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Assessment the potential of scale formation and the corrosivity of Al - Najebia thermal power plant cooling system water

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Abstract

The aim of this research is to study the potential of scale formation and corrosivity of the water using in Al-Najebia power station cooling system in Basrah province, south Iraq.

water indices such as langelier saturation index, Ryznar stability index, Pukuriuos scaling index and Larson ratio have been used for predicting the corrosive, scale forming .

The study is based on the obtained corrosion and scale data for the period from Jan.2012 to Dec. 2012 , samples were collected from Al-Najebia Power Station cooling system water , the analytical results were used to calculate the indices, because of seasonal flucations in water characteristics, sampling was performed twice monthly.

The quantitative analytical methods were employed. All indices were calculated the mean values of langelier saturation index (-0.3317), Ryznar stability index mean value was (7.7833), Puckurius scaling index mean value was (6.216) while the mean value of Larson Ratio was (29.59) and preliminary results confirmed that the studied water has a tendency to corrosion and scale formation, also the results revealed that the indices were correlated with measured metal ions.

Introduction

Water has many different uses in thermal electricity generation plants and its value can be very high. Power stations need access to secure and reliable water supplies so that they can provide secure energy to supply electricity to consumer and meet requirement for system reliability. Energy security is therefore depend on the availability of secure water supplies to power station[1]. The major use for water in thermal power station is for cooling, there are different cooling water systems technologies that employed in thermal power station [2]. In Najebia thermal power station once through cooling system employed. Once through cooling system is the most economic form of cooling system in the places where water is sufficiently available.

According to this principle, surface water is extracted from the sea, river, lake or canal, pumped to the turbine condensers (main cooling surcit) and to the coolers of the auxiliary circuit, and subsequently transported back to its origin [3].

Water is an excellent transporter of heat and quite inexpensive but in the same time it is an excellent polar solvent, which will dissolve about all known materials. Given this fact, the chemistry of all cooling system programs must be dealing with corrosion [4].

The term corrosion (in cooling water system) is defined as the electrochemical deterioration of a metal that is in contact with cooling water .Corrosion occurs when an electric current flows from one part of the thermal (anode) through the water (electrolyte) to another part of metal (cathode), corrosion takes at the anode only. The cathode is the driving force of corrosion action, as shown in the equation:

Metal→ Metal cat ion +electron

$M \rightarrow M^{+} + e^{-}$

This process degrades the metal ,reduces its strength, thickness and in some extreme cases , creates pits and then holes in the material .

At some point in the corrosion process, the metal can no longer do its job as a system component[5].Corrosion in general and pitting corrosion, in particular, must be guarded against in order to ensure the long term integrity of cooling system. The deposits that occur in cooling water systems are usually divided into two categories scale and fouling. The presence of either type of deposit in the heat reducing the efficiency of operation, deposit can also promote under-deposit corrosion[6].

Scale is formed from minerals formerly dissolved in water, that were deposited from the water in to heat transfer surface or in-flow water lines. As water is evaporated in a cooling pipes , the concentration of dissolved solids becomes greater until the solubility of a particular scale-causing mineral salt is exceeded. When this situation occurs in an untreated cooling water system, the scale will form on any surface in contact with the water , especially on heat transfer surface. The most common scaling minerals are calcium carbonate ($CaCO_3$),calcium phosphate $Ca_3(PO_4)_2$,Calcium sulfate ($CaSO_4$) and silica , usually in that order, formation of magnesium silicate scale is also possible under certain conditions[7,8]. Water can exhibit a tendency to either dissolve or deposit certan minerals in pipes , plumping and appliance surface , this tendency is known as stability. Water that tends to dissolve minerals is considered corrosive, while water that tends to deposit minerals is considered scaling[9].The most common methods used for calculating the stability of water are Langelier saturation index (LSI), Ryznar stability index (RSI), Puckurius scaling index (PSI) and Larson ratio (LnR)[10],so the main object of the present study is to assess cooling water tendency to corrosion or scale .

Materials and Methods

Water sample were collected in plastic bottles from Al-Najebia cooling system water showed in Fig 1 ,located at Basrah governorate during 2012 as shown in fig 1.

Fourteen parameters have been analyzed ,there are :

Electrical conductivity (EC), bicarbonate (HCO_3^-), total hardness (TH), Calcium (Ca^{+2}), Magnesium (Mg^{+2}), Chloride (Cl^-), Sulphate (SO_4^{-2}), total dissolved solid (TDS), M.Alk., Temperature (T),Chrome (Cr), Zinc (Zn),Iron (Fe), pH,Cupper (Cu) ,Silica (SiO_2) . Electrical conductivity and temperature and total dissolved solid was measured at sampling sites by using Horiba model W-2030 MFG. NO.812003 .Other parameters were analyzed at laboratory like bicarbonate, total hardness, Calcium, Magnesium, Chloride, M.alkalinity, according to [11]. Silica was determined colorimetrically by PU 8670 spectrophotometer at 810 nm according to [12], while metal ions like (Fe,Cu, Cr, Zn) were measured by flame atomic absorption spectrophotometer according to [11].Values of pHs(p[illegible]m saturation condition), LSI(Langlier saturation Index), RSI(Ryznar Stability Index), PSI(Pockurius Scaling Index) and LnR(Larson Ratio), calculated twice at month during 12 months. For determining the LSI and RSI, first must be determine the measures of pH and pHs. The value of pH and pHs are obtained by equation 1:

pHs= {(9.3+A+B)-(C+D)} -------- (1)

A= TDS (mg/l), B= Temperature °C, C= Calcium Hardness (mg/l $CaCO_3$), D= Alkalinity (mg/l $CaCO_3$) [13]. After calculating the pH and pHs, the value of LSI and RSI obtain by using of equations 2 and 3, respectively.

LI=pH-pHs ------------ (2)

RI=2pHs-Ph----------- (3)

pH: actual pH of water, pHs: pH of water at Carbonate Calcium saturation condition, LSI: Langlier saturation Index, RSI: Ryznar Stability Index[14].

Values of Pockurius Scaling Index are obtained by equation 4 and 5:

PSI=2pHs-pHeq ------------(4)

pHeq= pH of water at equilibrium condition

pHeq= 1.465+ log (T.ALK) + 4.54 ---------- (5)

T.ALK= Total alkalinity,

PSI: Pockurius Scaling Index [15]

Values of Larson Ratio are computed by using equation 6:

$$LnR = \frac{[Cl^-] + 2.[SO_4^{2-}]}{[HCO_3^-]} \quad \text{----(6)}$$

$[Cl^-]$ = Concentration of chloride ions in [mg/l],

$[SO_4^{-2}]$ = Concentration of sulfate ions in [mg/l],

$[HCO_3^-]$ = Concentration of the bicarbonate ions in [mg/l],

LnR = Larson Ratio [16].

The collected data were analyzed by use of packagesof SPSS16.0 and Microsoft Excel software for determining the corrosion and scaling indexes.

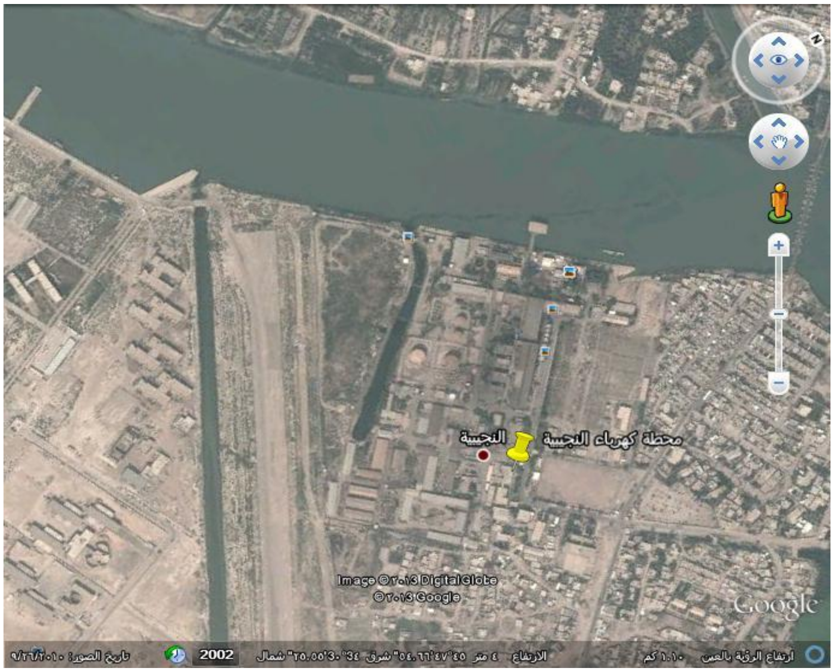


Fig 1:Najebia Power Plant in Basrah

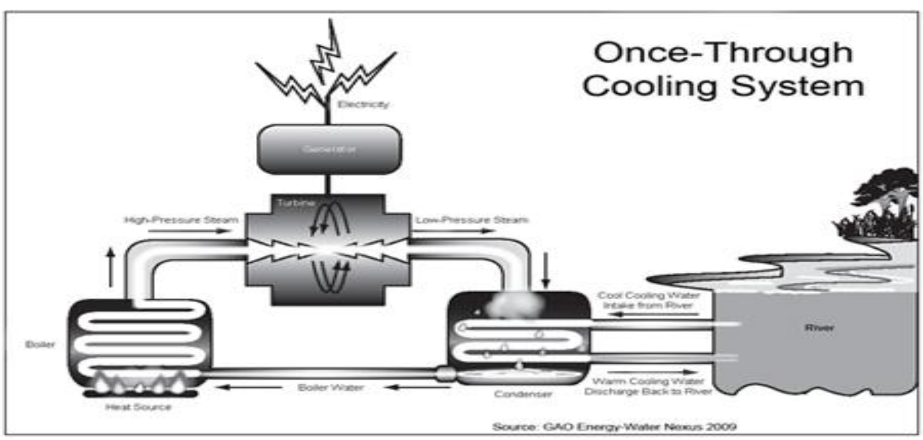


Fig 2: Cooling System in Najebia power plant (once-through cooling system)

Result and Discussion

For determining the water corrosion and scaling potential of Najebia power water station cooling system water, water quality parameters include, temperature, pH, total alkalinity, total hardness, Calcium ion concentration, Magnesium ion concentration, sulphate have been measured. The maximum, minimum, mean and standard deviation values of these parameters are shown in table (1).

Table 1: The maximum, minimum, mean and standard deviation of measured parameters.

Parameter	Unit	Max.	Min.	Mean	Standard deviations
T	c°	30.4	15.8	23.575	5.3115
pH		7.5	6.1	7.020	0.4391
TDS	ppm	3822	953	2194	837.3
TH	ppm	1225	530	816.666	151.0565
EC	µS\cm	5468	1850	3253	0.4391
Ca^{+2} as $CaCO_3$	ppm	650	300	478.1667	100.5856
Mg^{+2}as $CaCO_3$	ppm	575	237	363.5	68.55622
Cl^-	ppm	960	313	545.3333	139.2513
SO_4^{2-}	ppm	689	211	490.4542	113.4337
M.alk.as $CaCO_3$	ppm	90	37	68.60417	19.33551
Bicarbonate as $CaCO_3$	ppm	85	30	61.5	15.201
Dissolved Oxy.	ppm	6.8	5.7	6.25	0.488
SiO_2	ppm	8.5	5	6.966	1.1284
Total Iron as Fe	ppm	0.06	0.03	0.045	0.0081
Cu^{+2} ion	ppm	1.1	0.05	0.385	0.3225
Zn^{+2} ion	ppm	0.3	0.02	0.095	0.0819
Cr^{+3} ion	ppm	0.3	0.02	0.0955	0.0819

Then the corrosion and scaling indices (Langelier saturation index(LSI)),Ryznar stability index (RSI),Puckurius scaling index (PSI) and Larson Ratio were calculated each month for the period Jan.2012 to Dec.2012 by using the above equations. Table 2 illustrates the values of the calculated indices, figures 3,4,5,6 clarify the Indices Vs month

Table(2): The Maximum, Minimum, Mean and standard deviation of the calculated indices.

Index	**Max.**	**Min.**	**Mean**	**St.dev.**
Langelier Saturation Index (LSI)	-0.021	-0.96	-0.33	0.24
Ryznar stability index (RSI)	8.90	6.80	7.78	0.58
Puckurius Scaling Index (PSI)	7.22	4.49	6.21	0.83
Larson Ratio Index (LnR)	78.96	16.48	29.59	17.71

Corrosion and scaling may cause pipe blocking. As a result may reduce the flow and create some other problems in the pipelines .It can also damage the pipeline if it occurs, water leakage increases and so water loss will be high)[17] .By calculation of corrosion indices langlier saturation index (LSI) and Ryznar stability index (RSI) which are being used more than other corrosion indices [18] ,LSI values were negative and ranged from (-0.012) (slightly corrosive but non scale forming) to (-1.4)(Serious corrosion). RSI value ranged from 6.8 (heavy corrosion) to 8.9 (corrosion trouble) , the values indicate corrosion conditions[19].

The scaling index (PSI) values ranged from (4.49 to 7.2). Result show that water cooling system in Najebia power station had a potential to form scale. Water scaling can reduce the internal diameter of the water pipes so that the pipe will not transfer the expected capacity of water, therefor it is necessary to repair or replace the water distribution facilities that need high economic costs[19].

Larson Ratio is a new index, which is used in many parts of the world for determining the water corrosion potential. This index is based on measures of chloride and sulphate concentrations. It used for determined the corrosion potential of metallic pipes, LNR values indicates that the N.P.S.cooling system water had a sever corrosion potential [20].

Table (3) will illustrate the condition of Najibia power station cooling system water in view of scaling and corrosion indices **.**

Table (3) :The condition of Najibia power station cooling system water in view of scaling and corrosion indices

Month	**Langlier saturation index(LSI)**	**Ryznar stability index(RSI)**	**Pockarius scaling index (PSI)**	**Larson skold scaling index(LnR)**
1	Serious corrosion	Water is very aggressive causes heavy corrosion	Scaling	Moderate corrosion potential
2	Serious corrosion	Water is very aggressive causes heavy corrosion	Scaling	Moderate corrosion potential
3	Slightly corrosive but non scale forming	Water is very aggressive causes heavy corrosion	Scaling	Moderate corrosion potential
4	Slightly corrosive but non scale forming	Water is very corrosive Corrosion significant	Scaling	Moderate corrosion potential

5	Slightly corrosive but non scale forming	Water is very aggressive causes heavy corrosion	Scaling	Moderate corrosion potential
6	Serious corrosion	Water is very aggressive causes heavy corrosion	Scaling	Moderate corrosion potential
7	Serious corrosion	Water is very aggressive causes heavy corrosion	corrosive	Moderate corrosion potential
8	Water is supersaturated with respect to calicium carbonate ($CaCO_3$) and scale forming may occur	Little scale and corrosive	corrosive	Moderate corrosion potential
9	Serious corrosion But not scale forming	Water is very aggressive causes heavy corrosion	Scaling	Moderate corrosion potential
10	Slightly corrosive But not scale forming	Water is very aggressive causes heavy corrosion	Scaling	Moderate corrosion potential
11	Slightly corrosive But not scale forming	Water is very aggressive causes heavy corrosion	Scaling	Moderate corrosion potential
12	Slightly corrosive But not scale forming	Water is very aggressive causes heavy corrosion	Scaling	Moderate corrosion potential

There are a number of water quality parameter that need to be considered in addition to calcium carbonate solubility.

The water quality parameters listed by Singly were calcium, magnesium, alkalinity, pH, chloride, sulphate, conductivity, total dissolved solid, silica and temperature [21].

In general, when pH points to acidic environment, the chance of corrosion increase and when pH points to alkaline environment, the chances for scale increase [22], the pH values of the samples ranged from 6.1 to 7.5, so they indicated to corrosive environment.

TDS and chloride found to be high, the mean values of TDS and Cl^- were (2194.5, 545.33) mg/L respectively, both TDS and chloride considered to be the most aggressive agents that promoting general and localized pitting corrosion in the pipes system [23].

Water samples in this study exhibit high concentration of Cl^- SO_4^{-2}, as the major anions and Ca^{+2}, Mg^{+2} as the major cations.

The increase in total dissolved solid including calcium salts (the presence of Ca^{+2} is 478.1 mg/L) would promote a scale formation through its combination with carbonate or sulphate [24]. water samples of the study also revealed that trace metals Fe, Cu, Zn, Cr were significantly high, high pH values enhanced precipitation and retard mobility of these metals if exist in nature [25].

Dissolved oxygen naturally present within its equilibrium concentration is considered very deleterious because if there is more dissolved oxygen, then there is more hydrogen ions, therefore the metal is more likely to corrode if it is exposed to more hydrogen ions and that lead to more electrochemical exchange, so the hydrogen ions will pass into the metal, and the metal will lose electrons to the solution [26].

In cooling system, silica deposit as a scale on heat transfer surface and may therefore be the limiting parameter in cooling water treatment program, the scaling potential of magnesium silicate increase as the PH rise above 8but magnesium silicate is generally not usually en countered in cooling system unless the pH is above 9 [27], in this study pH value is below 8 so the silica doesn't encountered.

Static analysis of the results carried out, it revealed that Langelier stability index (LSI) was highly correlated to iron concentration with several regression models $p>0.001$,sig=0.001 ,fig (6) shows the several regression models that proved the correlation between LSI with iron concentration.

The static analysis also indicated that langelier stability index was correlated with Cupper concentration $p> 0.05$, fig(7) shows the positive regression of LSI on the concentration of cupper while the index Larson Ratio (LnR) was strongly correlated to Cupper concentrations in positive regression $p> 0.001$,sig=0.000 , fig (8) shows the several regression models of LnR on the concentration of Cupper concentration and it's also correlated to chromium concentration fig (9) shows the regression l that revealed the correlation between LnR and Cr concentration $p> 0.05$.

Table (4) illustrates the R square, sig., regression model of the indices with the correlated metal ions.

Table (4) Illustrate the R square , sig , regression model of the indices with correlated metal ions.

Index	Metal ion that correlate with Inds.	Reg. model	R^2	Sig.
LSI	Fe	Logarthmic	0.996	0.000
LSI	Fe	Inverse	0.983	0.000
LSI	Fe	S	0.996	0.000
LSI	Fe	Growth	0.996	0.000
LSI	Fe	Logistic	0.996	0.000
LS	Cu	Cubic	0.730	0.012
LnR	Cu	Liner	0.528	0.007
LnR	Cu	Quadratic	0.576	0.021
LnR	Cu	Cubic	0.627	0.040
LnR	Cu	Growth	0.417	0.023
LnR	Cr	cubic	0.540	0.036

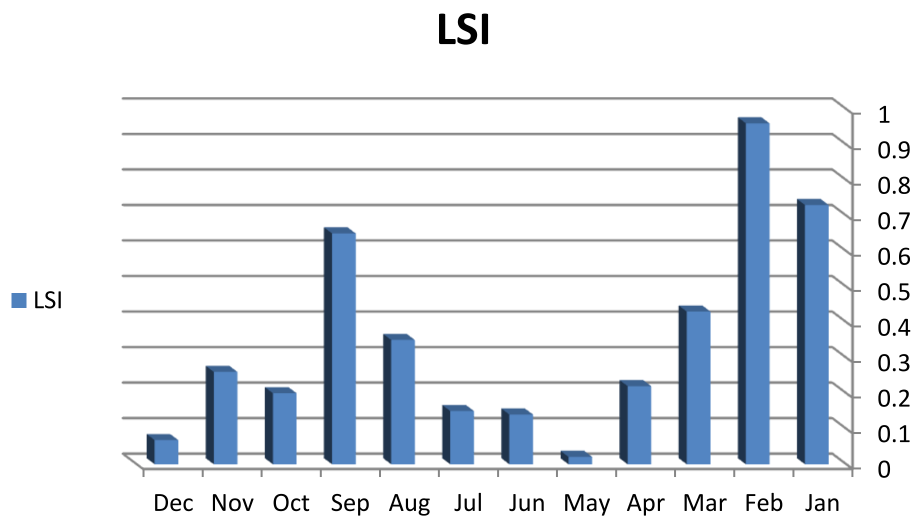


Fig 3: Values of Langlier saturation index vs. months

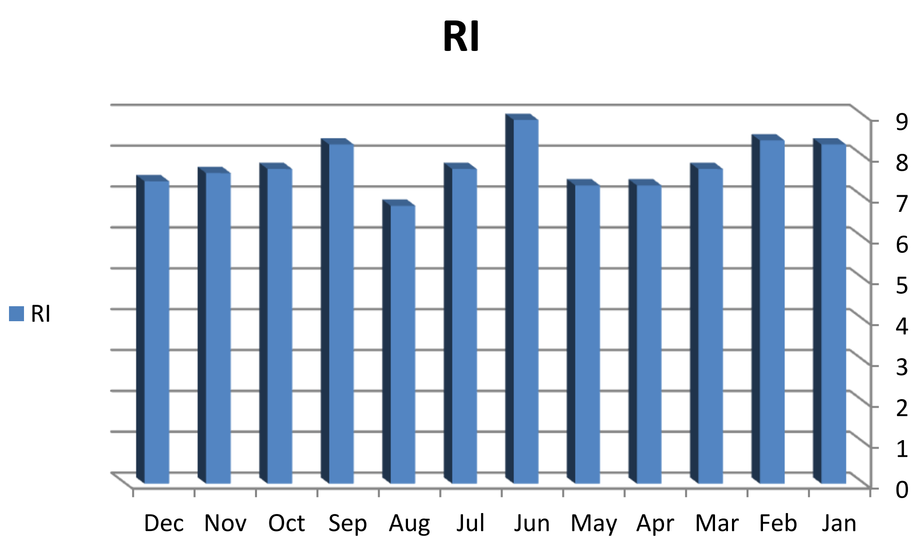


Fig 4: Values of Ryznar stability index vs months.

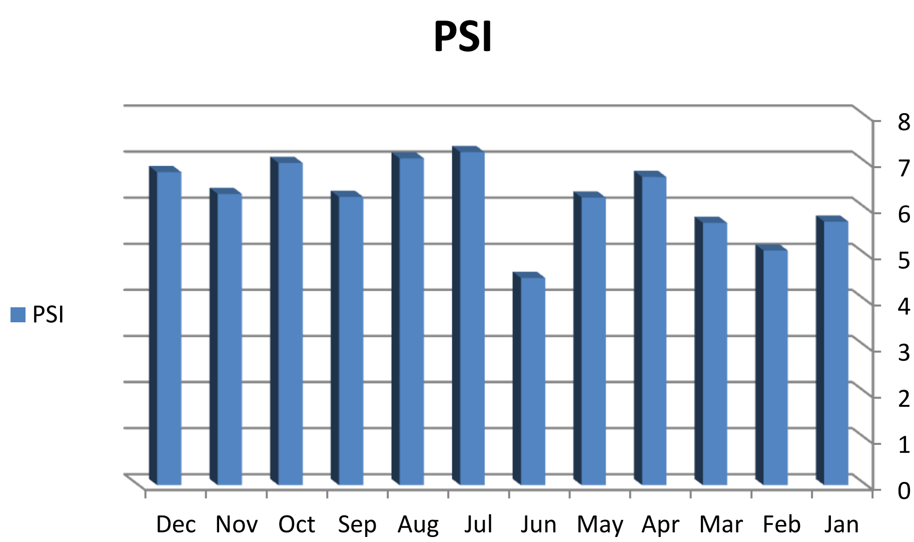


Fig 5: Values of puckarius scaling index vs. months.

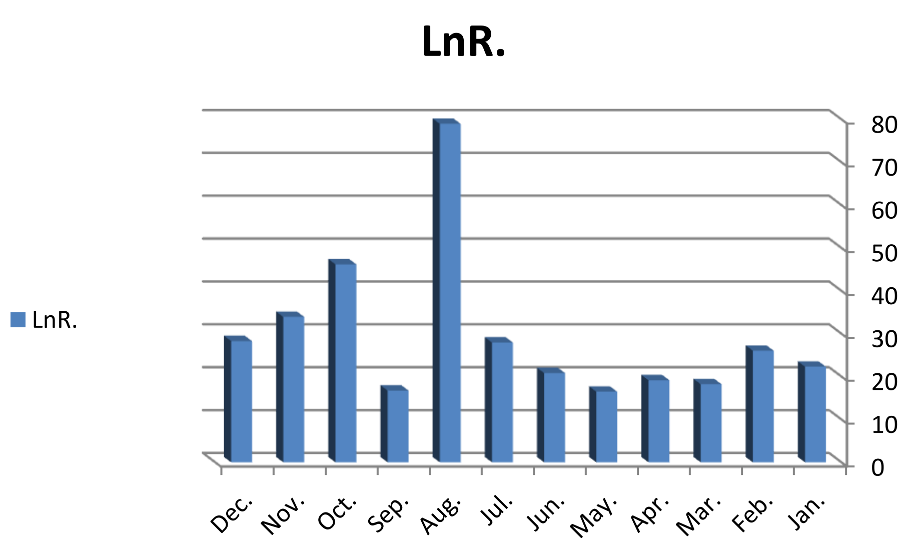


Fig 6: Values of Larson ratio index vs. months.

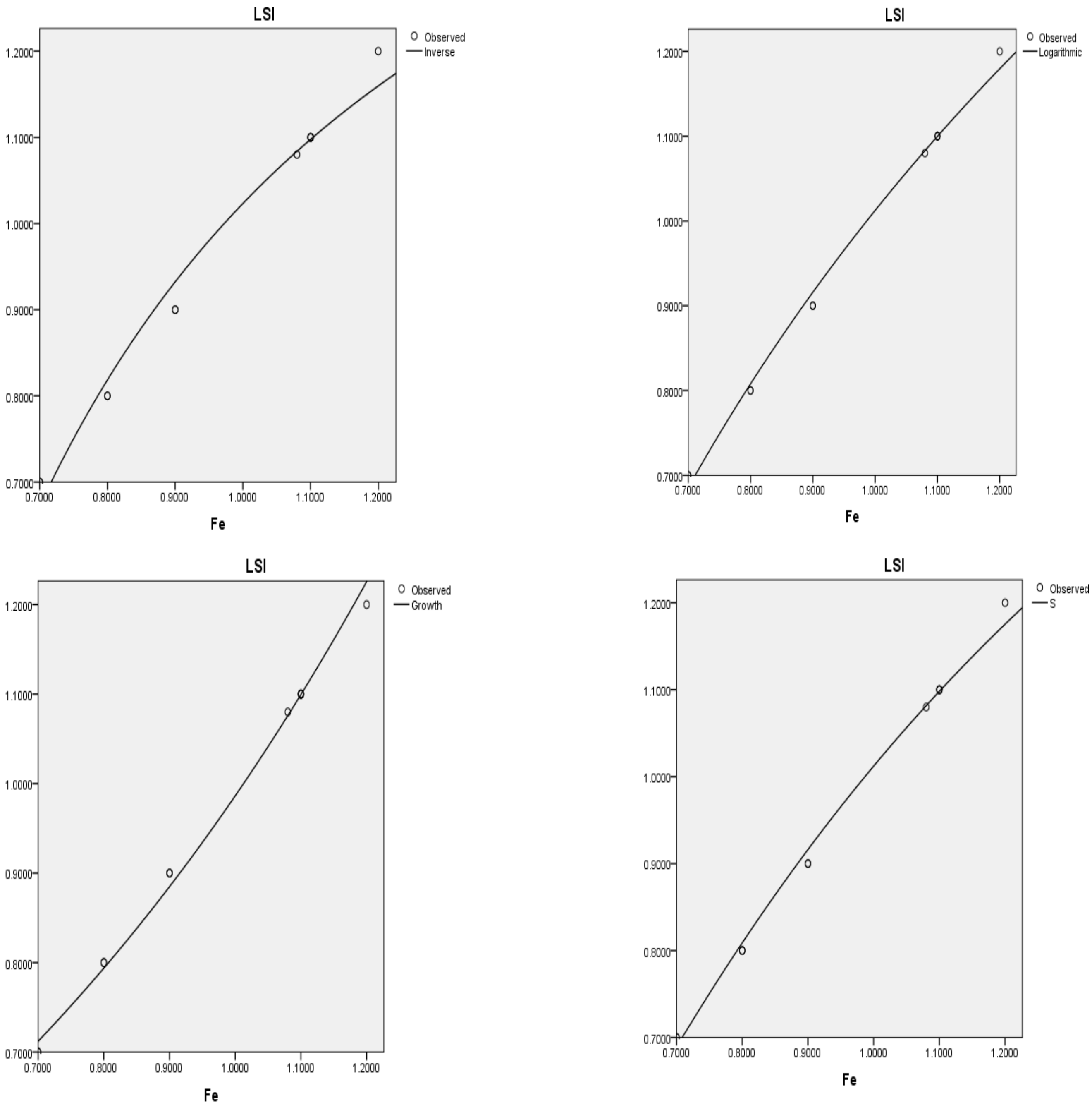


Fig (6): shows the several regression models that referred to the correlation 0f LSI with iron concentration.

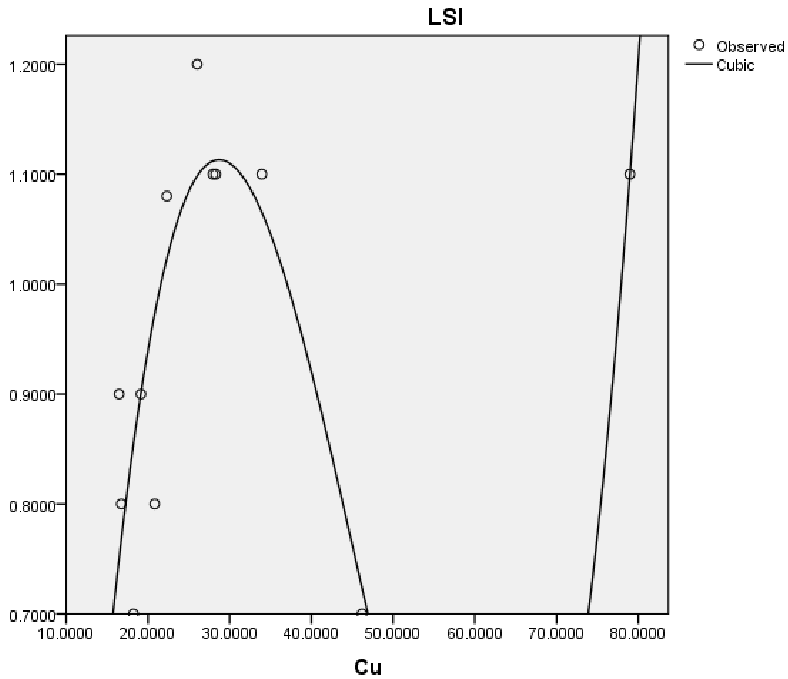
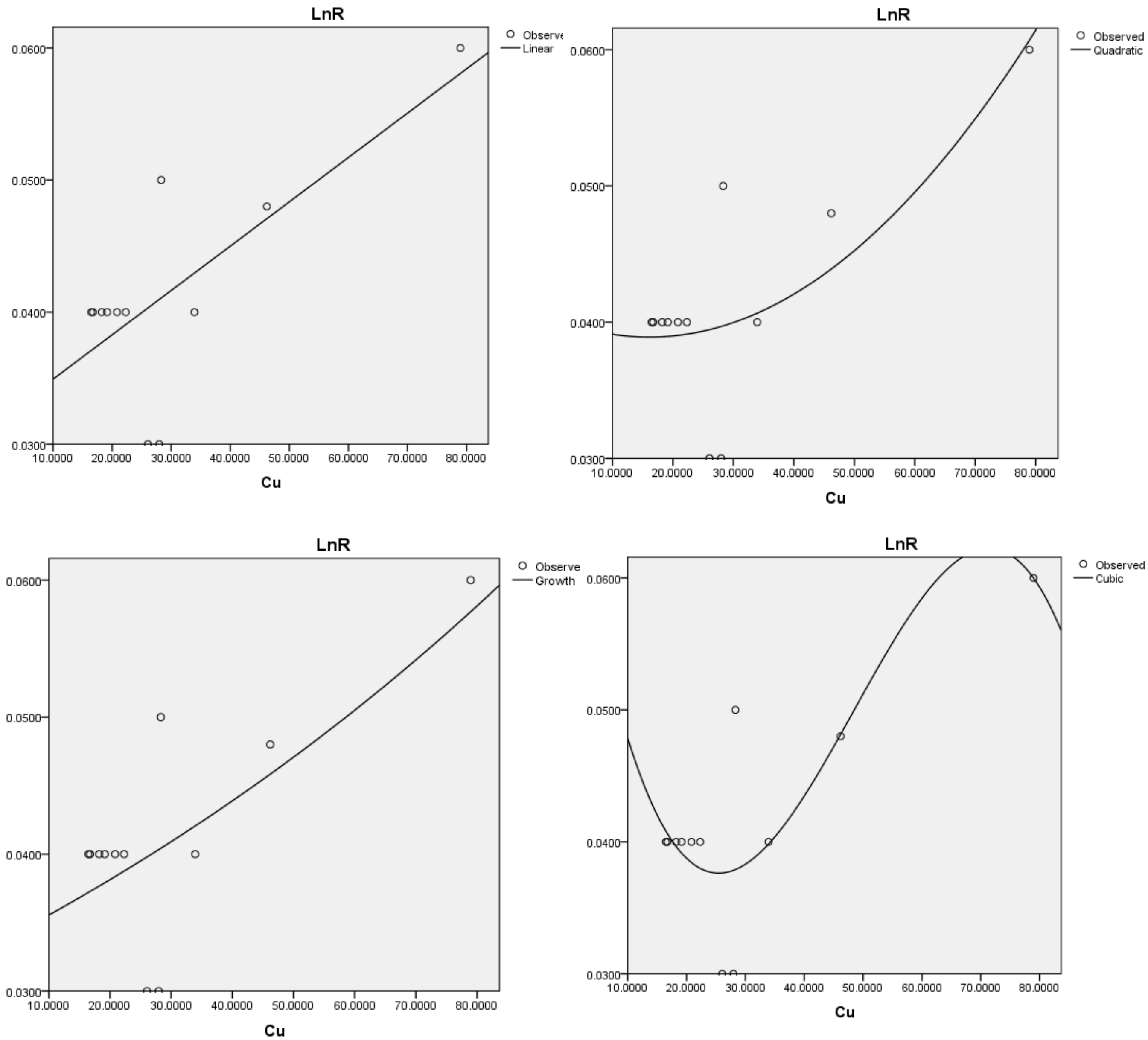


Fig (7) shows regression of LSI on the concentration of cupper



Fig(8): shows the several regression models that referred to the correlation of LnR with the concentration of Cupper concentration.

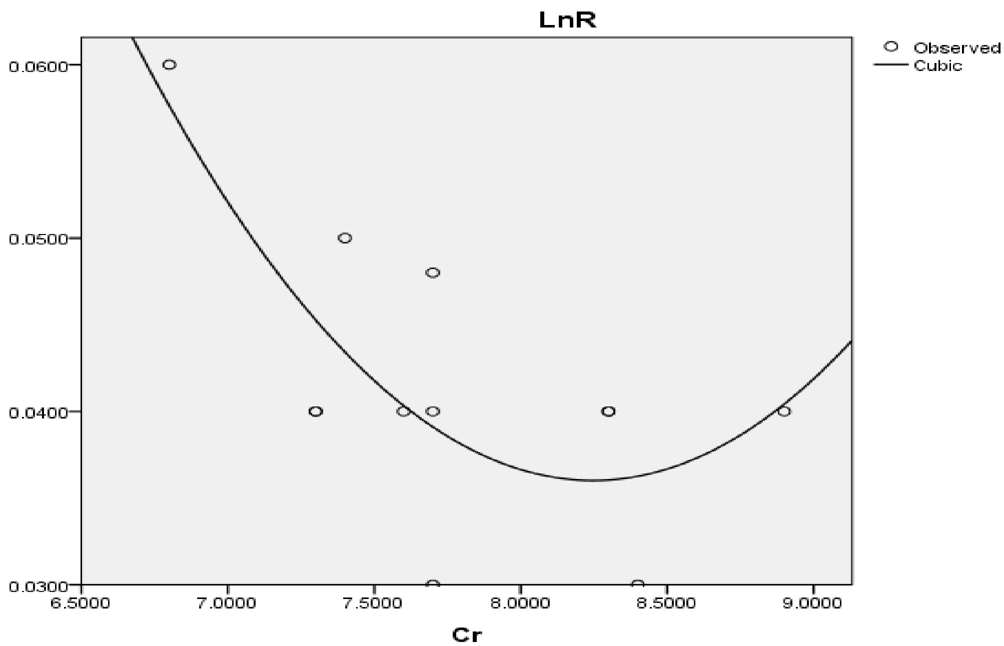


Fig (9): Shows the regression that revealed the correlation between LnR and Cr concentration

Conclusions

1- The calculated stability indices LSI, RSI, PSI and LnR indicated that water under study has the tendency to form scale and considered to be corrosive.

2- Water quality affect the corrosivity of the water that used in cooling purpose in the power plant cooling system, the parameters most influence the corrosion and leaching the material of the system pipes are:

A: Dissolved oxygen (DO):from the experimental investigation it was found that DO is the most critical parameter on the corrosion of the metal pipes. Internal corrosion of water pipes could be effectively prevented by reducing DO concentration.

B: TDS,SO_4^{-2} and Cl^- are considered to be the most aggressive agents that promoting general and localized pitting corrosion.

3- The parameters Ca^{+2} and allk. Are high in the study water which indicates that the water has the potential to form scale.

4- The indices were highly correlated.

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تقييم إمكانية الماء المستعمل في نظام تبريد محطة كهرباء النجيبية على تكوين الترسبات وإحداث التآكل

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المستخلص

ان الهدف من هذه الدراسة هو لاختبار امكانية المياه المستعملة في منظومة تبريد محطة توليد كهرباء النجيبية , البصرة .على تكوين الترسبات وعلى احداث التاكل داخل انابيب التبريد ولهذا الغرض فقد تم استخدام دلائل استقرارية الماء مثل Langelier saturation index,Ryznar stability index, Puckurius scaling index and Larson Ratio index لاختبار هذه القدرة .

تم حساب هذه الدلائل للماء قيد الدراسة بالاعتماد على النتائج المستحصلة من القياسات الحقلية للماء المستعمل في منظومة التبريد في المحطة للفترة من كانون الثاني 2012 الى كانون الاول 2012, وقد تم تطبيق التحاليل الكمية في قياس المتغيرات للماء قيد الدراسة وكان معدل قيم الدليل Langelir index (-0.3317)ومعدل قيم الدليل Ryznar index (7.7833), ومعدل قيم الدليل Puckurius index (6.216) أما معدل قيم الدليل Larson Ratio (29.59) واستنادا للنتائج المستحصلة فلقد تم اثبات ان الماء المستخدم في منظومة التبريد في محطة توليد كهرباء النجيبية له الميل لتكوين الترسبات وايضا له القدرة على احداث التاكل في انابيب المنظومة, وعند اجراء دراسة احصائية للنتائج وجد ان هناك علاقة ارتباط بين الدلائل المذكورة اعلاه وبعض تراكيز ايونات المعادن المقاسة.