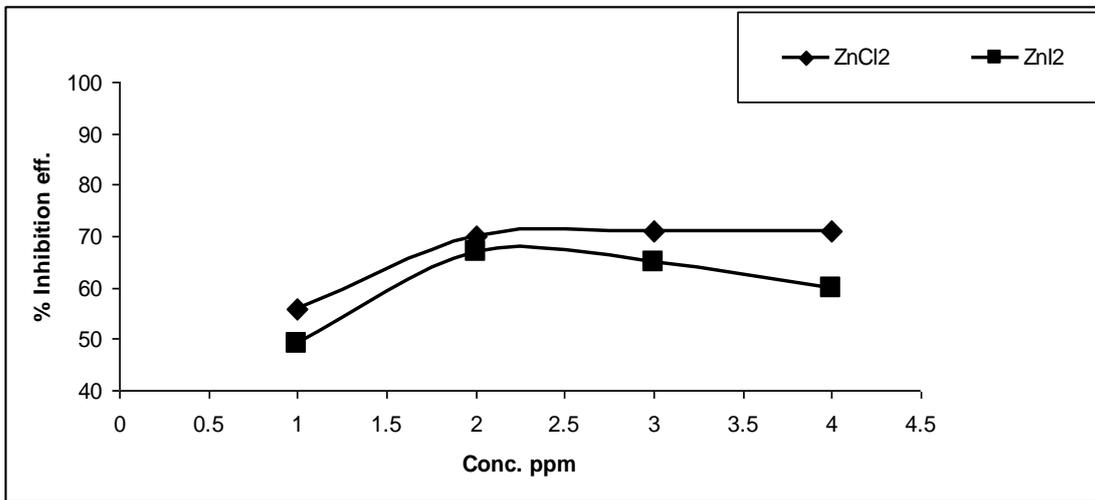


Fig. 5, Effect of concentration of ZnCl<sub>2</sub> and ZnI<sub>2</sub> on 304 SS in air cooler system for two weeks operation

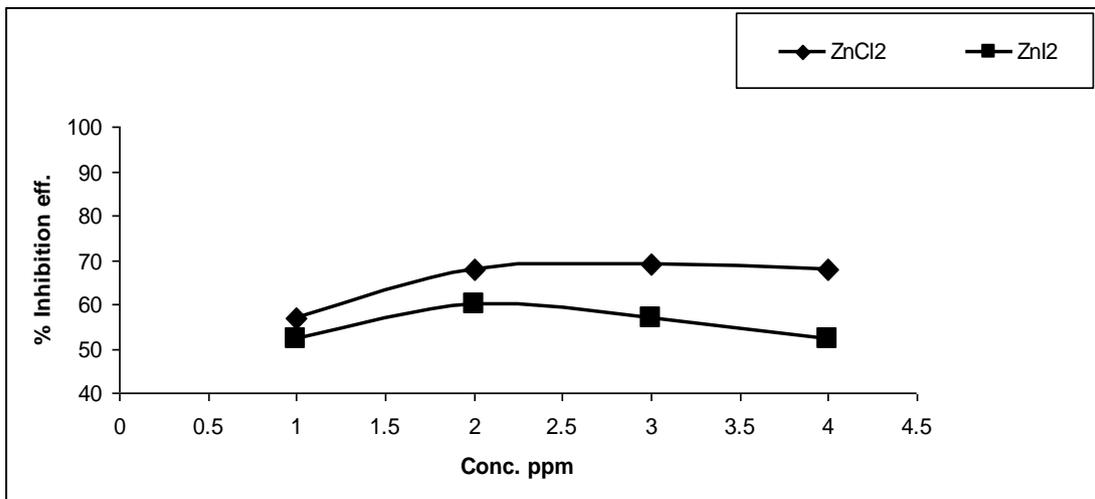


Fig. 6, Effect of concentration of ZnCl<sub>2</sub> and ZnI<sub>2</sub> on 316 SS in air cooler system for two weeks operation

## Conclusion

- 1- Zinc chloride was more effective than zinc iodide in all situations; this was attributed to the acidity of zinc chloride aqueous solution.
- 2- Zinc compounds were more effective on AISI 316 than 304.
- 3- Zinc compounds were more efficient in cooling tower system than in air cooler system, this can be imputing to the hot air effect in air cooler system.
- 4- Preferring of usage zinc salts instead of ammonium sulfate and (15ppm maleic acid and 6ppm phosphorous acid and 20ppm hydrogen peroxide) because of the latest environmental problem and corrosion action.

## References

- 1- Szymura, Teresa, Physicochemical problem of mineral processing, 40, 99-108, (2006).
- 2- Cho, Y.I., Liu, R., W.I., Mcfarland, and Fusegni," Study of scale removal method in double-pipe heat exchangers ", Heat Transfer Engineering, 21, 50-57, (2000).
- 3- Hasson, D., Dark, A., Semiat, R., Desalination 2003, 157,193-207.
- 4- Hong, Lu. "Composite fouling of heat exchanger surface ", Nova science books. N.Y. (2007)
- 5- Mulline, J.W., Crystallization, 3<sup>rd</sup>.ed; Butterworth Heinemann; Oxford, (1997).
- 6- Backer, J.S., Jadd, S.J.," Magnetic amelioration of scale formation ", Water Resources, 30,247-260, (1996).
- 7- Frayne, Colin, "cooling water treatment", Chemical Publishing Co.,Inc.,NewYork,NY, (1999).
- 8- Donaldson, J.D., Grimes, S. "Lifting the scale from our pipes", New Scientist, 117, 20-24, (1988).
- 9- Hsson, D., In understanding heat exchanger fouling and its mitigation; Bott, T.R. Ed.; Begell House: New York, (1999).
- 10- Shyu, L.L., United state patents, 5292449, Mar.8, (1994).
- 11- Coetzee, P.P., Yacoby, M., Howell, S., Mubenga, S., "Scale reduction and scale modification effecting induced by Zn and other metal species in physical water treatment", Water SA, 24(1), 77-84, (1998).
- 12- Pernot, B., Euvarard, M., Remy, F., Simon, P., "Influence of Zn (II) on the crystallization of calcium carbonate application to scaling mechanisms", J.Water Serv. Res. Tech. Aqua. , 48(1), 16-23, (1999).
- 13- Ascolese, C.R., Bain, D.J., "Take advantage of effective cooling water-treatment programs", Chemical engineering progress, 3, 49-54, (1998).
- 14- Loraine, A., Huchler, P.E.,"Non-chemical treatment systems: histories, principles and literature review". International Water Conference, 22 oct. (2002).
- 15- Yang, Q., "Inhibition formation of CaCo<sub>3</sub> scaling in reverse osmosis system by Zinc ions", Chinese J. Chem. Eng., 14(2)178-183, (2006).
- 16- Brown, D.I.," The chemical bonds in inorganic chemistry, the bond valance mode", oxford science publications, 2001.