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MAY 80 D P OKSANEN, A ZIRINO
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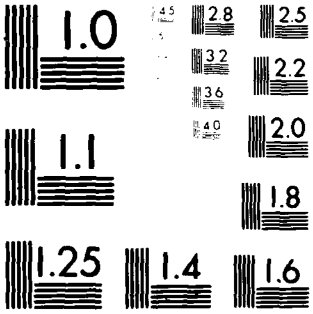

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THE pH RESPONSE OF A SHINY PLATINUM ELECTRODE

D. P. Oksanen and A. Zirino

1 May 1980

NAVAL OCEAN SYSTEMS CENTER
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INTRODUCTION

Platinum electrodes have been used by biologists and geologists to map variations in the level of oxidative degradation in the field and to draw conclusions about electron limits of particular environments based on assumptions as to actual reactions occurring on the platium (Pt) surface. Whitfield (Reference 1) suggests the possibility of the Pt surface acting as an oxide electrode responding to pH in the natural environment. In our work $E_{i=o}$ and Eh values for a shiny Pt tube are determined in seawater samples. The pH calibration of the Pt tube is investigated both polarographically and potentiometrically. The actual surface properties of the Pt tube were not explored; therefore, no conclusions were drawn as to the type of surface reaction occurring that permits pH calibration. Yet it is shown that the Pt tube does react to pH changes. If the Pt surface can be calibrated for its reaction to other seawater constituents, perhaps the Pt electrode can be used to measure one specific redox reaction and further define the natural seawater environment.

THEORY

The reaction: $H_2 \rightleftharpoons 2H^+ + 2e^-$

proceeds spontaneously on platinum surfaces immersed in aqueous solutions, even saline solutions such as seawater. At equilibrium, the potential (E) generated at the electrode by the reaction is given by the Nernst equation, i.e.:

$$E = E^o - \frac{RT}{nF} \ln \frac{pH_2}{(aH^+)^2} \qquad (1)$$

where E^o is the potential of the standard hydrogen electrode (SHE), pH_2 is the partial pressure of hydrogen gas in solution, aH^+ is the activity of hydrogen ion and R, T, n, F have their usual meanings (Reference 2). By convention, the potential of SHE is = 0.00. Thus,

$$E = -\frac{RT}{nF} \ln \frac{pH_2}{(aH^+)^2} \qquad (2)$$

in the ideal situation. For non-ideal situations E^o can be measured at the point where $pH_2 = (aH^+)^2$, or $\ln \frac{pH_2}{(aH^+)^2} = 0$, assuming that $H_2 \rightleftharpoons 2H^+ + 2e^-$ is in equilibrium and that Equation 2 holds.

In seawater E^o is the standard potential of the oxidation-reduction system of seawater and the Nernst equation now becomes:

$$E = E^o - \frac{RT}{nF} \ln \frac{[X]^x [Y]^y}{[A]^a [B]^b} \qquad (3)$$

with $aA + bB \rightleftharpoons xX + yY$ (Reference 3) as the general oxidation-reduction system of seawater. There is no universally established E^o for seawater because of the variations in different oxidation reduction systems in given samples (References 4, 5). Therefore, E must be measured for each sampled area. In principle when E equals $E^o - \frac{RT}{nF} \ln \frac{[X]^x [Y]^y}{[A]^a [B]^b}$ no net current is flowing and the system is in equilibrium. $E_{i=o}$ (E where the current i=o) can be measured polarographically by scanning a range of potentials and measuring the current flow. Once $E_{i=o}$ is established, changes in the oxidation-reduction system can be measured.

Changes in pH_2 may be determined, assuming the system in question stays in an equilibrium state during small fluctuations in pH_2 or aH^+. pH_2 may be measured by fixing aH^+ and determining the surface potential E or, alternatively, E may be set by a potentiostat and the current required to shift reaction (Equation 1) to the new equilibrium point may be measured. The first method is potentiometric while the second approach is polarographic in nature.

Initially we attempted to determine the feasibility of using a Pt electrode in seawater for polarographic and potentiometric measurements of H_2 in seawater. Two experimental approaches were used. In the first, $E_{i=o}$ was established by slowly scanning the electrode potential over a pre-selected range. This was done for unfiltered seawater and buffer solutions of constant pH values. In the second, the system was allowed to equilibrate and the potential (Eh)* reached by the Pt surface was noted. The pH was varied from 8.5 to 5.5 through the addition of CO_2 gas to unfiltered seawater (Reference 6).

Once $E_{i=o}$ and Eh were established for normal seawater they could be used as a baseline from which to measure Pt's response to H_2. The polarographically applied $E_{i=o}$ would develop a baseline of lowest background current and changes in pH_2 would shift the equilibrium point of reaction (Equation 1). Changes in current during the re-establishment of equilibrium could then be measured. The potentiometrically determined value for Eh under specific conditions would provide a baseline potential which is not constrained and would change in response to changes in pH_2 as indicated in the Nernst equation.

Ambient seawater pH values vary from about 7.5 to 8.8. The pH of a solution will affect the $E_{i=o}$ and the Eh values obtained as predicted in Equation 1. To predict Pt response to H^+ in seawater and to correct for changes in pH, a calibration of the Pt surface was made both polarographically and potentiometrically.

EXPERIMENTAL INSTRUMENTATION

All experimental determinations were done using a closed, continuous flow system (Figure 1). The system consisted of a teflon block, a peristaltic pump and a reservoir with a gas inlet, all connected with tygon tubing. A Corning No. 476056 combination semimicro electrode (with Ag/AgCl reference) sealed into the teflon block and a Corning Model 101 digital electrometer were used for pH measurements. A shiny Pt tube (0.122 inch inside diameter, 0.157 inch outside diameter, and 1.518 inch long) inserted into a break in the tubing was used for all Eh and $E_{i=o}$ determinations. A constant flow of solution was maintained at approximately 390 ml/min by a Cole-Parmer (Master-Flex) peristaltic pump. Gases were gently bubbled into 200 ml of solution contained in the reservoir and further mixed by the flow from the input and output tubes.

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*Eh rather than E, is used to refer to potentials potentiometrically obtained in seawater media.

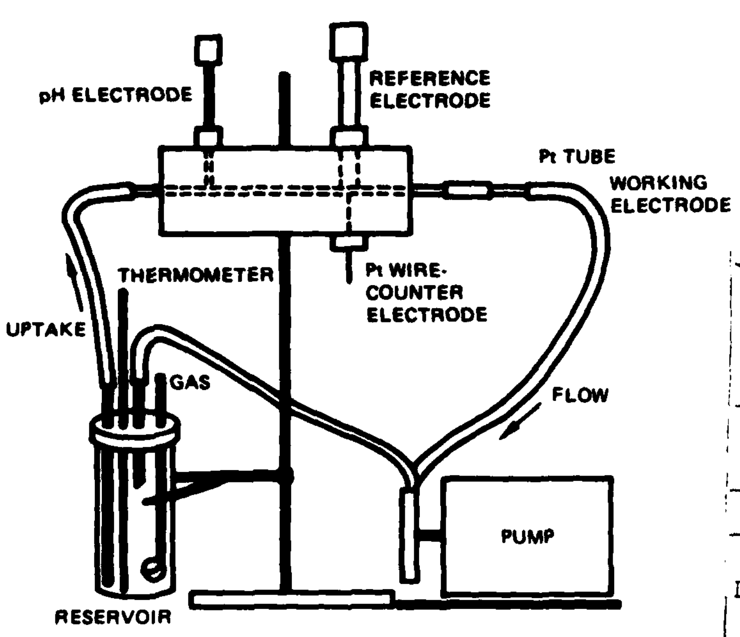

Figure 1. Closed continuous flow system.

For the polarographic determinations of $E_{i=0}$ current voltage measurements were made with a PAR #174-polarographic analyzer and recorded on a Rikadenki (Model B-361) three-pen strip-chart recorder. A Pt wire and a Fisher saturated calomel electrode (SCE) sealed separately into the teflon block were the counter and reference electrodes, respectively. The Pt tube was the working electrode.

Potentiometrically determined Eh values for the Pt surface were measured versus the SCE using an Orion Research Ion analyzer, Model 801 potentiometer and recorded on the Rikadenki three-pen strip-chart recorder.

Solutions:

Unfiltered Point Loma seawater sampled on 7 September 1979 was used for all determinations, 8N and 0.5 N HNO_3 solutions were used for cleaning the Pt surface. Dilute-it R brand pH 7 and 9 buffers prepared with distilled water were used for polarographically determined pH calibration. Pure CO_2 and a gas mixture of 300 ppm CO_2 with N_2 balance was used for the potentiometric pH measurements.

The Pt tube was cleaned by first immersing it in hot 8N HNO_3 for ten minutes and rinsing with distilled water. A potential of -750 mV versus SCE was applied using the potentiostat while a stream of 0.5 HNO_3 flowed through the tube. The tube was then rinsed with distilled water and placed in the set up shown in Figure 1.

Procedures:

Polarographic determinations were made by first establishing a constant flow of solution through the manifold system previously described. Then the potential was applied to the Pt tube from -375 to +370 mV at a rate of 0.1 mV/sec. Subsequently the potential was scanned in reverse from +370 to -375 mV. The cell current and pH were monitored on the three-pen recorder throughout both scans. The temperature was noted from the thermometer and recorded manually on the chart. The apparatus was rinsed with distilled water four times and conditioned with the sample twice before each set of scans was made.

Potentiometric determinations were made by establishing a constant flow of solution through the device and allowing the Pt surface to reach its equilibrium potential. Rinses were made as in polarographic determinations. Potentiometric pH calibration was done by establishing an initial pH value while bubbling the 300 ppm CO_2/N_2 gas mixture through the seawater in the reservoir and then lowering the seawater pH by increasing the concentration of CO_2 gas in the initial gas mixture. After each CO_2 increment the seawater pH was allowed to reach equilibriation and then the steady state value of Eh was obtained. Following each increase in CO_2 gas concentration, another increase was made in the same manner until several equilibrium points were obtained covering a pH range of 8.4 to 5.5. Again, pH and Eh were recorded on the three-pen recorder with the temperature noted manually on the stripchart recorder.

RESULTS AND DISCUSSION

Polarographic Scans:

When current was plotted as a function of applied potential, polarographic shaped curves were obtained for each scan (Figure 2). The $E_{i=o}$ values for seawater ranged from +38 to -7 mV for the scans in the positive direction and from 320 mV to 257 mV for scans in the negative direction (Table 1). For both positive and negative direction scans, anomalous currents were recorded. These typically result from oxide film formation (Reference 7). The difference in the anodically and cathodically determined $E_{i=o}$ values arises from the nonreversibility of the system in question and from the surface condition of the electrode. The Pt tube had been cleaned for scan 1 and remained in the set up uncleaned for scans 2 and 3 to observe any Pt surface aging that may have effected $E_{i=o}$. No conclusions could be made on aging effects. A fourth scan (not shown) was run on the Pt tube after it had been cleaned to obtain a fourth $E_{i=o}$ value. This $E_{i=o}$ value was 19 mV higher than the $E_{i=o}$ value determined for scan 1, although the anomalous currents recorded during previous scans were absent from both the positive negative directions scans for this last set of trials.

Potentials where the current first equaled zero during the scan, were selected only from the positive direction scans. This selection was based on the narrower ranges of $E_{i=o}$ values obtained from positive direction scans. As an example, the range of $E_{i=o}$ values obtained for seawater scans in the positive direction fall within a 45 mV range in comparison to the 63 mV range of $E_{i=o}$ values for the negative direction scans. A pH calibration plot derived from these $E_{i=o}$ values resulted in a scattering of data points. No predictions for the response of Pt to pH could be accurately made using the polarographic method.

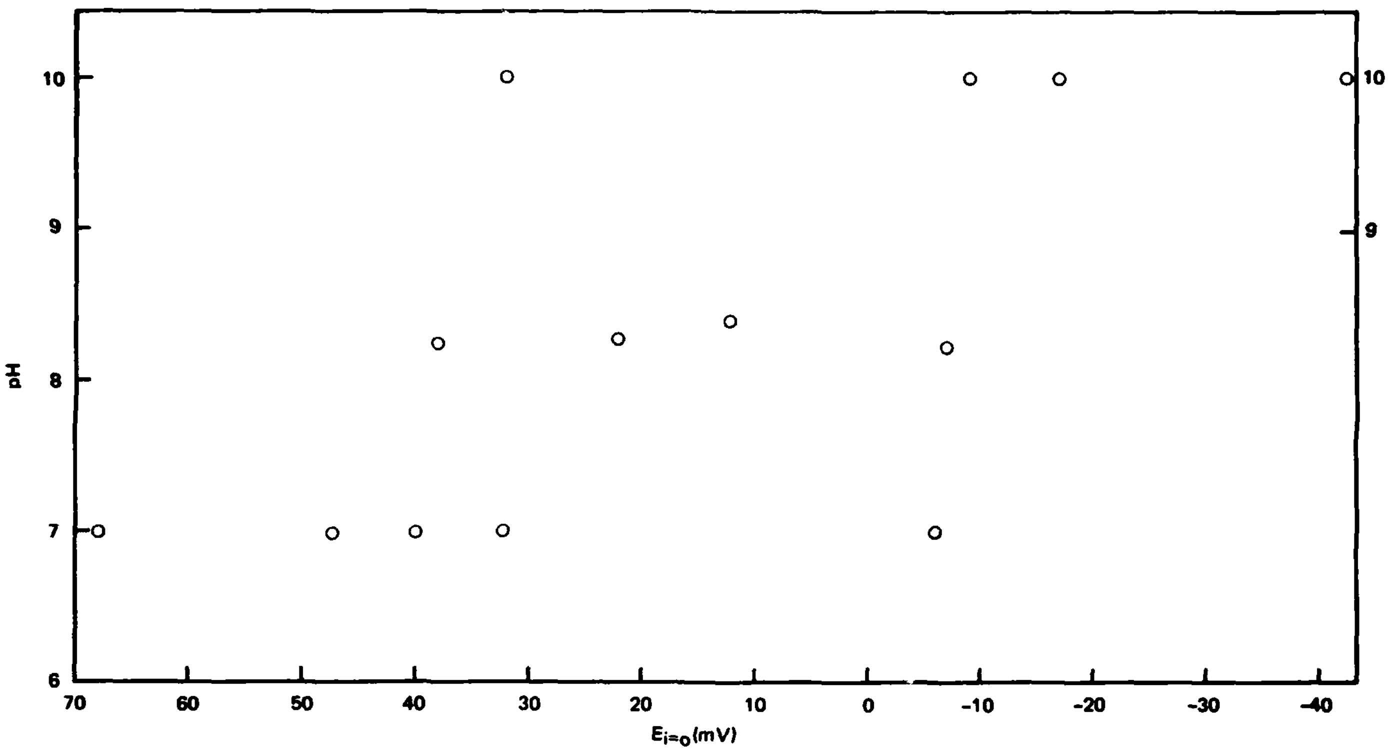

Figure 2. Polarographic calibration of Pt tube.

Potentiometrically Obtained Eh:

Eh values for seawater under a constant pCO_2 of 300 ppm and a pH value between 8.43 and 8.57 were between 186 mV and 208 mV (Table 2). The pH calibration for the Pt tube showed the Pt surface to respond to pH with one-third the response of the glass electrode, i.e., 59.03 mV/decade for the glass electrode and 21.67 mV/decade for the Pt tube. The calibration plot (Figure 4) was well defined and linear with a slope of 0.04 pH units/mV.

Scan Direction	pH	$E_{i=0}$ (mV) vs. SCE
+	7	+ 32*
+	7	+ 68*
+	7	- 6
-	7	+ 242
+	10	+ 42
-	10	+ 246
+	10	- 17
-	10	+ 249
+	10	+ 37*
+	10	- 9
-	10	+ 279
+	7	+ 47
-	7	+ 329
+	7	+ 40
-	7	+ 351
+	8.23	- 7
-	8.23	+ 320
+	8.26	+ 38
-	8.26	+ 287
+	8.26	+ 22
-	8.26	+ 257
+	8.42	+ 12
-	8.42	+ 281

(Scans are listed in sequential order)

*No reverse scans were obtained.

Table 1. Results of polarographic scans of pH buffers (7 and 10) and seawater.

pH*	Eh (mV) vs SCE
8.57	186.0
8.52	204.8
8.51	203.1
8.43	208.3

*Gas mixture of 300 ppm CO_2 balance N_2 bubbled through seawater samples to obtain pH.

Table 2. Eh of unfiltered Point Loma seawater.

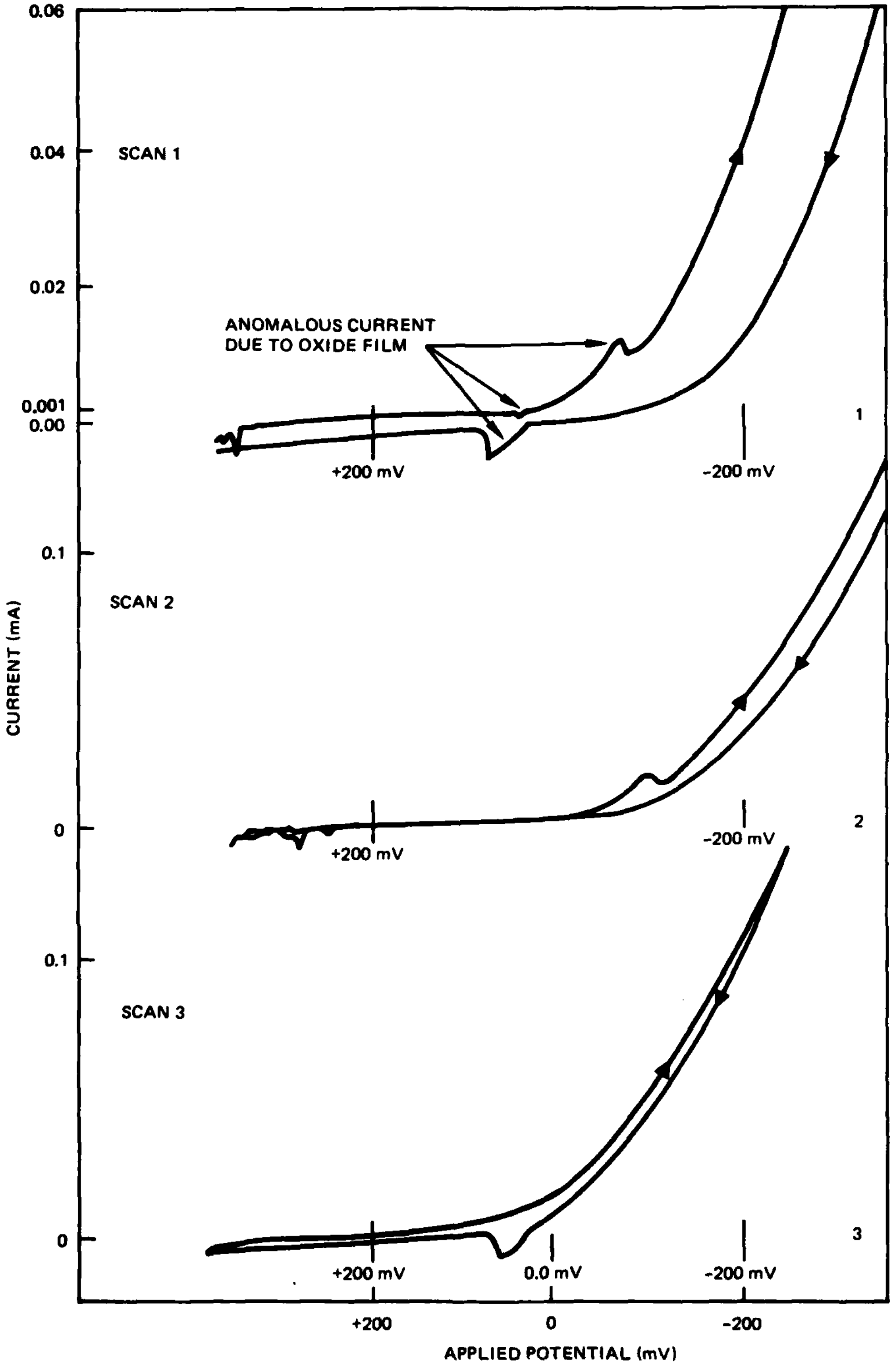

Figure 3. Polarographic scans of Pt tube in seawater.

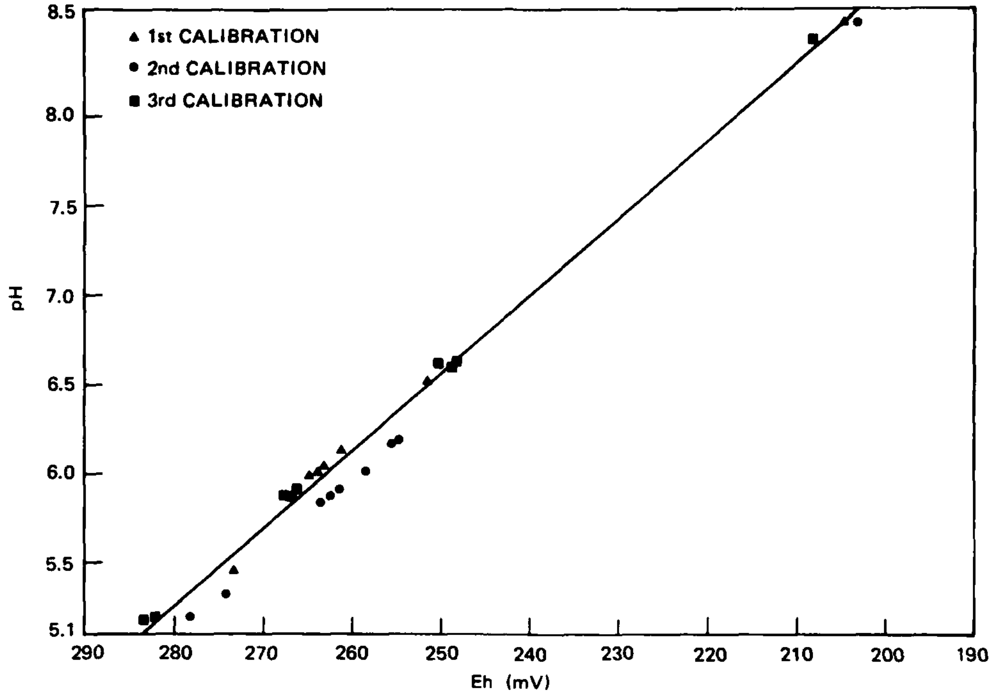

Figure 4. Potentiometric calibration of Pt tube.

CONCLUSION

Feasibility of Using a Pt Electrode in Seawater:

Detecting changes in solution will depend greatly upon the stability and reproducibility of the baseline from which to measure any changes. The Eh of seawater shows more promise as a baseline than the $E_{i=0}$ of seawater. The Eh values obtained appear to be more precise than the $E_{i=0}$ values; a 22 mV range versus 45 mV range. A reason for this difference in precision may be a result of no formation or extremely slow formation of an oxide film on the Pt surface in seawater without an applied potential. The oxide layer changes the surface characteristics of the Pt tube and it appears that oxide film formation lies at or near the $E_{i=0}$ determined by polarography. If this is the case an applied potential would be creating interference by changing the surface of the exposed Pt.

The sensitivity of the Pt tube to Ph was one-third that of the glass electrode used. Sensitivity may be increased by changing the exposed Pt surface from the shiny Pt used to a Pt black surface.

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