Corrosion Rate of Various Carbon Steels in Raw Water for Water Cooling System at Ammonia Plant

Ahmad Royani¹, Lutviasari Nuraini², Siska Prifiharni³, Gadang Priyotomo⁴ and Sundjono⁵ Research Center for Metallurgy and Materials - Indonesian Institute of Sciences, Kawasan Puspiptek 470 – Tangerang Selatan 15314, Indonesia

Abstract — The corrosion behavior of various carbon steels which simulated to raw water solutions from cooling water system in ammonia plant at different temperatures, was investigated. Polarization method was performed to investigate different types of carbon steel in raw water. The morphologies of various different types of carbon steel were studied. The water tendency was determined by the Langelier Saturation Index (LSI) method. The results of LSI method show negative values, which means, the corrosive tendency of raw water. The results, show that the variation in operating temperature of solution can affect the corrosion rate of materials, where that increases significantly with increasing the temperature of solutions. It was found that the corrosion resistance of materials was in the order of C1045 > A192 >A515-70 > C1015 for various temperatures of raw water.

Keywords — *Carbon steel, Corrosion, Raw water, Temperature.*

I. INTRODUCTION

The primary problems of cooling water systems are corrosion, scaling and biofouling, depending on raw water conditions, pretreatment, chemical treatment of cooling water and concentration cycle [1,2]. Water quality for cooling water can affect ammonia plant performance. Therefore, the criteria of cooling water for ammonia plants are stricter than those for refineries, which do not have this concern [3]. Raw water used in the recirculating system is usually provided from river, lake, reservoir, seawater and underground. The underground water is harder, containing more alkalinity and total dissolved solid (TDS) than the river water. However, the underground water is less turbid and less sensitive to microbiological contamination than surface water [4].

The three basic types of cooling water systems are once-through, closed recirculating, and open recirculating. Originally, the once-through was sufficient to pipe water through the plant and discharge it back to its natural source. Closed systems neither lose nor gain water during operation service. Open systems, however, must have water added to make up for losses. In closed systems where water loss is low, the total waterborne material entering the system is limited. Thus, deposited minerals accumulate at a much slower rate than in systems in which large amounts of make up water are added. Open recirculating and oncethrough systems are exposed to large quantities of solutes, suspended solids, and biological materials. As a consequence, scale, fouling and associated corrosion are generally more significant in open systems than in closed systems [5].

Depending upon the chemical composition of water, it can promote scaling, corrosion or both. Scale can be formed from a variety of dissolved chemical species, where there are two main reliable indicators such as hardness and alkalinity [6]. Calcium carbonate is the most common form of scale deposition in raw water, which used in water cooling systems [7]. Total hardness is primarily a measure of the calcium and magnesium salts in water. Two types of hardness are generally recognized: carbonate and non-carbonate hardness. Water hardness is classified according to a somewhat subjective criteria that varies from different of reference [4,5,8]. Table 1 shows the classification of water hardness which provides a common interpretation. Scaling problems typically occur above levels of 100 ppm hardness [8]. Calcium hardness is a key parameter in evaluating scale formation.

 TABLE I

 WATER HARDNESS CLASSIFICATION[8]

Hardness (as ppm CaCO ₃)	Classification
< 15	Very soft
15 - 50	Soft
50 - 100	Medium hard
100 - 200	Hard
> 200	Very hard

Alkalinity is a measure of a water's ability to neutralize acid. Like hardness it is usually expressed as ppm $CaCO_3$. In the range of normal groundwater chemistry, alkalinity is the result primarily of the bicarbonate content of the water. At pH values of greater than 8.3 carbonate and hydroxide can also contribute to alkalinity [8].

In order to evaluate the general character of a particular water sample it is necessary to know the total dissolved solids (TDS), pH and temperature in addition to the calcium hardness and the M alkalinity [9]. Total dissolved solid is a general indication of the quality of a water source. The increase of TDS can infuence water quality. The tendency of water to be corrosive or scaling also depends on other indicators. The pH value of most groundwater is in the range of 5.0 to 9.0. A common skaling problem occurs in pH values above 7.5 [9].

Two indices commonly used in the water treatment industry to evaluate the stability of a water source are the Langelier Saturation Index (LSI) and the Ryznar Stability Index (RSI). Both indices are based upon a calculated pH of saturation for calcium carbonate (pHs). The pHs value is then used in conjunction with the water's actual pH to calculate the value of the index as follows [5]:

LSI = pH - pHs.	(1)
RSI = 2pHs - pH.	(2)

Table 2 shows the interpretation of Langelier Saturation Index which indicate the tendency of water to scale or not . Moreover, Table 3 shows the interpretation of Ryznar Stability Index which elucidate in more detail description of the tendency of water such as scale and corrosion. Evaluation of the saturation index is as indicated in Table 2.

TABLE II INTERPRETATION OF THE LANGELIER SATURATION INDEX[5]

LSI Index	Indication
Value	
LSI < 0	No potential to scale
LSI = 0	Equilibrium
LSI > 0	Scale

TABLE III INTERPRETATION OF THE RYZNAR STABILITYINDEX[5]

RSI	Index	Indication
Value		
RSI < 6		Scale tendency
RSI > 7		Little scale or corrosive
RSI > 8		Heavy corrosive

On the other hand, carbon steel is widely used as construction material in many industries due to its excellent mechanical properties and low cost [10,11,12]. So, the evaluation of corrosion, scaling and biofouling problems on carbon steel is very important in the cooling water systems, as this phenomenon is responsible for costly social, economic and sometimes even human losses [13].

Heat exchanger and fluid management systems are key parameters in the water cooling system. Considering the fact that different of carbon steels are employed widely in pipelines and heat exchanger (condenser and cooler) tubes, corrosion, scaling and biofouling are usually studied on these alloys [14,15,16]. Deposition or precipitation of solids on the surfaces of heat exchanger tubes is a well reported problem commonly known as fouling [16]. Therefore, the common industry practice when designing heat exchangers is to have a fouling allowance by over sizing the heat transfer area. Meanwhile, an important factor involved in the process of corrosion, is the temperature, because the corrosion rate increases as the temperature increase in the corrosion medium on the reactions proceeding in solution [17].

The objective of this study is to elucidate the raw water tendency of cooling water system to corrosion or scale. The effect of various temperatures for the corrosion behavior for carbon steels is also investigated in raw water.

II. MATERIAL AND METHOD

A. Materials and Preparation

Various types of carbon steel of A 192, A 515-70, C 1015 and C 1045 were used in this study. The chemical composition of different carbon steels was analysed using spectrophotometer Hitachi U 2000. The results are shown in Table 4. Raw water for water cooling system at ammonia plant from Jatiluhur lakes was used as solution medium. The chemical compositions of raw water are shown in Table 5.

The test specimens were fabricated by cutting to a dimension of 10 mm x 10 mm. In order to supply an electrical connection, a suitable length of copper wire was spot welded to one end of sample. The samples were then mounted with Araldite resins and hardener.

B. Determination of the Langelier Saturation Index (LSI)

The method of Langelier Saturation Index (LSI) is used in this study. The Langelier Saturation Index (LSI) was obtained from the following expression (Roberge, 2008):

$$LSI = pH - pHs ..$$
 .. (3)

Where pH is the actual pH of the water, and pH_s is the pH of saturation. Water at equilibrium neither dissolves, nor precipitates calcium carbonate, so it is then characterized by its saturation pH, called pH_s . This is determined using:

$$pH_S = (9.3 + A + B) - (C + D)$$
. (4)

where A, B, C and D are coefficients that are estimated as follows:

A = (log [TDS] - 1)/10)		(5)
$B = -13.12 \times \log (°C + 100)$	+ 273) + 34.55 .	(6)
$C = \log [Ca^{+2}] - 0.4$.			(7)
$D = \log [Alk]$.			(8)

In above equations, TDS is the total dissolved solids, expressed in ppm; Ca^{2+} is the concentration of Ca (II) ions expressed as CaCO₃, in ppm; and Alk is the total alkalinity given in the equivalent CaCO₃, and expressed in ppm.

If LSI = 0, the water is considered to be neutral or at chemical equilibrium. Otherwise, when LSI < 0, the water has the tendency to be corrosive, whereas for LSI > 0, the water is supersaturated with respect to calcium carbonate (CaCO₃) and scale forming may occur, presenting encrusting trend.

TABLE IV	
CHEMICAL COMPOSITION OF CORROSION COUPON MATERIAL	LS

	Chemical Composition of Materials (%)										
Ν	Code	С	Si	Mn	Р	S	Ni	Cr	Мо	Al	Cu
0											
1	A 192	0.17989	0.23616	0.51519	0.0092	0.0203	0.07239	0.20573	0.04174	0.06928	0.07178
2	A 515-70	0.23718	0.25030	0.51917	0.0147	0.0124	0.12756	0.20798	0.04210	0.00462	0.19380
3	C 1015	0.17298	0.24139	0.51664	0.0092	0.0382	0.16836	0.05453	0.05280	0.03555	0.23134
4	C 1045	0.53836	0.20882	0.67844	0.0085	0.0030	0.01482	0.02739	0.00485	0.05266	0.02929

TABLE V CHEMICAL ANALYSIS OF RAW WATER IN A AMONIA PLANT WATER COOLING SYSTEM

Parameter	Unit	Composition
pН	-	8.05
Turbidity	NTU	0.37
Colour (Pt/Co)	-	0
Conductivity	μmhos	233
Dissolved solid	ppm	144
Calcium		17 91
Hardness	ppin,CaCO ₃	47.04
Total Hardness	ppm,CaCO ₃	65.52
Total Alkalinity	ppm,CaCO ₃	17.12
Bicarbonate	ppm	20.89
Total Chlorine,	nnm	0.00
Cl_2	ppm	0.00
Chloride, Cl ⁻	ppm	14.68
Hydroxide, OH ⁻	ppm	6.02
Free CO ₂	ppm	0.00
Nitrate, NO ³⁻	ppm	0.05
Sulphate, SO ₄ ²⁻	ppm	13.01
Sodium, Na	ppm	55.09
Potassium, K	ppm	11.79
Total Iron, Fe	ppm	1.07
Silica, SiO ₂	ppm	11.12

C. Polarization Measurements

Before measurements, the specimen was polished with emery paper up to 600 grade, degreased with ethanol and rinsed with demineralized water. After that, the working electrode was immersed in electrochemical cell, containing 1000 mL of raw water from ammonia plant. The experiments were conducted at various temperatures of 32 °C, 37 °C and 50 °C. The electrochemical cell was equipped with platina auxiliary electrode and a reference saturated silver electrode which was connected to the working electrode over Luggin capillary. Polarization measurements were performed on Corrosion Measurement System (CMS), Model 100. From Tafel polarization curves following corrosion rates were obtained.

D. Metallographic Exammination

The samples were first grinded, up to 1200 grade, and polished up to $0.5 \ \mu\text{m}$. The etching for revealing the microstructure was conducted in a 3 % of nital for 20 s. The samples were rinsed with ethanol and dried with hair dryer. A Meiji Techno Japan optical metallographic microscope was used to study the microstructure of the steel specimens. Metallographic specimens were prepared and investigated in the longitudinal and transverse directions of the castings. The results of the directions representing the exposed surfaces in the electrochemical study were obtained.

III.RESULT AND DISCUSSION

E. Tendency of Raw Water

To calculate the water indices, the samples of raw water were used with using standard methods and the water quality parameters such as temperature, electrical conductivity, total dissolved solids (TDS), pH, dissolved oxygen (DO), calcium hardness, alkalinity, chloride and sulphate were measured. The results of chemical analysis of raw water in ammonia plant water cooling system are shown in Table 5. The indices LSI are calculated using the data of Table 5. According to the results of chemical analysis in Table 5, the LSI index at 32 $^{\circ}$ C is obtained following:

LSI = pH - pHspHs = (0.3 + A + B) - (C - B)

pHs = (9.3 + A + B) - (C + D)where:

where:

A = [Log(144) - 1]/10 = 0.116B = -13.12 × Log10(32°C + 273) + 34.55 = 1.956

C = Log(47.84) - 0.4 = 1.279

D = Log(17.12) = 1.233

Calculation at 32 °C:

pHs = (9.3 + 0.116 + 1.956) - (1.279 + 1.233) = 8.86LSI = 8.05 - 8.86 = -0.81

Hence no tendency to scale.

The results of tendency of the raw water by LSI method at various temperatures were tabulated in Table 6. In the Table 6 shows negative LSI reading which indicate of slightly corrosive but non scale forming with increasing temperature of solutions. Therefore, the quality of the raw water at ammonia plant cooling water system is categorized as tend to be corrosive.

TABLE VI THE RESULTS OF WATER QUALITY INDEX FOR RAW WATER.

Tomp	Satura	tion Index of Raw Water
remp.	LSI	Tendency of Water
32 °C	0.810	Non scalling and slight
32 C -0	-0.010	aggresive
37°C	0.717	Non scalling and slight
57 C	-0.717	aggresive
50°C	0.483	Non scalling and slight
50 C	-0.465	aggresive

F. Electrochemical Measurements

Electrochemical measurement is considered to be a fast and efficient method for determining corrosion rate compared to weight loss. The results of polarization curve of various steels in raw water at various temperatures are shown in Figure 1. The corrosion rates and current densities of steels increase with increasing the temperature of solutions. From Tafel extrapolation curves, the the corrosion rate can be obtained easly. The summary of corrosion potential (E_{corr}), corrosion current (I_{corr}) and corrosion rate from Tafel measurement results were tabulated in Table 7.

TABLE VII
THE RESULTS OF CORROSION POTENTIAL
(E _{CORR}), CURRENT DENSITY (I _{CORR}) AND
CORROSION RATES FOR VARIOUS CARBON
STEEL

		Type of Carbon Steel					
Parameters	Temp.	A 102	A 515-	С	С		
		A 192	70	1015	1045		
	32 °C	-187.8	-139.3	-217.0	- 224,5		
E _{Corr} (mV)	37 °C	-143.3	-155.5	-226.3	- 176.3		
	50 °C	-237.3	-272.8	-168.8	- 214.3		
	32 °C	1.095	1.315	1.487	0.924		
I _{Corr} (A/cm ²) X 10 ⁻	.5 °C	1.686	2.089	2.239	1.289		
	50 °C	2.257	2.588	2.841	2.043		
a .	32 °C	5.009	6.016	6.805	4.219		
Rate	37 °C	7.716	9.558	10.243	5.896		
(mpy)	50 °C	10.327	11.839	12.998	9.348		

Figure 1 shows typical Tafel polarization curves obtained for various carbon steels in raw water solutions at various temperatures. With increasing temperature of solutions, the corrosion potential (E_{corr}) shifted to a positive value and almost unchanged. These curves had in common that the Tafel slopes were changed in the range of 40 to 80 mV and 120 to 160 mV (or even more) for the anodic and cathodic process, respectively.



a). Polarization Curves of Carbon Steel - type A 192 at Different Temperatures.



d). Polarization Curves of Carbon Steel - type C 1045 at Different Temperatures. Fig. 1 Polarization Curves of: a) A 192; b) A 515-70; c) C 1015; and d) C 1045.

G. Effect of Temperature

The experimental results obtained for various carbon steels in raw water conditions at various temperatures are shown in Figure 2. In general, the higher the temperature of solutions, the higher the corrosion rate [6]. It is found that the corrosion rate of each carbon steel increased significantly with increasing the temperature of solution from 32 °C to 50 °C.



Fig. 2 Corrosion Rates Obtained from Polarization Curves, for Various Carbon Steel at Different Temperatures.

The increase of solution temperature is followed by the increase of the solubility of oxygen in solution [5]. According to Ismail and Adan [18], the corrosion rates of carbon steel are higher in solutions with oxygen content in all solutions. Oxygen and carbon dioxide are the most important dissolved gases in water. Oxygen is an effective cathodic depolarizer and the cathodic reaction in water is generally oxygen reduction [18]. This causes an increase of reduction reaction on the cathode area that increases the corrosion rate [6]. Several preceding researchers had reported that the corrosion rate of carbon steel increases with increasing temperature due to increased oxygen solubility and corrosion reaction constant as well as the present results [17,18,19]. The corrosion rate results indicated that A C1015 carbon steel was subjected to severe corrosion in raw water from water cooling system at different temperatures.

H. Effect of Chemical Composition for Various Carbon Steel

The results of corrosion rate for steels in different temperature were shown in Figure 2. Figure 2 shows that corrosion rates of various carbon steels are different due to the addition of elements in carbon steel, as in Table 4. The corrosion rate of C 1045 steel was the lowest, where that of C 1015 steel was the highest. The corrosion rates of A 192 steel and A 515-70 steel with 0.20 % Cr were not much different. It was found that the corrosion resistance was in the order of C1045 > A192 > A515-70>C 1015 for various temperatures of raw water. Carbon steel C 1015 has lower chromium content comparing the other alloys, where the addition of chromium can increase the corrosion resistance of steel [20]. The carbon steel C 1045 has lower corrosion rate compares to other materials due to phase transformation occurred by heat treatment or tempering processes [6]. The content of carbon, chromium, copper and other elements can affect to corrosion resistance of the carbon steel [21,22].

I. The Relationship of Phase Structure of Steels for Corrosion

The results of metallographic images of the four types of steel are shown in Figure 3. Microstructure of carbon steel without heat treatment consists of two phase, ferrite and pearlite [23]. From Figure 3, it can be shown that percentage of pearlite phase on material C 1015 is relatively lower than that on carbon steel A 515-70 and A 192. Pearlite phase acts as a cathode and ferrite as anode so a galvanic cell formed [6]. Pearlite phase controls the oxygen diffusion rate on the metal surface, where it is higher as the pearlite phase content increases [24]. It imply that the increase of reduction reaction in cathodic area, increasing the corrosion rate. The pearlite grain size plays a primary role for the effect of the corrosion rate. The finer the grain size of pearlite will act as anode and will be easy attack by corrosion compares to coarser grain size that acts as cathode [6,24].

From Figure 3, it shown that the grain size of pearlite on the carbon steel C 1015 is finer than that of carbon steel A 515-70. Meanwhile, the microstructure of A 515-70 shown pearlite-ferrite elongated grain that is finer than that of carbon steel A 192. This is the result of rolling process during the fabrication. Carbon steel C 1045 without heat treatment has larger pearlite grain size because the carbon content of 0.538% compares to carbon steel A 192, A 515-70, and C 1015. However, microstructure of the carbon steel C 1045 shows one phase martensite. This is as the result of heat treatment process on austenizing temperature that follows by tempering process. Carbon steel C 1045 with martensite phases has a lower corrosion rate compares to carbon steel A 192, A 515-70 and C 1015 because there is no galvanic cell formation. this is due martensite is a single metastable phase with carbon in solid solution in interstitial positions of the body - centered tetragonal lattice of iron atoms. Random distribution of carbon atoms accompanied by with electronic interaction of carbon atoms neighboring iron atoms limits their effectiveness as cathodes of local - action cells [6].

IV.CONLUSIONS

Based on the results of water quality testing using the Langelier Saturation Index (LSI) method, the raw water from the cooling system at the ammonia plant tends to be corrosive. It was found that the corrosion resistance was in the order of C1045 > A192 > A515 $70 > C \ 1015$ for various temperatures of raw water. The corrosion resistance of materials tested using polarization method indicated carbon steel C1045 is higher than other materials. The increase of temperature in raw water can increase corrosion rate of various steels. It is essential to control the stability of raw water, which tends to be corrosive in various temperature of solutions.



Fig. 3 Metallographic images of the four types of carbon steel: a). A192, b). A151-70, c). C1015 d). C1045.

REFERENCES

- [1] Zlatanovic, L.J., Van der Hoek, J.P. and Vreeburg, J.H.G. An experimental study on the influence of water stagnation and temperature change on water quality in a full-scale domestic drinking water system. Water Research 123: 761-772. 2017.
- [2] Guolin, J., Shan, T., Xiaoxiao, L. and Huaiyuan., W. The analysis of scaling mechanism for water injection pipe columns in the daqing oilfield. Arabian Journal of Chemistry 10: S1235–S1239. 2017.
- [3] Shi-Meng, H., Sheng-Hui, W. and Zhen-Guo, Y. Failure analysis on unexpected wall thinning of heat-exchange tubes in ammonia evaporators. *Case Studies in Engineering Failure Analysis 3:* 52–61. 2015.
- [4] Palazzo, A. J., Van der, M and Combrink, G. The accuracy of calcium-carbonate based saturation indices in predicting the corrosivity of hot brackish water towards mild steel. The Journal of The South Arfican Institute of Mining And Metallurgy 115: 1229-1238. 2015.
- [5] Roberge, P.R. 2008. Corrosion Engineering: Principles and Practice. McGraw-Hill. New York.
- [6] Revie, R.W and Uhlig, H.H., 2008. Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering. Fourth Edition. John Wiley & Sons. Canada.
- [7] Saifelnasr, A., Bakheit, M., Kamal, K and Lila, A. Calcium carbonate scale formation, prediction and treatment: Case study gumry oilfield-PDOC. International Letters of Chemistry, Physics and Astronomy 12: 47-58. 2013.
- [8] Carrier Air Conditioning Company, 1965. Handbook of Air Conditioning System Design. McGraw-Hill Books. New York.
- [9] Roberge, P.R. 2000. Handbook of Corrosion Engineering. McGraw-Hill. New York.

- [10] Dobatkin, S., Zrnik, J. and Mamuzic, I. Mechanical and service properties of low carbon steels processed by severe plastic deformation. *Metalurgija* 48 (3): 157-160. 2009.
- [11] Gandy, D. 2007. Carbon Steel Handbook. Final Report. Electric Power Research Institute. California, USA.
- [12] Moller, H., Boshoff, E.T. and Froneman, H. The corrosion behaviour of a low carbon steel in natural and synthetic seawaters. *The Journal of The South African Institute of Mining and Metallurgy* 106: 585-592. 2006.
- [13] Cesen, A., Kosec, T., Legat, A. and Violeta B. B. Corrosion properties of different forms of carbon steel in simulated concrete pore water. *Materials And Technology* 48 (1): 51–57. 2014.
- [14] Sadiq, J.Z., Blair, C.W. and Chris, M. Silica scaling in geothermal heat exchangers and its impact on pressure drop and performance: Wairakei Binary Plant, New Zealand. *Geothermics* 51: 445–459. 2014.
- [15] Ibrahim, M.G., Abdel Hamid, Z. and Gomaa, N. A case study: corrosion failure of tube heat exchanger. *Journal of Metallurgical Engineering (ME)* 4: 57-61. 2015.
- [16] Behbahani, R.M., Muller-Steinhagen, H. and Jamialahmadi, M. Heat Exchanger Fouling in Phosphoric Acid Evaporators: Evaluation of Field Data. *ECI Digital Archives*. 2003.
- [17] Zuniga, E.M.E., M.A. Veloz, R., Chavarin, J.U. and V.E. Reyes, C. Corrosion of carbon steel in sour water from the oil industry: the effect of temperature. *Int. J. Electrochem. Sci.* 6: 5016 – 5030. 2011.
- [18] Ismail, A. and Adan, N.H. Effect of oxygen concentration on corrosion rate of carbon steel in seawater. American Journal of Engineering Research (AJER) 3 (1): 64-67. 2014.
- [19] Yameng, Q., Hongyun, L., Shuqi Z., Changfeng, C., Zhenguo, L. and Maoxian, X. Effect of temperature on the corrosion behavior of carbon steel in hydrogen sulphide

environments. Int. J. Electrochem. Sci. 9: 2101 – 2112. 2014.

- [20] Terachi, T., Yamada, T., Miyamoto, T., Arioka, K. and Fukuya, K. Corrosion behavior of stainless steels in simulated pwr primary water: Effect of chromium content in alloys and dissolved hydrogen. Journal Of Nuclear Science And Technology 45 (10): 975–984. 2008.
- [21] Park, S.A., Le, D.P. and Kim, J.G. Alloying effect of chromium on the corrosion behavior of low-alloy steels. *Materials Transactions* 54 (9): 1770-1778. 2013.
- [22] Baorong, H., Yantao, L., Yanxu, L. and Jinglei, Z. Effect of alloy elements on the anti-corrosion properties of low alloy steel. *Bull. Mater. Sci.* 23 (3): 189-192. 2000.
- [23] Amin, M.A., Saracoglu, M., El-Bagoury, N., Sharshar, T., M. Ibrahim, M., Joanna, W., Stefan, K. and Jacek, R. Microstructure and corrosion behaviour of carbon steel and ferritic and austenitic stainless steels in NaCl solutions and the effect of p-Nitrophenyl phosphate disodium salt. *Int. J. Electrochem. Sci.* 11: 10029 – 10052. 2016.
- [24] Sami I. A, Eman A. A and Mahdi M. H. The Influence of Microstructure on the Corrosion Rate of Carbon Steels. Eng. & Tech. Journal 31 (10):1825-1836. 2013.