

Evaluating a Multifactorial Model for the Predication of Relationship Between Sea Water pH and its Major Elemental Constituents

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Abstract: This paper presents a model for the prediction of the relationship between sea water pH and its major elemental constituents; chlorides, calcium, magnesium and potassium. The sea water constituent were determined using Atomic Absorption Spectrometer and average values recorded correspondingly against each pH. Response coefficient of the sea water pH ξ to the resultant influence of these constituents was evaluated to ascertain the reliability of the highlighted dependence. A multi-factorial model was derived, validated and used for the predictive evaluation of the sea water pH. The validity of the model;

$$\xi = 0.0129\delta + 0.2373\vartheta + 0.3202\varepsilon + 0.0004\gamma - 7.9959$$

was rooted on the core model expression $\xi + 7.9959 = 0.0129\delta + 0.2373\vartheta + 0.3202\varepsilon + 0.0004\gamma$ where both sides of the expression are correspondingly approximately equal. Standard errors incurred in predicting the sea water pH for each value of the highlighted elemental constituents as obtained from experiment, derived model & regression model-predicted results were 0.0480, 0.0037 & 1.9115×10^{-5} , 0.0418, 0.0041 & 1.9237×10^{-5} , 0.0487, 0.0031 & 2.7337×10^{-5} and 0.0649, 0.0128 & $27331 \times 10^{-5}\%$ respectively. Furthermore the minimum correlation between sea water pH and its major elemental constituents as obtained from experiment, derived model and regression model was > 0.7 . The maximum deviation of the model-predicted in situ sea water pH (from experimental results) was less than 2.5%. This translated into over 97% operational confidence for the derived model as well as over 0.97 response coefficients for the dependence of the in situ sea water pH on its major elemental constituents.

Key words: Mathematical relationship • Sea water pH • Elemental Constituents

INTRODUCTION

The need to carry out oil industry based engineering operations using metallic equipment and also submerge steel pipes (for conveying petrol and gas) and across the sea water has raised the need for intensive research on the in situ sea water with the aim of finding better ways of determining accurate sea water pH. This is because sea water is corrosive, as a result of presence of dissolved compounds and elements. These are chlorides, magnesium, oxygen potassium, calcium, hydrogen etc. Most abundantly, dissolved ions in sea water are sodium, chloride, magnesium, sulfate and calcium [1].

Report [2] has shown that sea water or salt water is water from a sea or ocean. On average, sea water in the world's oceans has a salinity of about 3.5% (35g/L, or

599mM). This implies that every kilogram (roughly one litre by volume) of sea water has approximately 35 grams of dissolved salts predominantly sodium and chlorine. The report revealed that the average density at the surface is 1025 kgm^{-3} . The research indicated that sea water is denser than both fresh water and pure water (density $1.0\text{g/ml @ } 4^\circ\text{C}$) because the dissolved salts add mass without contributing significantly to the volume. The freezing point sea water decreases as salt concentration increases. At typical salinity, it freezes at about $- 2^\circ\text{C}$. The coldest sea water ever recorded (in liquid state) was in 2010, in a stream under an Antarctic glacier and measured $- 2.6^\circ\text{C}$ [3].

Mathematically, pH is the negative logarithm of the activity of the (solvated) hydronium ion more often expressed as the measure of the hydronium ion

concentration [4]. Some researcher [5] expressed pH as the decimal logarithm of the reciprocal of the hydrogen ion activity, a_{H^+} , in a solution.

Research [6] has shown that sea water pH is typically limited to a range between 7.5 and 8.4.

The determination of the pH of seawater has always been a rather difficult problem (using the conventional pH scale) due to ionic strength differences between the sea water and buffer solutions used for pH scale calibration. For example while the sea water ionic strength is ≈ 0.7 , that of the buffer solutions is ≈ 0.1 [8]. Past findings [4] have shown that the measured pH “value” in saline solutions is probably not a reliable indication of the actual value of the hydrogen ion activity. Only for dilute solutions of simple solutes, whose pH values match closely that of a standard, can the “pH be regarded as an approximate measure of the hydrogen ion activity of the solution.

Further research [7] has shown that pH measurement is complicated by the chemical properties of sea water, leading to existence of several distinct pH scales in chemical oceanography. Researchers [8] realized this difficulty and proposed the establishment of a suitable operational scale for the pH of seawater using high ionic strength standards. Based on the foregoing, three different pH scales were developed [8] for measuring the pH of sea water; free pH scale pH_f , total pH scale pH_t and sea water pH scale pH_{sws} . The free pH scale determines the sea water pH just by evaluating only the concentration of hydrogen ion H^+ present in the water. The total pH scale gives the sea water pH by evaluating the hydrogen ions and sulphate ions present in the sea water. The sea water pH scales reads the pH by evaluating the hydrogen ions, sulphate ions and the fluoride ions. However, in sea water where fluoride ion is very negligible, the total pH scale is used since the difference between it and the sea water pH scale is insignificant.

In practice, the pH of seawater is measured at a constant temperature on board ship. The in situ value of the pH must then be computed. Scientists [9] used technique from earlier research [10] to determined coefficients for the pressure correction. And so, the pH at the in situ temperature could then be calculated from:

$$pH(\text{in situ temp } t_2) = pH_t + 0.0114(t_1 - t_2) \quad (1)$$

A similar equation has been reported [11] for the range of oceanographic interest, even though equation (1)

is applicable for all salinity and temperature ranges. The calculated pH at the equilibration temperature is then corrected to the in situ value using an equation similar to equation (1).

The pH of sea water plays an important role in the ocean’s carbon cycle and there is evidence of ongoing ocean acidification caused by carbon dioxide emission [12]. Research results [13] therefore go to show that the value of the pH of seawater is obtained to gather information on the carbonate equilibria.

Studies [11] have indicated that in situ sea water pH could be calculated using measurements of total carbon dioxide and of the partial pressure of CO_2 . The report indicates that apparent dissociation constants from earlier work [14] were used.

The aim of this research is to give a simulative evaluation of the sea water pH as function of its major metallurgical constituents. An empirical model will be derived, validated and used for the simulative evaluation. It is expected that if the work is successful, the model would predict the pH of sea water if dissolved concentrations (in sea water) of the considered elements are known and within the dissolved solids-boundary condition in this work. Furthermore, the success of the work would eliminate the issue of debating for the choice of most suitable or appropriate pH scale to use.

MATERIALS AND METHODS

Materials used for the experiment are sea water (collected from in situ sea located in Port Harcourt, Nigeria) flying boat, beakers, conical flasks. The other materials used were analytical digital weighing machine and pH meter.

Specimen Collection and Measurement of Electrical Conductivity: Flying boat was used in plying around the in situ sea water. The specimens were collected within a space of 6weeks, to accommodate and integrate any change in the salinity and pH of the sea water. Each week, 60 samples of the sea water were collected from 60 different points in the sea. The pH of these sea water samples were respectively measured and average value recorded against each week. Furthermore, the concentrations of chlorides, calcium, magnesium and potassium present in each sea water samples (whose pH was already measured) were determined using AAS and average values recorded correspondingly against each pH.

RESULTS AND DISCUSSION

Variation of Sea Water pH with its Major Elemental Constituents: Table 1 shows that pH of the in situ sea water increases with increase in its major elemental constituents such as chlorides, calcium, magnesium and potassium. Since sodium chloride (NaCl); salt, is the principal constituent of sea water [2], it follows that increase in the in situ sea water saltiness as a result of increase in the constituent chlorides will lead to increase in the in situ sea water pH as shown in Table 1. Furthermore, Ca, Mg and K form basic oxides. Therefore, increase in there respective concentrations in situ sea water will shift the pH increasingly away from acidity implying increasing pH as shown in Table 1. Based on the foregoing, in situ sea water pH could be determined as a function of the concentrations of chlorides, calcium, magnesium and potassium in the sea water.

Model Formulation: Computational analysis of generated experimental data shown in Table 1 gave rise to Table 2 which indicates that;

$$\xi + S = N\delta + S_c \vartheta + K\varepsilon + N_c \gamma \tag{2}$$

Introducing the value of S, N, S_c, K and N_c into equation (2) reduces it to;

$$\xi + 7.9959 = 0.0129\delta + 0.2373 \vartheta + 0.3202\varepsilon + 0.0004 \gamma \tag{3}$$

$$\xi = 0.0129\delta + 0.2373 \vartheta + 0.3202\varepsilon + 0.0004\gamma - 7.9959 \tag{4}$$

where,

S = 7.9959, N = 0.0129, S_c = 0.2373, K = 0.3202 and N_c = 0.0004. These are empirical constant (determined using C-NIKBRAN [15])

- (ξ) = In situ sea water pH
- (δ) = Conc. of chlorides in the sea water (ppm)
- (ϑ) = Conc. of calcium in the sea water (ppm)
- (ε) = Conc. of magnesium in the sea water (ppm)
- (γ) = Conc. of potassium in the sea water (ppm)

The derived model is equation (4). Computational analysis of Table 1 gave rise to Table 2. The derived model is multivariate in nature since it is composed of many input process parameter. This implies that the predicted in situ sea water pH is dependent on Cl, Ca, Mg and K content of the sea water.

Table 1: Variation of in situ sea water pH with its elemental constituents

(ξ)	(δ)	(ϑ)	(ε)	(γ)
6.57	89.2	40.41	11.98	7.685
6.58	89.4	40.42	12.00	7.703
6.60	89.8	40.44	12.01	7.725
6.64	90.5	40.46	12.03	7.732
6.65	90.8	40.50	12.05	7.738
6.80	91.1	40.52	12.06	7.741

Table 2: Variation of ξ + 7.9959 with 0.0129 δ + 0.2373 ϑ + 0.3202ε + 0.0004γ

ξ + 7.9959	0.0129 δ + 0.2373 ϑ + 0.3202ε + 0.0004ε
14.5659	14.5791
14.5759	14.5905
14.5959	14.6035
14.6359	14.6238
14.6459	14.6435
14.7959	14.6553

Boundary and Initial Conditions: Consider in situ sea water, interacting with some corrosion-induced agents. The sea water is assumed to be affected by unwanted dissolved gases and minerals. Range of the sea water pH considered: 6.57 – 6.80 respectively. Also range of chlorides, calcium, magnesium and potassium content of the in situ sea water considered: 89.2-91.1, 40.41- 40.52, 11.98- 12.06 and 7.685- 7.741 respectively.

The boundary condition is: aerobic environment, since the atmosphere contains oxygen.

Model Validity: The validity of the model is strongly rooted on equation (3) (core model equation) where both sides of the equation are correspondingly approximately equal. Table 2 also agrees with equation (3) following the values of ξ + 7.9959 and 0.0129δ + 0.2373 ϑ + 0.3202ε + 0.0004 γ evaluated from the experimental results in Table 1. Furthermore, the derived model was validated by comparing the sea water pH predicted by the model and that obtained from the experiment. This was done using various analytical techniques.

Statistical Analysis

Standard Error (STEYX): The standard errors incurred in predicting the sea water pH for each value of its major elemental constituents; chlorides, calcium, magnesium and potassium considered as obtained from experiment & derived model were 0.0480 & 0.0037, 0.0418 & 0.0041, 0.0487 & 0.0031 and 0.0649 & 0.0128% respectively. The standard error was evaluated using Microsoft Excel version 2003.

Correlation: The correlation coefficient between sea water pH and its major elemental constituents; chlorides, calcium, magnesium and potassium were evaluated (using Microsoft Excel Version 2003) from results of the experiment and derived model. These evaluations were based on the coefficients of determination R^2 shown in Figs. 1- 8.

$$R = \sqrt{R^2} \quad (5)$$

The evaluated correlations are shown in Tables 3-6. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from actual experiment.

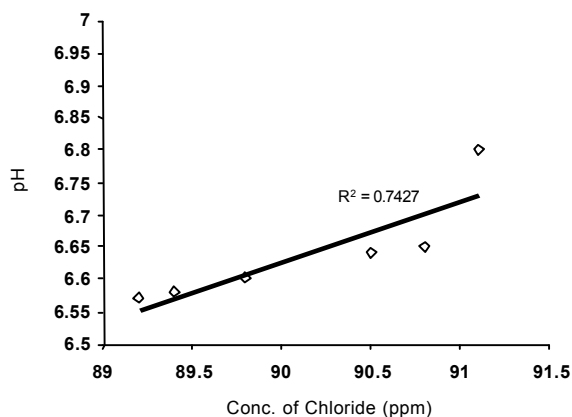


Fig. 1: Coefficient of determination between in situ sea water pH and its chloride content as obtained from the experiment

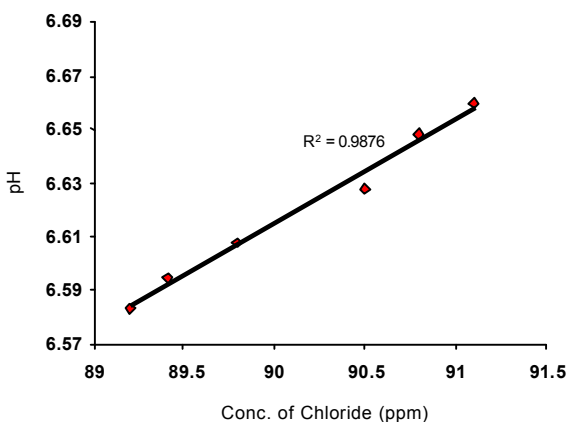


Fig. 2: Coefficient of determination between in situ sea water pH and its chloride content as obtained from derived model

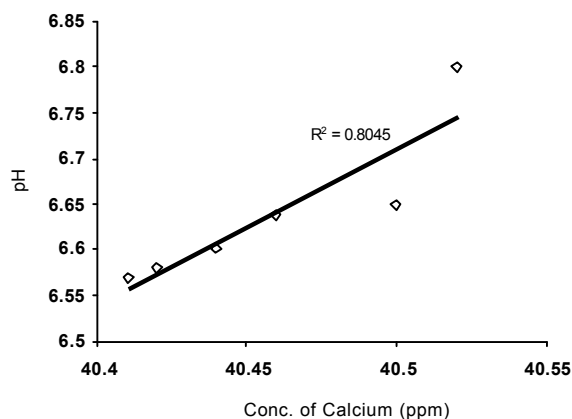


Fig. 3: Coefficient of determination between in situ sea water pH and its calcium content as obtained from the experiment

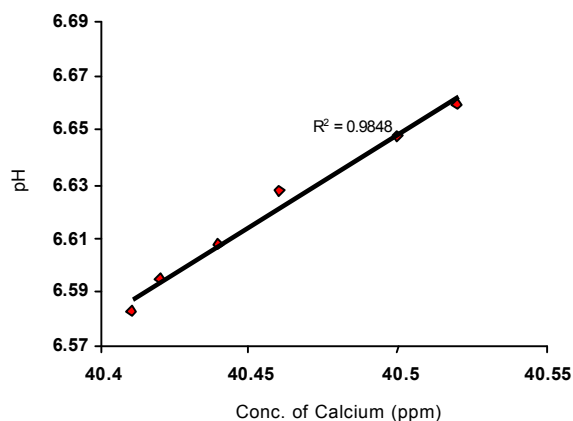


Fig. 4: Coefficient of determination between in situ sea water pH and its calcium content as obtained from the derived model

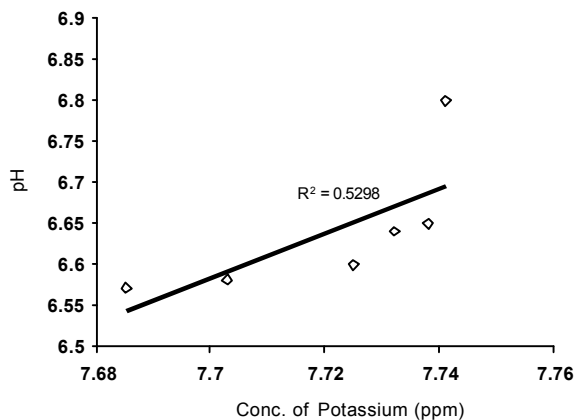


Fig. 5: Coefficient of determination between in situ sea water pH and its potassium content as obtained from the experiment

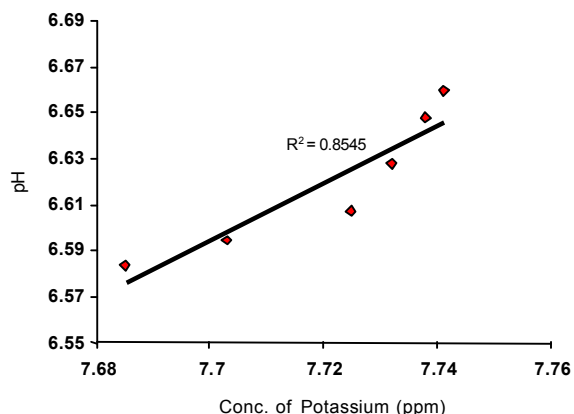


Fig. 6: Coefficient of determination between in situ sea water pH and its potassium content as obtained from derived model

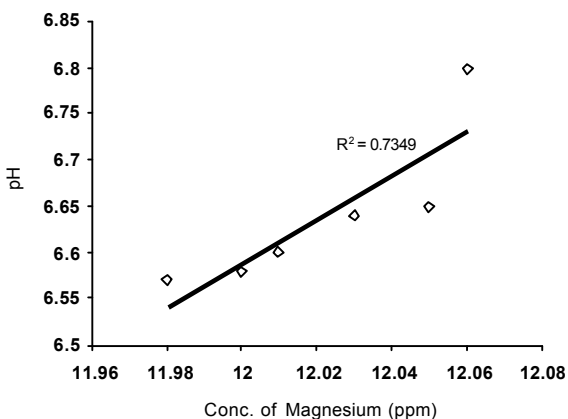


Fig. 7: Coefficient of determination between in situ sea water pH and its magnesium content as obtained from the experiment

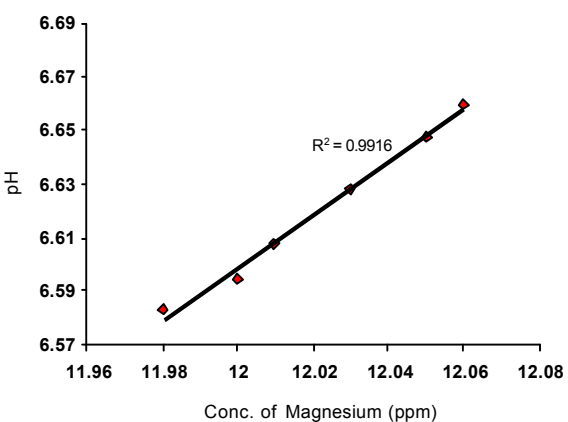


Fig. 8: Coefficient of determination between in situ sea water pH and its magnesium content as obtained from derived model

Table 3: Comparison of the correlations between sea water pH and its chloride content as evaluated from experimental (ExD) and derived model (MoD) predicted results

Analysis	Based on chloride content	
	ExD	D-Model
CORREL	0.8618	0.9938

Table 4: Comparison of the correlations between sea water pH and its calcium content as evaluated from experimental (ExD) and derived model (MoD) predicted results

Analysis	Based on calcium content	
	ExD	D-Model
CORREL	0.8969	0.9924

Table 5: Comparison of the correlations between sea water and its potassium content as evaluated from experimental (ExD) and derived model (MoD) predicted results

Analysis	Based on potassium content	
	ExD	D-Model
CORREL	0.7279	0.9244

Table 6: Comparison of the correlations between sea water pH and its magnesium content as evaluated from experimental (ExD) and derived model (MoD) predicted results

Analysis	Based on magnesium content	
	ExD	D-Model
CORREL	0.8573	0.9958

Graphical Analysis: Graphical analysis of Fig. 9-12 shows very close alignment of curves from derived model and experiment. It is strongly believed that the degree of alignment of these curves is indicative of the proximate agreement between ExD and MoD predicted results.

Comparison of Derived Model with Standard Model:

The validity of the derived model was also verified through application of the regression model (ReG) (Least Square Method using Excel version 2003) in predicting the trend of the experimental results.

Comparative analysis of Figs. 13-16 shows very close alignment of curves which precisely translated into significantly similar trend of data point's distribution for experimental (ExD), derived model (MoD) and regression model-predicted (ReG) results of in situ sea water pH. Also, the evaluated correlations (from Figs. 3-6) between in situ sea water pH and its major elemental constituents; chlorides, calcium, magnesium and potassium for results obtained from regression model were 0.9882, 0.9839, 0.9955 and 0.9474 respectively.

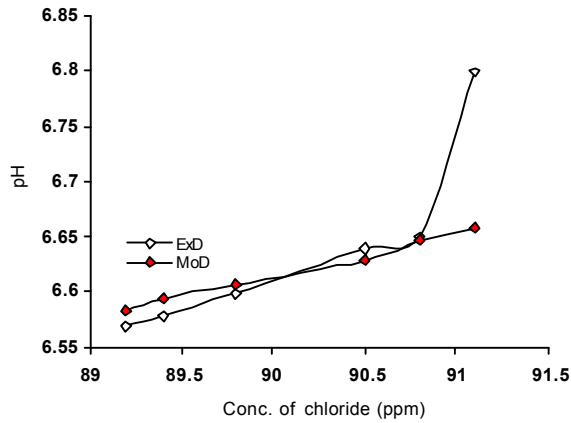


Fig. 9: Comparison of the sea water pHs (relative to its chloride content) as obtained from experiment and derived model

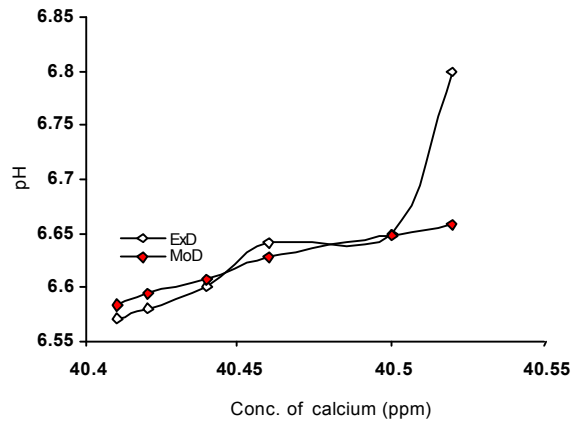


Fig. 10: Comparison of the sea water pH (relative to its calcium content) as obtained from experiment and derived model

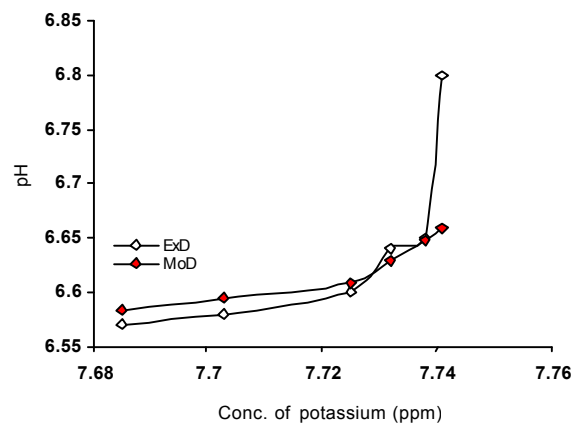


Fig. 11: Comparison of the sea water pH (relative to its potassium content) as obtained from experiment and derived model

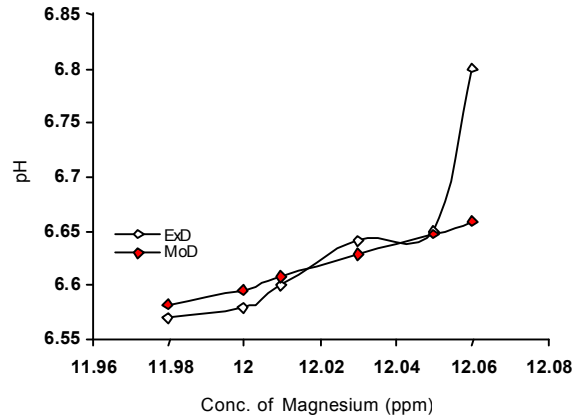


Fig. 12: Comparison of the sea water pH (relative to its magnesium content) as obtained from experiment and derived model

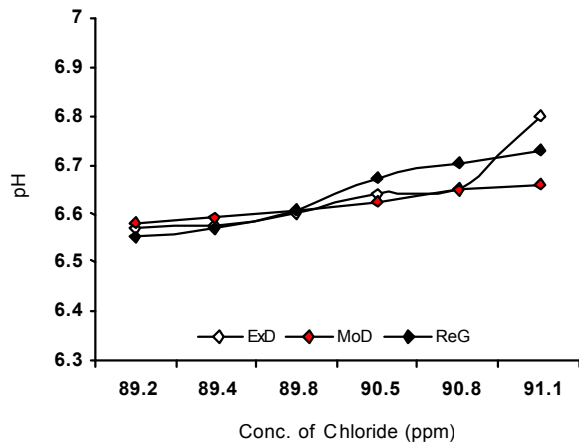


Fig. 13: Comparison of the sea water pH (relative to its chloride content) as obtained from experiment, derived model and regression model

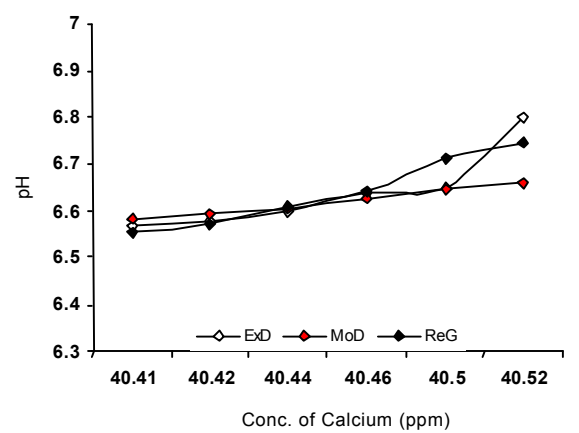


Fig. 14: Comparison of the sea water pH (relative to its calcium) as obtained from experiment, derived model and regression model

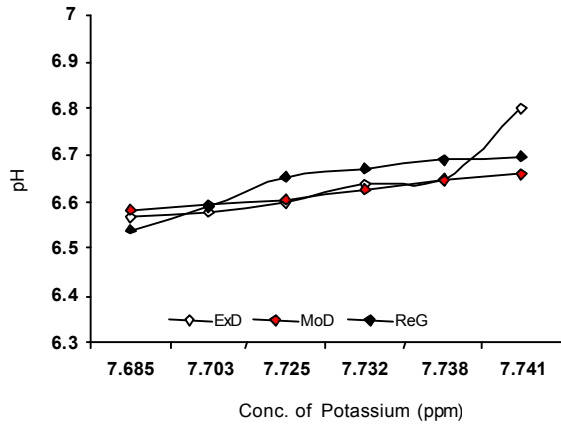


Fig. 15: Comparison of the sea water pH (relative to its potassium content) as obtained from experiment and derived model

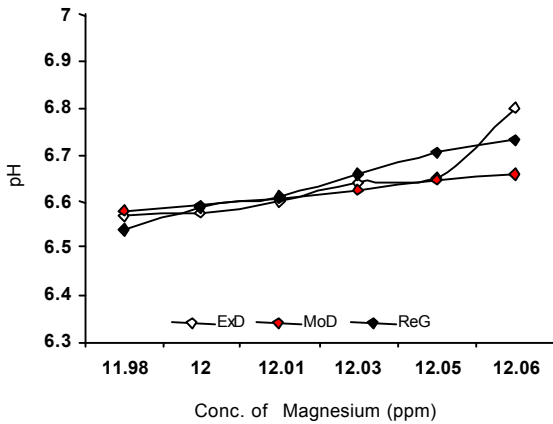


Fig. 16: Comparison of the sea water pH (relative to its magnesium content) as obtained from experiment, derived model and regression model

These values are in proximate agreement with both experimental and derived model-predicted results. The standard error incurred in predicting in situ sea water pH for each value of the major elemental constituents considered as obtained from regression model were 1.9115×10^{-5} , 1.9237×10^{-5} , 2.7337×10^{-5} , 2.7331×10^{-5} respectively.

Deviational Analysis: Comparative analysis of the in situ sea water pH precisely obtained from experiment and derived model shows that the model-predicted values deviated from experimental results. This was attributed to the fact that some process conditions involved in pH measurement which affected generated results were not considered during the model formulation.

This necessitated the introduction of correction factor, to bring the model-predicted seawater pH to those of the corresponding experimental values.

The deviation D_v , of model-predicted seawater pH from the corresponding experimental result was given by;

$$D_v = \left(\frac{\zeta_{MoD} - \zeta_{ExD}}{\zeta_{ExD}} \right) \times 100 \quad (6)$$

where,

ζ_{ExD} and ζ_{MoD} are sea water pH evaluated from experiment and derived model respectively.

Table 7 shows that the least and highest magnitudes of deviation of the model-predicted sea water pH (from the corresponding experimental values) are -0.04 and -2.07% . It could be seen from Table 7 that these deviations correspond to in situ sea water pH: 6.65 and 6.80, chloride content: 90.8 and 91.1, calcium content: 40.5 and 40.52, magnesium content: 12.05 and 12.06 as well as potassium content: 7.738 and 7.741 ppm respectively.

Analysis of Table 7 also shows that the maximum deviation of model-predicted in situ sea water pH from the experimental results was less than 2.5%. This translated into over 97% operational confidence and response level for the derived model as well as over 0.97 response coefficients for the dependence of in situ sea water pH on its major elemental constituents; chlorides, calcium, magnesium and potassium.

It is strongly believed that the model's confidence level and the insignificant level of deviation of model-predicted sea water pH (from experimental results) positions the model to be more reliable than other pH scales [7] in terms of readily, offering a direct prediction of in situ sea water pH (if the various concentrations of its highlighted major elemental constituents are known) without the inconveniencies of evaluating the temperature of the in situ sea water or making any correction to whatsoever pH recorded.

Correction factor, Cf to the model-predicted sea water pH was given by;

$$Cf = \left(\frac{\zeta_{MoD} - \zeta_{ExD}}{\zeta_{ExD}} \right) \times 100 \quad (7)$$

Table 7 indicates that the evaluated correction factors are negative of the deviation as shown in equations (6) and (7).

The correction factor took care of the negligence of some process conditions involved in sea water pH measurement, which actually affected generated results.

Table 7: Deviation of model-predicted sea water pH (from experimental results) and its associated correction factor

Dv (%)	Cf (%)
+ 0.20	- 0.20
+ 0.22	- 0.22
+ 0.12	- 0.12
- 0.18	+ 0.18
- 0.04	+ 0.04
- 2.07	+ 2.07

The model predicted results deviated from those of the experiment because these conditions were not considered during the model formulation. Introduction of the corresponding values of Cf from equation (7) into the model gives exactly the corresponding experimental in situ sea water pH.

Table 7 shows that the least and highest magnitudes of correction factor to the model-predicted in situ sea water pH are + 0.04 and + 2.07%. Since correction factor is the negative of deviation (equations (6) and (7)), Table 7 indicates that these correction factors correspond to in situ sea water pH: 6.65 and 6.80, chloride content: 90.8 and 91.1, calcium content: 40.5 and 40.52, magnesium content: 12.05 and 12.06 as well as potassium content: 7.738 and 7.741 ppm respectively.

It is important to state that the deviation of model predicted results from that of the experiment is just the magnitude of the value. The associated sign preceding the value signifies that the deviation is a deficit (negative sign) or surplus (positive sign).

CONCLUSION

A correlative mathematical relationship between sea water pH and its major elemental constituents; chlorides, calcium, magnesium and potassium was carried out. A multi-factorial model was derived, validated and used for the predictive evaluation of the sea water pH. The validity of the derived model was rooted on the core model expression $\xi + 7.9959 = 0.0129 \eta + 0.2373 \theta + 0.3202\varepsilon + 0.0004 \gamma$ where both sides of the expression are correspondingly approximately equal. Standard errors incurred in predicting the sea water pH for each value of the highlighted elemental constituents as obtained from experiment, derived model & regression model-predicted results were 0.0480, 0.0037 & 1.9115×10^{-5} , 0.0418, 0.0041 & 1.9237×10^{-5} , 0.0487, 0.0031 & 2.7337×10^{-5} and 0.0649, 0.0128 & 27331×10^{-5} % respectively. The minimum correlation between sea water pH and its major elemental constituents as obtained from experiment, derived model and regression model was > 0.7 . The maximum

deviation of the model-predicted in situ sea water pH (from experimental results) was less than 2.5%. This translated into over 97% operational confidence for the derived model as well as over 0.97 response coefficients for the dependence of the in situ sea water pH on its major elemental constituents.

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