

Diagnosis of Heat Exchanger Scales in Cooling Water Systems

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ABSTRACT: *An experimental database is compiled in order to fingerprint the scales formed over the hot surfaces of heat exchangers, in cooling water systems or other systems with similar chemistry. To collect these data, a dynamic simulating pilot plant was designed with considerable application flexibility among which simultaneous flow of water with different velocity and heat fluxes to three simulating heat exchangers can be mentioned. Changing the water chemistry and using various inhibitors composition known in the art, the nature of scale deposits formed on the heating elements was studied by scanning electron microscopy (SEM) coupled with Energy Dispersive X-ray instrument. The heat flux of the elements ranges from 9.46×10^4 to 1.45×10^5 J/m².sec, which depending on the velocity of fluid passing through the orifice of pipe, give rise to skin temperatures of 80 °C to 230 °C. The flow velocities used in this study were 0.21 and 0.46 m/sec. Phosphonates and most popular polymers were studied as scale inhibitors.*

KEY WORDS: *Heat exchanger, Cooling water, Deposit, Scale inhibitors, Scale, Water chemistry.*

INTRODUCTION

The control of deposits in cooling water systems is necessary to maintain maximum heat transfer efficiency. In addition, the formation of deposits may cause flow obstruction of cooling fluids, impedance of heat exchanger, shortening of equipment life, under-deposit corrosion, poor corrosion inhibitor performance, unscheduled equipment shutdown and increased costs in maintaining aqueous systems. These problems can arise in water or oil wells, water pipes, steam power plants, water desalination plants, reverse osmosis equipment utilizing aqueous solutions, heat exchange devices and equipment concerned with the transport of products in aqueous media.

Preventing deposits from adhering to heat exchange surfaces is the most important objective of virtually all cooling water treatment programs. Deposition problems are usually divided into two types, fouling and scale. Fouling, due to the presence of suspended solids in the circulating water, is the physical accumulation of these matters on heat exchanger surfaces.

High iron content in the water source and/or microbiological activity may also cause fouling [1.2]. The iron is oxidized and precipitates onto the system surfaces. Municipal and well water sources normally do not cause problems related to fouling by suspended solids, but may introduce iron fouling problems.

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1021-9986/08/1/65

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Scales can be caused by mineral salt precipitation, co-precipitation of a suspended material with another precipitating mineral, trapping of particulates by adherent films, or simply the settling of particulate matter under gravity. These deposits are typically dense, non-conducting, hard, tightly bound particles that tenaciously adhere to metallic surfaces. Calcium carbonate (CaCO_3) is the most frequently encountered scale or deposit because of its very limited water solubility and the high concentration of calcium and bicarbonate alkalinity normally found in cooling waters [1-4]. Other mineral scales that can form on heat exchange surfaces are calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), calcium sulfate (CaSO_4), iron oxides and iron phosphate (FePO_4).

Most of these inorganic salts have the property of inverse solubility and are therefore less soluble in hot water. Silicate scale can also form in cooling systems that are on high soluble silicate waters. In such waters, silicate transforms to high molecular-weight silicate polymer deposit or so called amorphous silica. Silicate scale is tenacious and difficult to remove [5].

The composition and quantity of a silica deposit and the rate at which it forms are dependent on pH, temperature, the ratio and concentration of calcium to magnesium, and on the concentration of other polyvalent ions in the water.

The use of scale or deposit inhibitor programs can control the level of scaling and modify the character of deposits throughout the cooling water system [6-14]. Several mechanisms are proposed to account for the ability of these programs to control scaling or deposition that consist of: chelation and solubilization, threshold inhibition by surface adsorption, modification of crystal composition and morphology, stabilization of specific crystal phases, dispersion of particles and particle size control [15]. A specific scale or deposit inhibitor may act by one or more of these mechanisms, and the mechanisms may change depending on the type of impurity being inhibited.

Various biodegradable scale inhibitor formulations based on biodegradable carboxylic acids have been developed recently and exhibit good scale inhibition performance in pilot plant test along with low toxicity and reasonable raw material cost [16, 17].

Serious controversy can arise after the annual, or bi-annual overhauls in industry, after examination of

equipments and heat exchangers, between operation engineers and water treatment chemical suppliers. The focal point is who and what caused the problem of scaling, corrosion, microbiological fouling, etc.

It is also a normal practice to change water treatment suppliers every now and then due to price bids, after sale engineering services or dissatisfaction with performance. Considering the aforementioned problems, our goal in two-decade investigation has been to address these problems, and find a systemic qualitative or semi quantitative approach to find when and who did what in the past that resulted in malfunctions.

Various methods have been reported for evaluation of scale inhibitors. A new rapid test has been developed, based upon solution conductivity measurements. It consists of determining a super saturation level of any scale-forming compound in given water, at defined conditions, in the presence of a specified amount of scale inhibitor and also without inhibitor [18]. The solubility and solubility product were critically evaluated for each solid polymorph (amorphous CaCO_3 , ikaite, vaterite, aragonite and calcite) using a hydrated ion pair model and were given coherent explanations for the calcium carbonate precipitation/dissolution process and the existence of supersaturated waters [4]. The static laboratory tests were designed to give a measure of the ability of scale inhibitors to prevent the precipitation of calcium carbonate and calcium sulfate from solution at 71 °C [19]. In addition, screening tests were described for evaluating the effectiveness of gypsum scale removers [20].

Experimental results of CaCO_3 precipitation kinetic have been reported [21]. Several kinetic studies have also been undertaken to monitor the growth of precipitating CaSO_4 and CaCO_3 [22, 23, 24, 25]. The scale formation has occurred in geothermal systems under a wide range of enthalpy and chemical conditions. The predominant factors found to control the solubility of scale-forming minerals include changes in temperature and pH with lesser control being exerted by the concentrations of other ionic species and by kinetic effects [26]. Other studies have investigated the effect of flow velocity using an electronic-antifouling (EAF) treatment, which was considered to mitigate mineral fouling in a heat exchanger connected to a cooling tower water [27].

Table 1: Comparative study of pilot test results with A. P. Complex.

Composition under evaluation	Corrosion rate (mpy)		Scale inhibition
	Admiralty brass	Carbon steel C1018	
Treatment A pilot test	0.06 mpy	0.14 mpy	Very good
Treatment A field results in A. P. complex	Average of 3 month coupon test		Very good
	0.10	0.16 mpy	
	Average of 8 month coupon test		
	0.12	0.33 mpy	

Although, laboratory scale inhibitor evaluation by various test procedures, such as dispersion methods, compares fairly well with actual field results, the same is not true for the scale inhibitors screening, testing and evaluation of scale inhibitor for specific targets in cooling systems. Among numerous laboratory test methods, the actual field condition is not properly modeled. Very often the mechanism of the scale formation in the field is not well understood. Therefore by inappropriate treatments, significant financial losses are imposed to the industry.

To overcome the stated problems a dynamic simulating pilot plant was designed and after years of evaluations which proved to match well with actual industrial field results, the innovation was patented [28a]. Results of an eight months case study in A. P. Complex, manifested that our pilot test results reproduced quite well with the field monitoring data (table 1) [28b].

It is noteworthy to state that, only a few studies have been carried out in order to fingerprint the scales formed over the hot surfaces of heat exchangers and correlate it to the composition of scale inhibitors.

To carry out a detailed study of these correlations, a laboratory size, pilot plant was designed with extensive capabilities. The fingerprint of scale deposit formed on heating elements was exposed using a scanning electron microscope (SEM) coupled with an Energy Dispersive X-ray instrument.

EXPERIMENTAL

Materials

Amino tri(methylene phosphonic acid) (AMP), 50 % aqueous solution of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), 60 % aqueous solution 1-hydroxy-ethylidene-1,1-diphosphonic acid (HEDP) and commercial $ZnCl_2$ solution (45 % wt).

Maleic anhydride copolymer (50 % solution from FMC), Polyacrylic acid (50 % solution) and Carboxylate/sulfonate /nonionic terpolymer (40 % solution from Rohm & Haas),

Methods

Dynamic testing system

As mentioned before, this system has been developed for simultaneous evaluation of cooling water, corrosion and scale inhibitors. Deposits were obtained from the surfaces of heating elements that were used in the dynamic testing system. Fig.1 shows the schematic diagram of the dynamic testing system. In the system an acid resistant centrifugal pump draws the testing liquid from the tank and pumps it through the erosion-corrosion device, corrosion coupons, heating elements, heat exchanger and back to the sump. The fresh inhibitors and the test liquid are injected to the sump by a dual head peristaltic pump and the aged inhibitor is bled off through side tubing in the middle of the sump. A pH controller actuates a solenoid valve connected to an acid feed tank to maintain a target pH. Other safety devices and temperature controllers are also installed to keep the temperature constant. The coupon and element holders are threaded into transparent acrylic pipes with different diameters, such that to allow various fluid velocities in each test. The heat flux of the elements ranges from 9.46×10^4 to 1.45×10^5 J/m².sec (30,000 to 46,000 Btu/hr.ft²) which depending on the velocity of fluid passing through the orifice give rise to skin temperatures of 80 °C to 230 °C.

Simulation of industrial heat exchangers was achieved using high flux stainless steel cartridge type heating elements (10 mm O.D., 10 cm long) with fairly uniform skin temperature. A stable desired heat flux is maintained using a voltage variac.

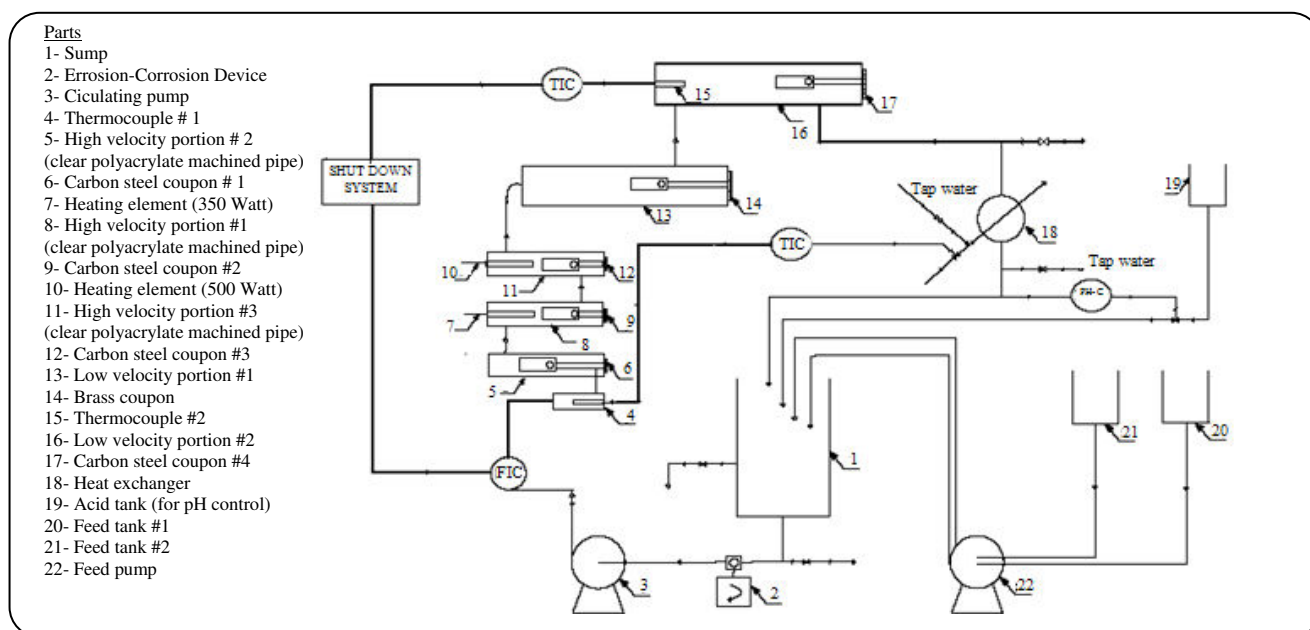


Fig. 1: Dynamic testing system for cooling water corrosion inhibitors.

Since the objectives of dynamic tests are quantification of scaling rate, the elements are dried at 110 °C for four hrs then weighed prior to analysis by EDX. More often the scales are thin enough such that the element's shell also appears in the scale's spectrum. To overcome this problem, the elements shell spectra are eliminated from the scale spectra. Then the elemental composition of scale is calculated. Fig. 2 shows the elemental spectra of heating cartridge without any scale.

Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray

EDX/SEM instrument Stereo scan 360 from Cambridge Co was used for analysis. Using standard scale samples made in our laboratory, the instrument can semi quantitatively analyse all elements heavier than sodium. Standard samples were made using an IR-compressed disk maker.

To perform the scale analysis, depending on the aims and objectives, one of the following sample preparation methods is selected.

1- The heating element containing a skinny scale is placed under the EDX probe.

2- A cross-section of the scale accumulated on the interior of a heat exchanger, during various chemical treatments, is mounted in epoxy resin. Then it is placed

under the probe and each layer is scanned. Referring to the history of the system, one can determine which chemical treatment has contributed more to scalings.

RESULTS AND DISCUSSION

Although the scale composition is highly affected by the ingredients of an inhibitor and the water chemistry, nevertheless the scaling rate depends upon the linear velocity of the cooling water contacting the heating element (heat exchanger), skin temperature or heat flux of the same and the temperature of cooling water.

Investigation of phosphonate effects on scale composition

Zinc phosphonate formulations were prepared, in order to investigate the effects of various popular phosphonates on scale composition. Since the treatment A¹ (table 2, Fig. 3) has performed well in industrial cooling systems within pH=8.2, Cl=600 ppm and total hardness (T.H)= 600ppm as CaCO₃, water conditions, therefore it was selected as a starting point or reference formulation. When in Treatment B, 10 % more HEDP was added to the reference formulation, the scaling rate jumped from 416 to 708 mgr/m².day and calcium phosphonate content has also increased (see P and Ca in table 2), however, the sulphate content was eliminated

Table 2: Elemental composition of deposits formed during Treatments A-E.

Treatments	Element Flux(flow) mg/m ² .day	T.H Cl pH	HEDP	AMP	Ca %	P %	Zn %	Mg %	S %	Cl %	Si %	Na %	Cu %	Fe %	Corrosion Rate of Admiralty Brass (mpy)	Corrosion Rate of Carbon Steel C-1018 (mpy)
Treatment A	31600(1.5) 416	600 600 8.30	-	-	23.7	1.3	52.2	0.7	0.7	1.3	0.0	3.0	0.0	0.1	0.06	0.14
Treatment B	31600(1.5) 708	600 600 8.30	10%	-	33.4	22.2	38.0	2.0	0.0	1.3	0.0	1.3	0.9	0.9	0.05	0.50
Treatment C	31600(1.5) 478	600 600 8.30	-	10%	31.4	21.3	32.9	1.8	5.1	0.0	0.0	1.7	2.9	2.8	0.28	3.50
Treatment D	45500(1.5) 125	1000 1100 8.20	-	-	38.8	10.4	28.9	2.9	1.9	5.6	2.9	1.8	2.9	3.8	0.30	10.40
Treatment E	45500(1.5) 1724	1000 1100 8.20	50%	-	33.0	18.4	34.0	2.0	0.8	0.4	0.0	1.0	1.5	9.0	0.20	1.46

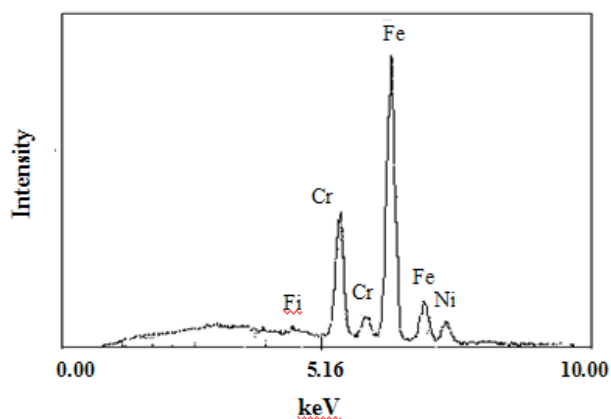


Fig. 2: EDX spectrum of a clean stainless steel heating cartridge.

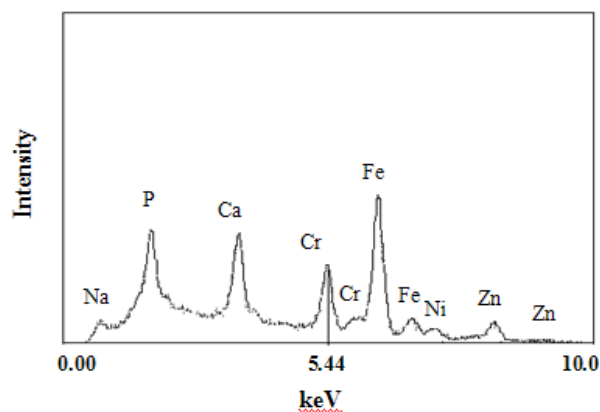


Fig. 3: EDX spectrum of scale formed during Treatment A test.

(see S in table 2). Instead, addition of 10 % AMP to the reference, forming treatment C has increased the scaling rate slightly (from 416 to 478 mgr/m².day), further, comparing Treatment A and C and EDX spectra, copper is noticeably present in Fig. 4. When the water chemistry is changed, and the HEDP content is increased to 50 % (treatment E as compared with treatment D²) a rise in scaling rate from 125 to 1724 mgr/m².day has occurred and surprisingly calcium carbonate content has also been increased (compare Ca & P in table 2 for treatment A and E). Further, dissolved and dispersed iron has also been co-deposited on the element while in test with much higher corrosion rate the iron content of the scale has been much lower (compare Fe content for treatment D & E in table 2). This indicates that the

composition has a very good iron oxide dispersion capability.

Investigation of polymers effect on scale composition

Scrutinizing table 3 and comparing F³ and G spectra (Figs. 5, 6), while having in mind that Treatment F contains, polyacrylic acid, maleic anhydride co-polymer and terpolymer, the following conclusions can be expressed.

1- Increasing terpolymer content by 50 % (treatment F) result in more stability of soluble Ca and Mg salts, decreasing their deposition, while increasing the zinc content most probably by an organo zinc composition. However, the overall deposition rate has decreased significantly.

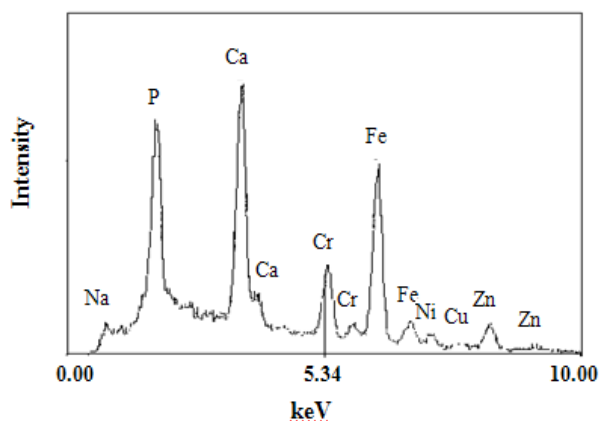


Fig. 4: EDX spectrum of scale formed during treatment C test.

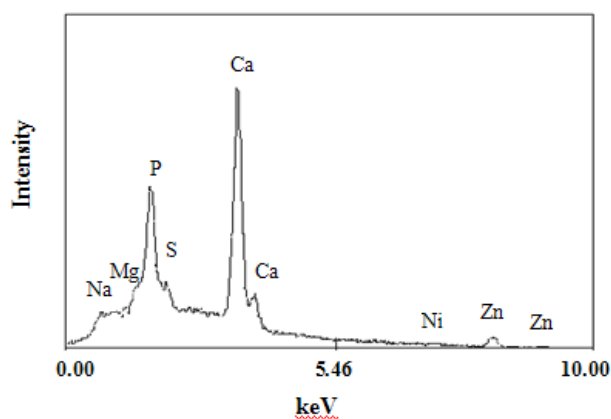


Fig. 5: EDX spectrum of scale formed during treatment F test.

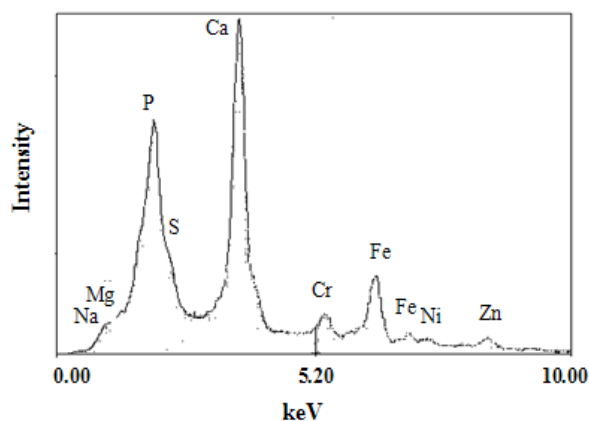


Fig. 6: EDX spectrum of scale formed during treatment G test.

2- Increasing polyacrylic acid, co-polymer and terpolymer content by 40 % (Treatment H) not only has not been able to lower the deposition rate, but also has increased the Ca content significantly and therefore intensified the rate of deposition.

3- Accordingly, in industrial applications one should be very careful to maintain the recommended ratio of corrosion inhibitor and dispersant and also the overall feed rate, as overfeeding may significantly increase the scaling rate.

CONCLUSIONS

1- Normally an increase in phosphonate (e.g. HEDP-AMP) content may improve the surface corrosion inhibition property of the composition, but in some cases it can increase the scaling rate and initiate under/deposit localized corrosion. Addition of 10 % HEDP or 10 % AMP has increased scaling rate about twice. In another water chemistry, when 50 % HEDP has been added to the base formulation, the scaling rate has increased about thirteen times.

2- Increasing the polymer content of an inhibitor composition, does not necessarily decrease the scaling rate, as normally is expected. Concentration and type of cations present in water affect various polymer structures differently. Increase by 50 % of the terpolymer content (i.e. treatment G) lowered the scaling rate 4.5 orders of magnitude as compared with treatment F, but addition of polyacrylic acid, co-polymer and terpolymer content by 40 % (i.e. treatment H) have increased the scaling rate about 1.5 times as compared with treatment F. When an increase in polymer content results in higher scale, it is either due to formation of insoluble polymer-cation compounds and/or iron salt deposits resulting from an increase in corrosion rates.

3- Certain phosphonate/polymer ratios have synergistic effect in corrosion and scaling mitigation. The most synergistic effect is observed when the ratio of phosphonate to polymers is 1:1 as in the treatment A.

4- Preparing a cross section of a scale removed from the interior of industrial heat exchanger tube side, one can determine the history of chemical treatments used in the system. Further it can pinpoint if the system, in the past, has been operated without any inhibitor for a while.

5- Scales resulting from each inhibitor composition in the same water chemistry is always identical and by

Table 3: Elemental composition of deposits formed during Treatments A-E.

Treatments	Element Flux(flow) mg/m ² .day	T.H Cl pH	Polymers	Terpolymer	Ca %	P %	Zn %	Mg %	S %	Cl %	Si %	Na %	Cu %	Fe %	Corrosion rate of admiralty brass (mpy)	Corrosion rate of carbon steel C-1018 (mpy)
Treatment F	45500(0.4) 12936	1000 1100 8.3	-	-	49.4	18.4	24.1	3.1	3.0	0.0	0.0	1.3	0.5	0.2	0.37	0.46
Treatment G	45500(0.4) 3015	1000 1100 8.3	-	50%	38.3	18.2	34.8	1.9	2.2	1.2	0.4	1.6	0.6	0.9	0.03	7.90
Treatment H	45500(0.4) 16579	1000 1100 8.3	40%	-	66.0	15.0	8.0	3.0	4.8	0.5	0.0	1.0	1.1	0.7	0.11	0.17

changing the inhibitor system in the same, the scale chemistry also follows.

Acknowledgements

The financial support by the Research Institute of Petroleum Industry is gratefully acknowledged

Received : 12th November 2006 ; Accepted : 23th December 2007

REFERENCES

- [1] Hasson, D., Semiat, R., Bramson, D., Busch, M., Limoni-Relis, B., *Desalination*, **118**, 285 (1998).
- [2] Qingfeng, Y., Yangqiao, L., Anzhong, G., Jie, D., Ziqiu, S., *Chemical Engineering Science*, **57**, 921 (2002).
- [3] Neville, A., Morizot, A. P., *Chemical Engineering Science*, **55**, 4737 (2000).
- [4] Jean-Yves, G., Jean-Claude, B., Tolosa, H., Nathalie, G., *Talanta*, **43**, 1497 (1996).
- [5] Konstantinos, D.D., *Journal of Chemical Technology & Biotechnology*, **80**, 630 (2005).
- [6] Kmec, P., Emerich, D.E., US Patent 6207079, (2001).
- [7] Shakkthivel, P., Sathiyamoorthi, R., Vasudevan, T., *Desalination*, **164**, 111 (2004).
- [8] Richard W. Goeldner., *Desalination*, **47**, 25 (1983).
- [9] Shakkthivel, P., Ramesh, D., Sathiyamoorthi, R., Vasudevan, T., *Journal of Applied Polymer Science*, **96**, 1451 (2005).
- [10] Yong-Wook, K., Jung-Gu, K., Dong-Jin, C., *Materials and Corrosion*, **52**, 697 (2001).
- [11] El-Shall, H., Rashad, M. M., Abdel-Aa, E. A., *Crystal Research and Technology*, **37**, 1264 (2002).
- [12] Amjad, Z., Zuhi, R. W., NACE International, Paper 02401, Corrosion (2002).
- [13] Carey, W. S., Park, A. S., Donald, T. F., Libardo, A. P., US Patent 5378372 (1995).
- [14] Yang, B., Tang, J., US Patent 5788857 (1998).
- [15] Morizot, A. P., Neville, A., *Journal of Colloid and Interface Science*, **245**, 40 (2002).
- [16] Dong-Jin, C., Seung-Jae, Y. and Jung-Gu, K., *Materials Science and Engineering A*, **335**, 228 (2002).
- [17] Nowack, B., *Water Research*, **37**, 2533 (2003).
- [18] Dreila, I., Falewicz, P., Kuczkowska, S., *Water Research*, **32**, 3188 (1998).
- [19] NACE TM0374-2001
- [20] NACE TM 0397-2002
- [21] Roques, H., Girou, A., *Water Research*, **8**, 907 (1974).
- [22] Gill, J. S., Nancollas, G. H., *Journal of Crystal Growth*, **48**, 34 (1980).
- [23] Kjellin, P., Holmberg, K., Nydén, M., *Journal of Crystal Growth*, **48**, 34 (1979).
- [24] Shinichi, T., Katrin, I. P., Joseph, L. K., *Journal of Crystal Growth*, **143**, 261 (1994).
- [25] Ferguson, R. J., *Materials Performance*, November 25 (1984).
- [26] Thomas, D. M., Gudmundsson, J. S., *Geothermics*, **18**, 5 (1989).
- [27] Sung, H. L., Young, I. C., *International Journal of Heat and Mass Transfer*, **45**, 4163 (2002).
- [28] a) Kameli, M., Moradmand, M., Rahimi, H., Esmaili, N., Iranian Patent 27248, July (2001).
b) Mosayyeb, B., Kameli, M., Bahrami, G. R., Proceeding of 2nd Conference of Corrosion in Petroleum Industry, Tehran, Iran, 18-19 Feb. (2003).