Effect of acidic water on physio-mechanical properties of building stone- a case study

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Abstract: The physico-mechanical properties of rocks play an important role in planning and designing of civil constructional works. These properties are adversely affected by acidic and alkaline environments, where they are exposed for a longer time. The natural forces and agents of weathering have a degrading effect on the appearance and structural soundness of Kota Stone. These agents include rain, temperature, wind and atmospheric pollutants. Weathering agents almost never work individually or in isolation, they always act in combination with one another or with other agents of deterioration.

The durability of building stones is primarily judged by its reactivity with acidic and basic water of different pH values. The conditions are very obvious in any of the large-scale constructions that use building stones like Kota Stone.

In this paper, an attempt has been made to assess the variation in the physico-mechanical properties of Kota Stone under different moisture conditions. In the present study, NX size cylindrical cores were prepared with the help of a diamond core drilling machine as per the ISRM standard. The prepared samples were dried in an oven for 24 hours at 104^0C to eliminate the moisture present. They were then submerged in water having different pH values ranging from nearly 0.89 to 12 for 24 hours till fully saturated at room temperature. The study revealed that there is a prominent change in strength properties under acidic and alkaline conditions. The strength reduction is due to the chemical reaction (corrosion) of the solution and Kota Stone. In acidic conditions, this is because higher concentration of hydrogen ions accelerates the rate of corrosion. However, under alkaline conditions that reduction in the strength properties of Kota Stone is also due to the fact that the liquid influences the surface energy of the specimens. As new surfaces are created during loading of the specimen, the fluid, which wets the surface of the rock, invariably decreases the surface energy and hence the strength properties. Rock is considered as a neutral substance so at pH 7, Kota stone shows maximum strength due to the non-reactive nature of the solution.

Résumé: Les propriétés physico-mécaniques des roches jouent un rôle important la planification et en concevant des travaux de construction civils. Ces propriétés sont compromises par les environnements acides et alkalins, où elles sont exposées pendant un plus long temps. Les forces et les agents normaux de survivre à ont un effet dégradant sur l'aspect et la solidité structurale de la pierre de Kota. Ces agents incluent la pluie, la température, le vent et les polluants atmosphériques. Survivant à les agents ne fonctionnent individuellement presque jamais ou en isolation, ils agissent toujours en combination avec un un autre ou avec d'autres agents de détérioration.

La longévité des pierres de bâtiment est principalement jugée par sa réactivité avec de l'eau acide et de base de différentes valeurs du pH. Les conditions sont très évidentes dans n'importe laquelle des constructions à grande échelle qui emploient des pierres de bâtiment comme la pierre de Kota.

En cet article, une tentative a été faite d'évaluer la variation des propriétés physico-mécaniques de la pierre de Kota sous différents états d'humidité. Dans la présente étude, des noyaux cylindrique de taille de NX ont été préparés à l'aide d'une foreuse de noyau de diamant selon la norme d'ISRM. Les échantillons préparés ont été séchés dans un four pendant 24 heures à 1040C pour éliminer le présent d'humidité. Ils ont été alors submergés dans l'eau ayant différentes valeurs du pH s'étendre presque de 0.89 à 12 pendant 24 heures jusqu'entièrement à saturé à la température ambiante. L'étude a indiqué qu'il y a un changement en avant des propriétés de force dans des conditions acides et alkalines. La réduction de résistance est due à la réaction chimique (corrosion) de la solution et de la pierre de Kota. En conditions acides, c'est parce qu'une concentration plus élevée des ions d'hydrogène accélère le taux de corrosion. Cependant, dans des conditions alkalines que la réduction des propriétés de force de la pierre de Kota est également due au fait que le liquide influence l'énergie extérieure des spécimens. Pendant que de nouvelles surfaces sont créées pendant le chargement du spécimen, le fluide, qui mouille la surface de la roche, diminue invariablement l'énergie extérieure et par conséquent les propriétés de force. La roche est considérée comme substance neutre ainsi à pH 7, force maximum d'expositions de pierre de Kota due à la nature non-réactive de la solution.

Keywords: physico-mechanical properties, pH, Kota Stone, corrosion.

INTRODUCTION

All carbonate materials are sensitive to acidic environments. Concern over the effect of pollutants on carbonate stone is directed to the economic consequences of damage to the stone used in construction as well as to the loss of the aesthetic value of historic buildings and monuments. In acid rain the primary contributions of hydrogen ion besides the natural sources of acidity are sulfurous, sulfuric, and nitric acids, which lower the pH of rain and accelerate weathering processes.

The incremental impact of hydrogen ion on carbonate rock is always not same. In equilibrium conditions, the incremental impact of hydrogen ion is expected to be small (~ 6 %) because of the dominant contribution to the equilibrium solubility of calcite (5.5 × 10 -4 M) by the reaction with carbonic acid from atmospheric CO_2 dissolved in rain water:

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3,$$

where,

$$H_2CO_3 \sim CO_2 (aqueous) \sim CO_2 + H_2 0.$$

However, under non-equilibrium conditions, the incremental impact of H^+ is difficult to predict, and can be quite significant if the dissolution process is controlled by reaction kinetics (Baedecker and Reddy, 1991). Many important structures, buildings and dams are exposed to acidic and alkaline environments in many countries. The degradation in physico-mechanical properties of Kota Stone (Limestone), in acid and alkaline conditions relates directly to the prediction of durability of project life and the evaluation of project benefit of the investors (Singh *et al*., 1999). The experimental study carried out by Dubey and Singh (2000) showed that the uniaxial compressive strength (UCS), tensile strength, shear strength, and cohesive strength observed in sandstone increased with increase in pH of water, while the angle of friction decreased with increase in pH of the saturating medium, i.e. water.

Kota Stone is basically a special type of limestone occurring in the Kota District of Rajasthan, India. Kota Stone is readily dissolved due to the presence of acidic agents, even low strength acids. However, the actual results of acidic exposure will vary with the nature of the acid. Chlorides, nitrates, sulfates and other chemical compounds react differently with carbonate rock and produce various by-products, which have a wide range of solubility and impact on the durability of calcium carbonate (Nierode and William, 1971).

Amongst the building stones, Kota Stone occupies a unique position in Indian construction and building industries. Since time immemorial, in India Kota Stone has been used in temples, mosques, churches, palaces, monuments etc. as an ornamental and decorative stone because of its pleasing colours, attractive patterns and designs. The natural forces and agents of weathering may have a degrading effect on the appearance and structural soundness of Kota Stone. These agents include rain, snow, temperature, wind and atmospheric pollutants. Weathering agents almost never work individually or in isolation, they always act in combination with one another or with other agents of deterioration (Baedecker and Reddy, 1991). Acid rain, especially in combination with atmospheric gases, results in dissolution of the Kota Stone, creating higher levels of salt movement within the micro-structure. Temperature can affect rates of deterioration and movement of the individual grains, as well as patterns of salt migration within the rock.

Boozer *et al*. (1962) reported that the deformational behaviour of Indiana Limestone and Navajo Sandstone are affected by fluids which are strongly absorbed on the surface of the grains of these rocks. The predominant effect of these fluids was observed as a decrease in ultimate strength of the sandstone and a decrease in the yield strength in the case of Indiana Limestone, which deformed in a ductile manner. In certain cases, it was observed that the type of failure of Indiana Limestone was ductile when the specimen was saturated with an inert liquid and brittle when the limestone was saturated with oleic acid. A study of the effect of moisture content on UCS revealed that the uniaxial compressive strength is almost inversely proportional to the surface tension of different acidic liquids with which the specimen is saturated (Colback and Wiid, 1965).

One principal theory has been proposed to explain the mechanism by which the liquids affect the compressive strength of various rocks. The strength is altered by a change in the surface free energy of the developing crack or the fracture due to the absorption of the liquid (Rehbinder *et.a.l*, 1944). In a study of the effect of water on the physico-mechanical behaviour of rock, results revealed that the acidic water changed the behaviour and strength of the rock. The strength decreased linearly from neutral pH to the acidic condition (Singh *et.al.*, 1999).

Most of the researchers have investigated the rock response behaviour under acidic conditions i.e. pH below 7, but the effect of alkalinity on the strength of the rock has not been fully understood. In the present paper, an attempt has been made to study the effect of the entire range of pH (0.89 to 12) on the physico-mechanical properties of Kota Stone.

METHODOLOGY

The representative Kota Stone blocks were collected from the quarry of Kota district, Rajasthan for coring and facing. These blocks were drilled by a coring machine using a NX size drill core bit. These samples were prepared as per the ISRM standard (ISRM, 1981). The prepared samples were put into the oven for 24 hours at 104^0C to eliminate the moisture present within them and then treated and tested under the different pH solutions. Then, these samples were tested to understand the behaviour of Kota Stone in various moisture conditions.

The different physio-mechanical properties of Kota Stone such as, uniaxial compressive strength (UCS), tensile strength, shear strength, triaxial strength (cohesive strength and angle of internal friction), point load strength index, density, Young's modulus, Poisson's ratio, and P-wave velocity were determined at different pH values in the laboratory. The NX size rock specimens were placed in between the platens of a Universal Testing Machine (UTM) and loaded at constant loading rate of $3.5 x 10^3$ Pa/sec until they failed (ISRM, 1979). The load and deformation curve obtained from the UTM was utilized to determine the modulus of elasticity and uniaxial compressive strength of the Kota Stone.

The specimens were tested at different pH values 0.89, 1.9, 4, 6, 7, 8, 10 and 12 to determine the uniaxial compressive strength (ISRM, 1979). The maximum value of UCS was found at pH 7 whereas the lowest was at 0.89 pH (Figure 1). The strength reduction under acidic conditions is due to the chemical action of the pH solution on rock composition. Rock is considered as a neutral substance so at pH 7, Kota Stone shows maximum strength due to non-reactive nature of the solution and subsequently deteriorates in strength under acidic and alkaline conditions. Calcium carbonate, however, of which Kota Stone is mainly composed, is highly susceptible to attack by acidic agents. Kota stone is readily dissolved under acidic condition, even though very dilute solution. However, the actual results of acidic exposure vary with the nature of the acids. At low pH value, dissolution of Kota Stone is faster because acid has more free charged particles that bind to the CO_3 of the Kota Stone. In all the cases, fractures were originated near the centre of the specimens, and migrate towards periphery where the axial stress is higher.

The tensile test was conducted to determine the strength of Kota Stone. In this test, a circular disc (1:1) was compressed across the diameter till the failure occurred. It was found that at 0.89 pH the tensile strength was 80.81 kgf/cm^2, which was the lowest, while at 7.0 pH, 108.8 kgf/cm^2 which was the highest. Figure 2 shows that tensile strength increases up to pH 7.0 and then started decreasing afterwards. The fracture initiated from the central part of the disc and propagated radially. The decrease in tensile strength of Kota Stone is due to the fact that the liquid influences the surface energy of the specimens and, as new surface originates during loading of the specimen, the liquid, which wets the surface of the rock, invariably decreases the surface energy of the rock specimen and hence the tensile strength of the same.

To determine the shear strength of the Kota Stone core specimens were tested on a universal testing machine with double shear box (ISRM, 1974). The results showed maximum shear strength at pH 7 and minimum shear strength at 0.89 pH (Figure 3). The Kota Stone specimens were tested to determine the point load strength index by using a point load testing machine. The maximum point load strength index was found at 7 pH. However, it decreased under acidic and alkaline conditions with minimum value at 0.89 pH (Figure 4).

P-wave velocity depends upon the density, water content, strength and discontinuity. The P-wave velocity was found to be maximum at 7 pH while decreasing in acidic and alkaline conditions (Figure 5). The trend indicates that percentage reduction in P-wave velocity is sharper in acidic environment and gentle in alkaline environment. Density of the Kota Stone is found maximum at 7 pH and minimum at 0.89 pH. The chemical reaction of acidic agents with the Kota Stone has reduced the density (Figure 6). Young's modulus was measured as 28407.31 kg/cm^2 at 7 pH. However, it shows a decreasing trend in acidic and alkaline condition similar to the other physico-mechanical properties (Figure 7).

Poisson's ratio has an inverse relationship with strength so it was found minimum at 7 pH and was showing an increasing trend in acidic and alkaline conditions. The Poisson's ratio was found maximum at 0.89 pH (Figure 8). The UCS is lower at pH 0.89 whereas Poisson's ratio shows higher at the same pH values. It is true for all the strength properties like tensile strength and shear strength. The surface damage is maximum as compared to its inner surface; this might gives higher lateral deformations.

RESULTS AND DISCUSSION

Table 1 lists average geotechnical properties of Kota Stone in varying pH solutions. Figures 1-8 show the plots between the pH and UCS, tensile strength, shear strength, point load index, P-wave velocity, density, Young's modulus and Poisson's ratio. The trend of all the graphs is best correlated by a parabolic curve fitting, which provides a better coefficient of correlation.

Table 1. Physico-mechanical properties of Kota Stone at different pH.

pH Value	Uniaxial Compressive Strength (Kgf/cm^2)	Tensile Strength (Kgf/cm^2)	Shear Strength (Kgf/cm^2)	Point load strength index (Kgf/cm^2)	P Wave Velocity (m/s)	Density (g/cc)	Young's Modulus ($10^3 Kgf/cm^2$)	Poisson's Ratio
0.89	695	80.81	132.61	30.2	6258	2.52	23.96	0.17
1.9	750	85.22	137.82	32.6	6437	2.59	24.85	0.21
4	866	99.54	144.52	35.46	6667	2.68	25.99	0.23
6	924	103.8	154.67	38.5	7016	2.83	27.73	0.26
7	980	108.8	158.63	40.4	7152	2.88	28.41	0.27
8	980	96.3	157.17	40.36	7102	2.86	28.16	0.25
10	954	94.3	152.17	38.4	6949	2.80	27.39	0.23
12	882	89.2	148.18	36.4	6793	2.74	26.62	0.20

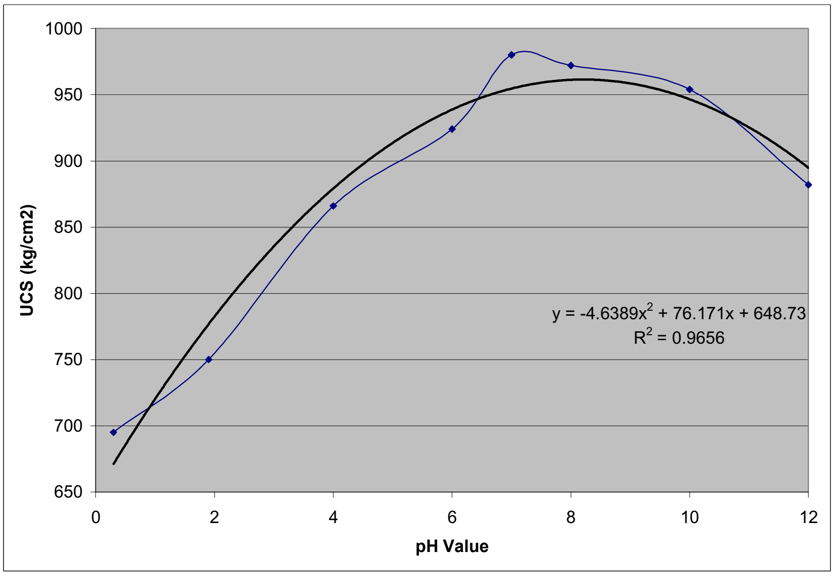

Figure 1. Relation between pH and uniaxial compressive strength.

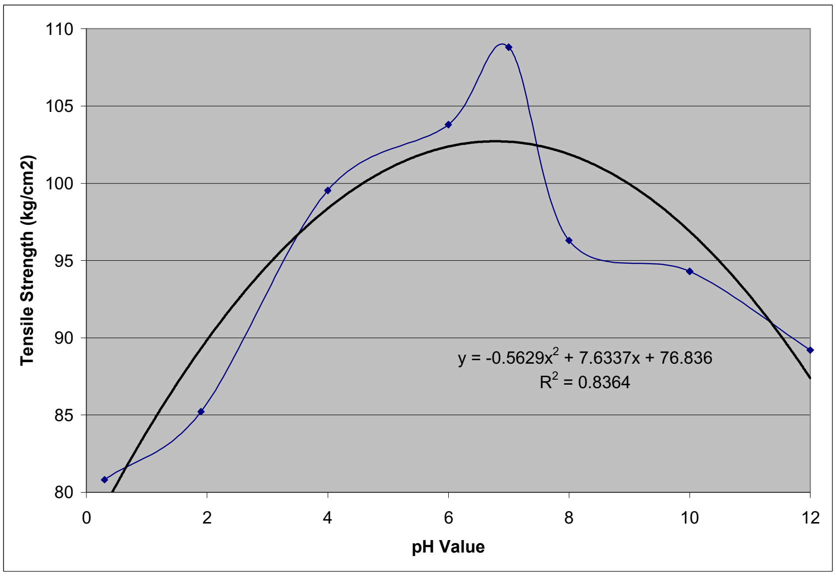

Figure 2. Relation between pH and tensile strength.

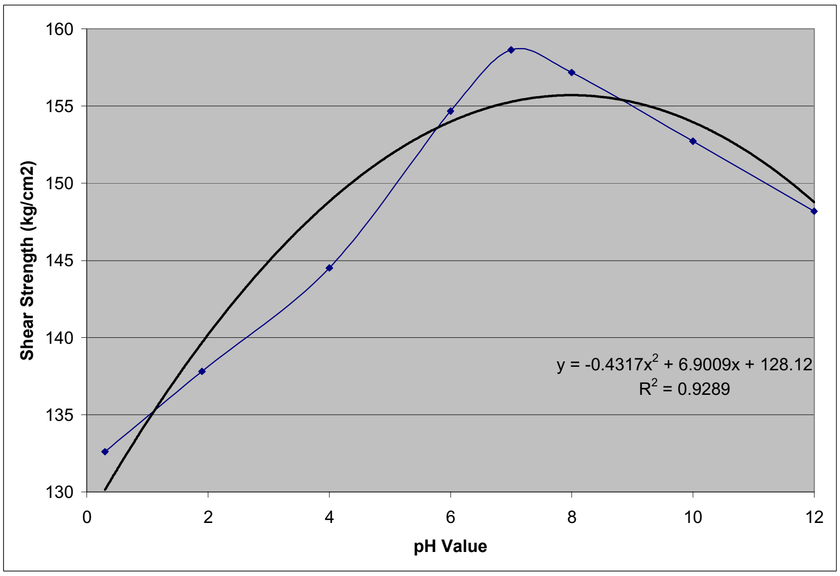

Figure 3. Relation between pH and shear strength.

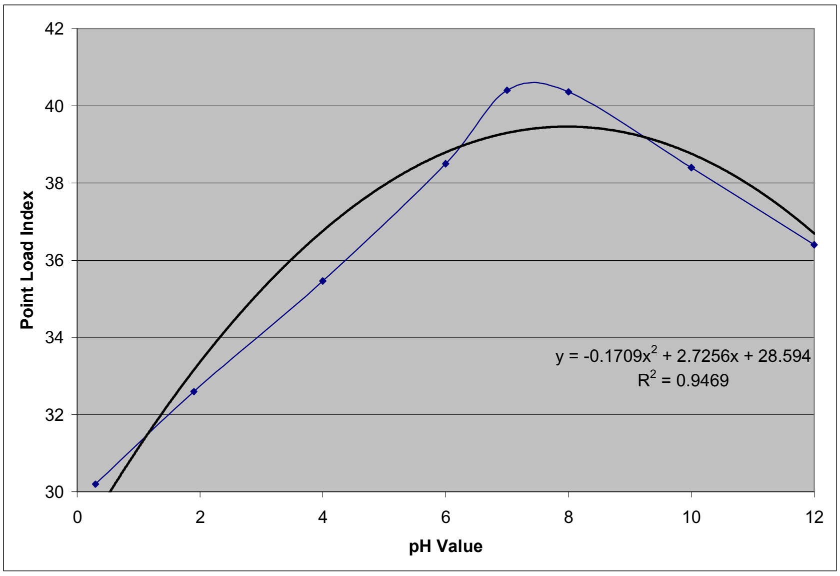

Figure 4. Relation between pH and point load index.

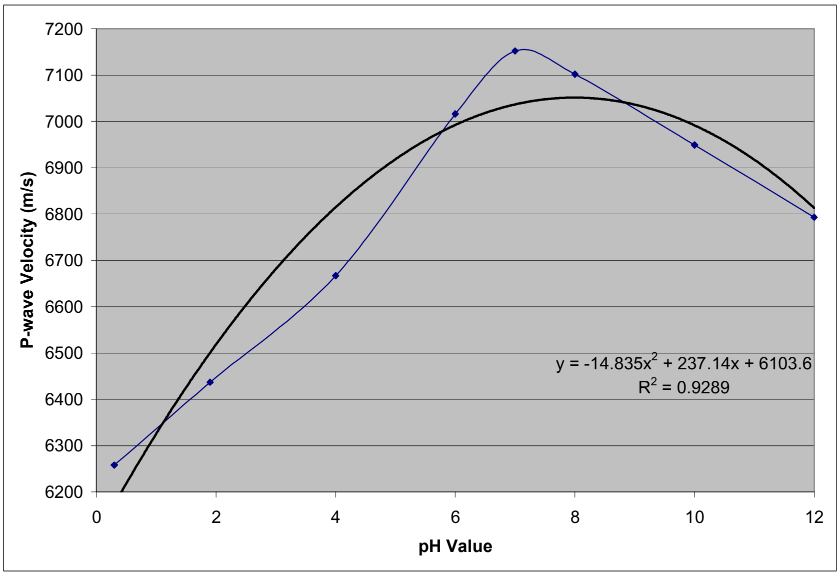

Figure 5. Relation between pH and P-wave velocity.

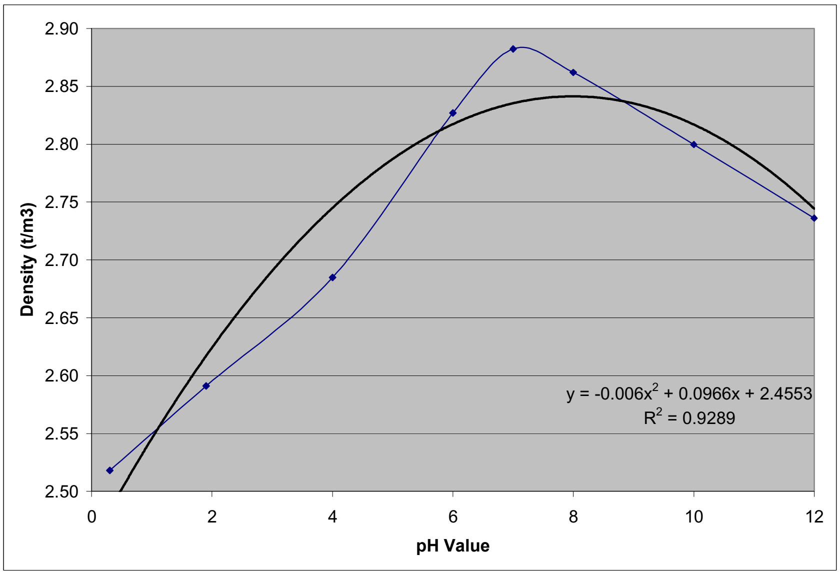

Figure 6. Relation between pH and density.

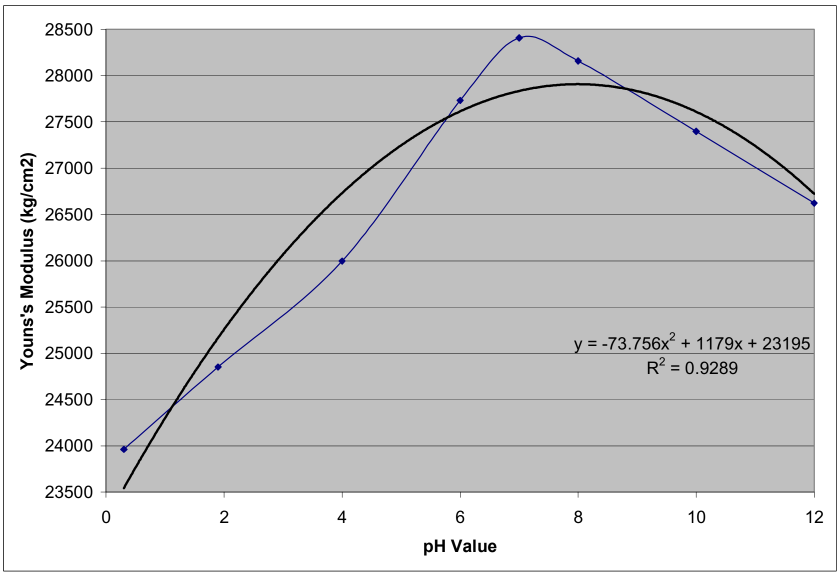

Figure 7. Relation between pH and Young's modulus.

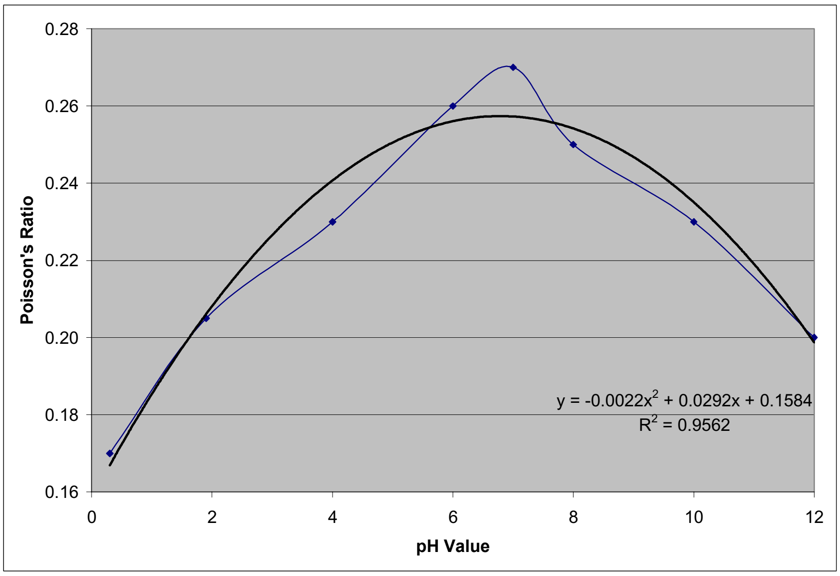

Figure 8. Relation between pH and Poisson's ratio.

CONCLUSIONS

The study reveals that the physico-mechanical properties of Kota Stone are adversely affected by the acidic and alkaline moisture conditions. The reduction in strength properties is higher in an acidic environment as compared to an alkaline environment. In acidic conditions higher reduction in strength is due to the fact that higher concentration of hydrogen ions accelerates the rate of corrosion.

The correlation coefficient varies from 0.9289 to 0.9656 for different physico-mechanical properties. From these correlation coefficients it can be said that these empirical equations can be used for the estimation of physico-mechanical properties of calcareous rocks at different pH ranges. This study will help to understand the behaviour of rock structures, which are suffering due to the presence of different moisture environments. However, more tests and data are required to determine a generalized empirical equation.

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