Characterization and Compositional Analysis of Indian Black Aggregate as a Concrete Raw Material

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Abstract

The study is conducted to find the applicability of Indian black aggregate as a concrete material through a series of physiochemical and surface morphological investigation. The report reveals the effects of different chemical properties on concrete performance which ultimately affect the life period of any structure. Mineralogical and Chemical characterization of the aggregate was analyzed by UV visible spectroscopy (UV-vis), X-Ray Fluorescence (ED-XRF) and X-Ray Diffraction (XRD). Scanning electron microscopy (SEM) used to know Surface morphology of the aggregate. It was observed that studied aggregate containsthe a high amount of MgO (4.36%) and Fe_2O_3 (14.84%). However, it is quite stable up to 800 °C with a a loss of only 1.58% of gross weight. The surface morphology analysis clearly revealed the existence of Calcite, Quartz and Dolomite materials in studied aggregate.

Keywords: Black aggregates; physiochemical properties; surface morphology, minerals.

1. Introduction

One of the fundamental elements of concrete construction is stone aggregate which is produced around 10 billion cubic meters in a calendar [1] which are basically mine based whose significant production and use as reinforcement in concrete started during Roman empire. It has an urgency to know the physiochemical properties and their effects of stone aggregates as they are the major part of any concrete and serving as a reinforcement by adding strength to overall concrete structure. Durability problems of the concrete structure are frequently observed for the last few decades which are majorly due to the exposed to the watery environment [2-4] where corrosion is propagated through a series of steps [5]. Concrete foundation deterioration was also occurred in a few housing developments in the Trois-Rivières area (Québec, Canada) just after two to four years of construction [6]. Presence of pyrite (FeS2) and pyrrhotite in construction aggregates are one of the predominating reasons to cause concrete deterioration [7-9]. Other sulphide minerals are also responsible for such problems [10-13]. Underground foundations, roads, and railroads use aggregates as a low-cost extender that combines with more costly cement or asphalt to form concrete. The use of qualified aggregates is very important for sustainable concrete structure [14-16].

It is well known that the strength, stiffness, retraction and permeability and durability of fresh concrete completely depends on the texture, shape and gradation characteristics of the used aggregates. The influence of aggregate characteristics on the overall quality and durability of concrete is reported by many researchers [17-19]. Hardened concrete behavior such as shape and texture; gradation; absorption; mineralogy; compressive strength and elasticity modulus; maximum size; specific gravity; sulfates attack resistance and hardness are found to depend on characteristics fresh aggregate [19-21]. To know surface morphology of the aggregates and concrete, scanning electron microscopy (SEM) measurement is very common [20-21]. The SEM observation provides information on the network of external and internal pores of the aggregates [20-21] which has an extensive effect on water absorption; concrete formation and final hardened strength (after 28 days) of the structure.

The study was performed to understand the physiochemical and mineralogical composition of widely used natural Indian black aggregate to find its applicability in the concrete structure, which included the assessment of their influence on concrete properties. It was also aimed to explain the surface morphology of the studied aggregate.

2. Materials and Methods

2.1 Sample processing

Samples collected for the experiments were in different shapes and size form different part of raw materials stock imported from India. After screening with the sieve, aggregates of the desired shape were obtained which were used for sample preparation. Four types of samples were prepared which were coarse aggregate, fine aggregate, powdered sample and aqueous stock solution for physiochemical experiments. The stock solution was prepared by transferring 50 gm dry sample in a 500 ml volumetric flask which was up to marked with distilled water then stirring was done for 15hr on a magnetic stirrer when the temperature was maintained below 60℃. Final stock solution was obtained after centrifugation at 4000 rpm and filtration which was used for wet chemical analysis. Powdered sample (sieve-200) was prepared by grinding collected aggregates with a hammer which was used for elemental and morphological analysis.

Table 1: Name of different tests and their standard testing methods

Name of Tests	Standard Testing Methods
Physiochemical Tests	
Moisture content (%)	ASTM C70
Water absorption (%)	ASTM C127
Density (kg/m^3)	ASTM C29
Specific gravity	ASTM C127
Porosity (%)	ASTM C29
Chemical Tests	
Nitrate (NO_3^-)	ASTM C1580
Chlorine (Cl^-)	ASTM C1218
Phosphate (PO_4^{2-})	-
Sulphate (SO_3^{2-})	ASTM C1580
pH	ASTM C33

2.2 Aqueous stock solution

The aqueous stock solution was prepared for wet chemical analysis. The sample was prepared by ASTM standard method. 50 gm sample was weighed and transferred to the 500 ml volumetric flask. Volumetric flask filled up with distilled water. Kept the volumetric flask for 15hr on a magnetic stirrer for digestion and temperature maintained up to 60 ℃. Sample transferred to centrifuge equipment after digestion, set the motion of centrifuge at 4000 rpm and continue this process for 10 min. After that clean solution was collected in a beaker for continue wet chemical analysis.

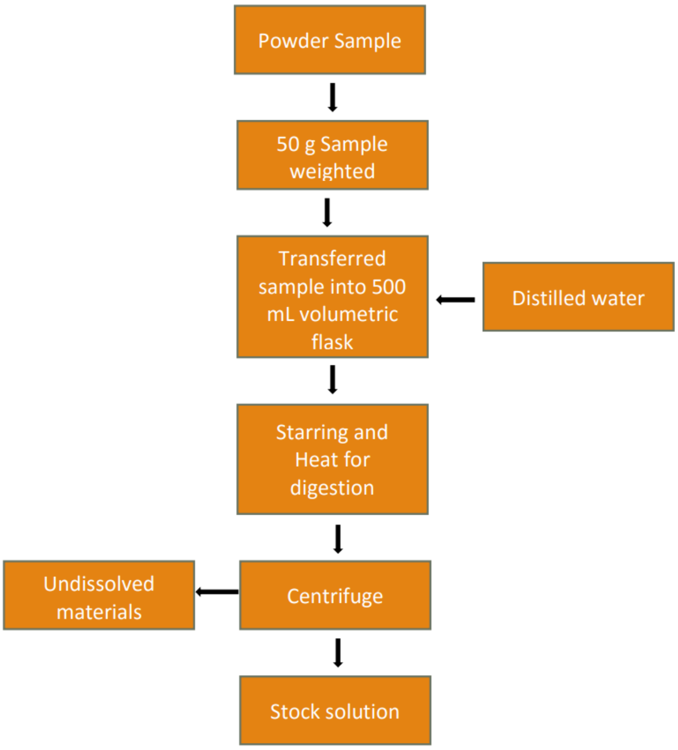

Figure 1: Block diagram presentation for aqueous stock solution preparation technique.

2.3 Quantitative analysis

For qualitative analysis, we prepared two types of sample one were powder sample and other was solution base. We used UV spectrophotometer for measuring the concentration of ion present in the sample solution. XRD and EDXRF was used for measuring the composition of different compound present in powder sample aggregates.

2.4 Characterization of sample

For characterization of sample, various instruments were used. Scanning electron microscope (SEM) used for morphology analysis, stability measurement and helps to analyze the behavior of the component. X-Ray Detraction (XRD) used for identified the crystal structure, metallic component identification (Dolomite, Calcite etc.) and XRD pattern also used for investigation of reaction occur in construction. Energy Dispersive X-ray Fluorescence (EDXRF)for non-destructive elemental analysis. EDXRF spectrometers are the elemental analysis tool for analysis Cement and raw metal: sulfur, iron, calcium, silicon, aluminum, magnesium, etc; Kaolin clay: titanium, iron, aluminum, silicon, etc. Durable Analyzers for thermogravimetric analysis (TGA) of organic & inorganic samples.

3. Results and Discussions

3.1 Physiochemical analysis

All aggregates contain some moisture depending on the porosity of the particles and the storage condition, which is an important factor while developing the proper water/cementitious material ratio for a concrete structure. This experiment shows moisture content of the aggregate about 1.65% whereas the maximum limit is

1-2% which are represented in Table 1. The porosity of the assigned aggregates found nearly 39% which may influence water absorption and influence bonding between aggregates and surrounding hydrates paste of cement while concrete formation. It was also found that the density of the aggregate is about 19% more numerically 2858.2 Kg/m^3 than the standard value which is 2400 kg/m^3 which is acceptable because it will not affect construction design remuneration which would have to do if density were too high.

The acid test is another important experiment performed to check the insoluble residues in aggregate. A good aggregate maintains its sharp edges instead of breakdown and keeps its surface free from powder at the end of acid test which also indicates better weather ability of aggregates. From the report of acid test experiment, we observed stable edges of the studied aggregate beside the formation of traces of powders on the surface with a change of color which is acceptable. This experiment has also confirmed good crystalline stability of the aggregates.

Volumetric percentage of silt in fine aggregate another crucial parameter which affects overall strength and durability of any concrete structure. In this test, mixed aggregate chosen from a different part of aggregates stock were sieved with 4.75 mm sieve and silt content measurement was done following BS 882. Based on the analysis, the maximum silt content was observed about 2.3`% whereas BS 882 and ASTM C40 recommends that fines aggregates should not be used in concrete structure if its silt content is more than 6% [10]. Previous studies indicate that concrete's durability is intensively affected by silt content, especially when it is more than 5% [10]. So, from the observation of this, silt content is within the allowable limit so it will not affect concrete durability and strength.

Table 2: Physiochemical properties of coarse aggregates

Test type	Measured value	Permissible/Standard limit	Testing method
Moisture content (%)	1.65	1-2%	ASTM C70
Water absorption (%)	0.50	Max 2%	ASTM C127
Density (kg/m^3)	2858.02	2400	ASTM C29
Specific gravity	2.85	2.6-2.9	ASTM C127
Porosity (%)	38.7	-	ASTM C29
pH (%)	7.89	7.5-9.5	ASTM C33

3.2 Wet Chemical Analysis

Chloride is one of the corrosive species, when present sufficiently, has a potential threat to accelerate corrosion of metallic components of concrete, such as steel. ASTM C1218/C1218 Method has been used to determines water-soluble chloride which was found 0.12 mg ion/Kg much lower than the permissible limit. so, this aggregate has no certain tendency to cause chloride-based trouble inside the concrete. Similarly, Nitrate and phosphate are within the standard limit, so they are also not a matter of major concern. Excessive amounts of mobile Sulphate, derived from aggregates or other constituents in concrete, can cause disruption due to expansion. The concentration of different ion present in aggregates was analyzed by Ultraviolet-Visible Spectrophotometer (UV-vis) and the obtained results are shown in Table 2. It was observed that the amount of dissolved sulfate ion presented in Indian black aggregates are within standard limit but very close to the upper limit. So, this parameter may have trace impact on the concrete for a long duration.

Table 3: Water-soluble ion content amount present in aggregate

Ion name	Measured value (mg ion/kg sample)	Standard Limit	Method
Nitrate (NO_3^-)	0.8	Max. 3%	ASTM C1580
Chlorine (Cl^-)	0.12	Max. 0.1 % by mass	ASTM C1218
Phosphate (PO_4^{2-})	0.54	No data	No data
Sulphate (SO_3^{2-})	44.98	15-55	ASTM C1580

3.2 Chemical composition Analysis

We have done EDXRF measurement for elemental analysis to check the presence of the major and minor element in wt/wt percentage in the black aggregate which shown in details in Table 3.

Table 4: Percentage of elements present in black aggregates

	Na_2O (wt.%)	MgO (wt.%)	Al_2O_3 (wt.%)	SiO_2 (wt.%)	CaO (wt.%)	K_2O (wt.%)	Fe_2O_3 (wt.%)
Value	2.3032	4.365	16.1343	45.6864	12.8355	0.7599	14.8465

The obtained EDXRF result resembling that black aggregate is enriching in Fe_2O_3 and MgO. An aggregate with a high unbound iron content may result in oxidation, discoloration, softening, and loss of the mineral over time. An increasing free iron oxide content in aggregates has an adverse effect on the soil-concrete interface which ultimately decreases the strength of the concrete and increases surface roughness [24]. Magnesium hydroxide and Magnesium carbonate have an aggressive behavior toward dolomite whose presence is confirmed by X-ray diffraction (XRD) in the working aggregate [25].

X-ray diffraction analysis concluded that silica is represented by low-quartz, and reactive silica (amorphous silica and quartz high) was not determined (Fig. 2). There is no single pattern indicating intense curve matched with opal (amorphous silica; reactive silica). According to them, there is no other reactive high-quartz in the sample as silica scanning does not reveal such. Reactive silica is therefore absent from the studied black aggregates. The existence of feldspar is more likely to have a solid origin. Therefore, percentages of constituent minerals indicate that the rock can safely be used as an aggregate with ordinary Portland cement and high alkali cement.

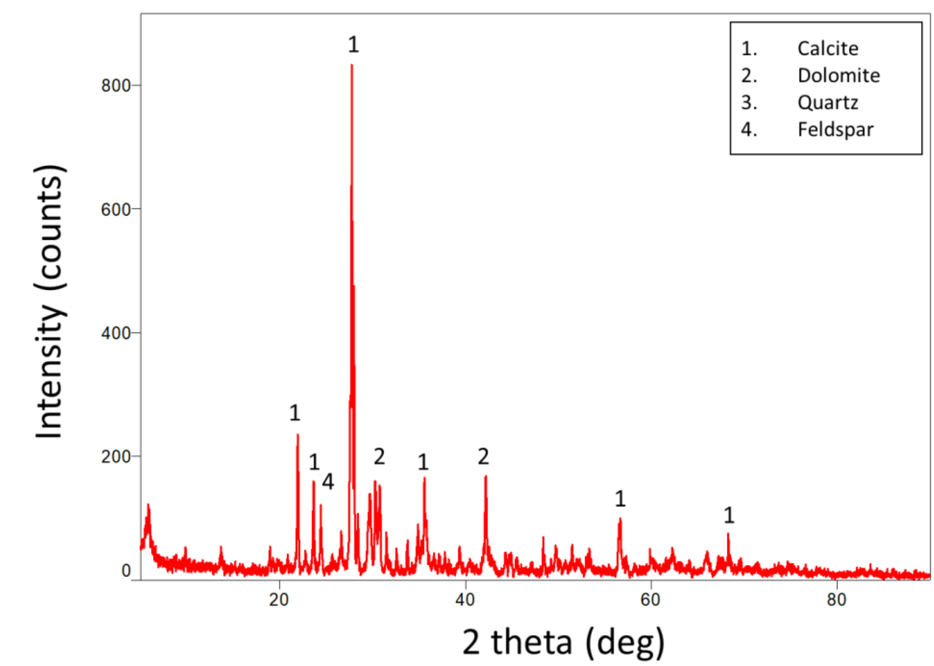

Figure 2: XRD spectra of black aggregate

3.3 Surface morphology study

SEM experiment was done to check the microcrystalline structure of the aggregates. Figure 3 shows the SEM image of black aggregate which shows the presence of calcite, dolomite and some quartz. The Dolomites are frequently attacked by magnesium base compounds in some specific conditions whereas quartz and calcite are almost stable. On heating beyond 573 °C, quartz undergoes rapid expansion due to phase transition whereas calcite shrinks due to decomposition at 900 °C [25].

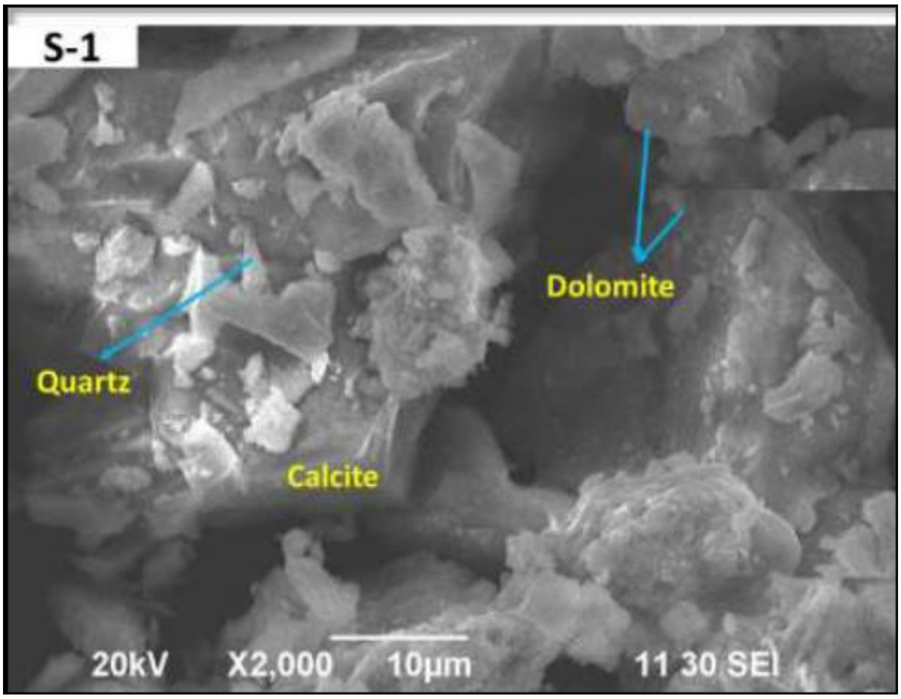

Figure 3: SEM image of the black aggregate

3.4 Thermogravimetric Analysis:

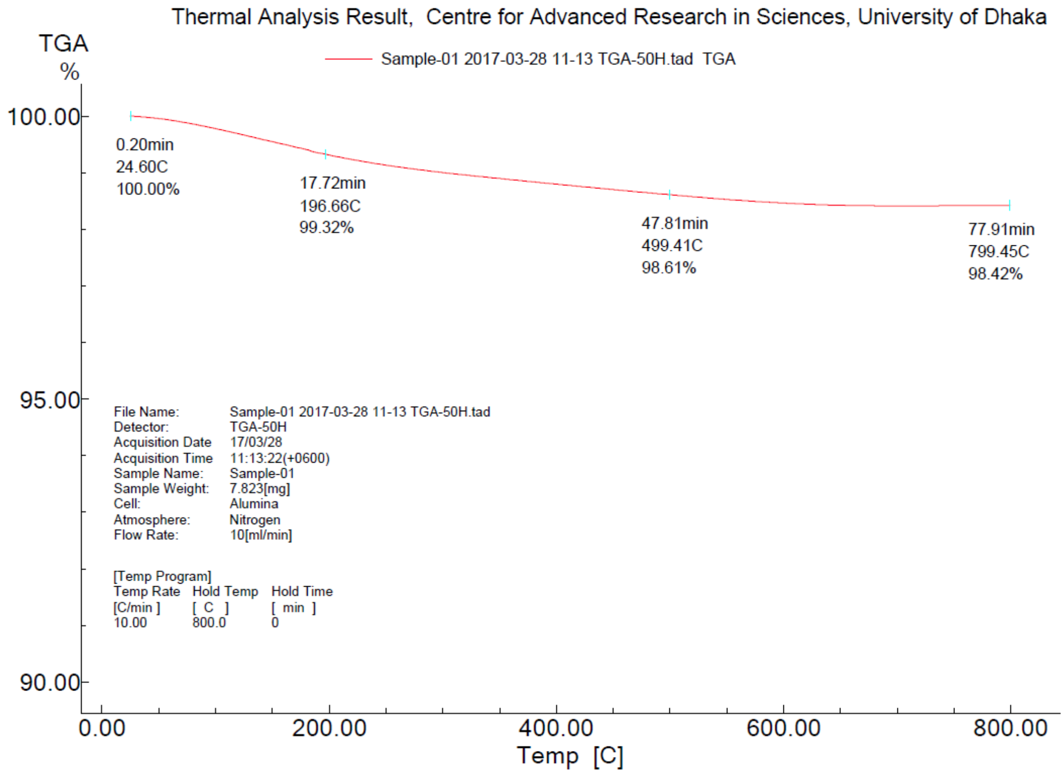

Figure 4: TGA image of black aggregate

Data form TGA analysis shows that the aggregate is quite stable till 100 ^{o}C and they undergo normal thermal expansion beyond that weight loss started which may be simply moisture loss by the aggregates which continues until complete removal of moisture. Hydrate decomposition started at around 450-550 °C at the same time coarsening of pores also take place which may responsible for the observed weight loss [25]. Quartz undergoes rapid expansion because of the phase transition at 573 °C whereas calcium carbonate decomposes at 600 °C but calcite is indecomposable bellow 900 °C [25]. Similarly, rehydration of any structure undergoes expansion [25] which is also a point of concern. As a structure in general, are not exposed to so high temperature as shown in the above Figure 4 and there in no sharp decrease of weight loss found in TGA analysis, the aggregate can be safe for constructing roads and buildings and other structures.

4. Conclusion

Indian black aggregate studied in this work contains a very small amount of silt materials was Indian black aggregate which is about 2.3%, whereas, world standard limit is maximum 4-6%. From EDXRF, it is clear that black aggregate contains a high amount of silica Fe_2O_3 and MgO. Moreover, the durability of any concrete depends on many parameters in which, silica is very important who manipulates the alkali-silica reaction. From SEM, it was observed that calcite, Quartz, and Dolomite clearly exist in studied aggregate.

5. References

1. Meyer C. The greening of the concrete industry. *Cem Concr Compos* 2009;31(8):601–5.

2. Zivica V, Bajza A. Acidic attack of cement based materials - a review. Part 1. Principle of acidic attack. *Construct Build Mat* 2000; **15:331**-40.

3. Collepardi M. Simplified modelling of calcium leaching of concrete in various environments. *Mat Struct Mat Const* 2002;**3**:633-40.

4. Beddoe RE, Dorner HW. Modelling acid attack on concrete: Part I. The essential mechanism. *Cement Concrete Res* 2005;**35**:2333-39.

5. Vollertsen J, Nielsen AH, Jensen HS, Andersen TW, Jacobsen TH. Corrosion of concrete sewers—The kinetics of hydrogen sulfide oxidation, *Sci Envi* 2008;**394**:162-170.

6. Josée Duchesne and Benoît Fournier, Deterioration of Concrete by the Oxidation of Sulphide Minerals in the Aggregate, Journal of Civil Engineering and Architecture, Aug. 2013, Volume 7, No. 8 (Serial No. 69), pp. 922-931 ISSN 1934-7359, USA

7. J.P.R. de Villiers, D.C. Liles, The crystal-structure and vacancy distribution in 6C pyrrhotite, American Mineralogist 95 (2010) 148-152.

8. D.C. Liles, J.P.R. de Villiers, Redetermination of the structure of 5C pyrrhotite at low temperature and at room temperature, American Mineralogist 97 (2012) 257-261.

9. M. Becker, J. de Villiers, D. Bradshaw, The mineralogy and crystallography of pyrrhotite from selected nickel and PGE ore deposits, Economic Geology 105 (2010) 1025-1037.

10. I. Casanova, L. Agullo, A. Aguado, Aggregate expansivity due to sulphide oxidation—I. Reaction system and rate model, Cement and Concrete Research 26 (1996) 993-998.

11. J. Berard, R. Roux, M. Durand, Performance of concrete containing a variety of black shale, Canadian Journal of Civil Engineering 2 (1975) 58-65.

12. . S. Chinchon, C. Ayora, A. Aguado, F. Guirado, Influence of weathering of iron sulfides contained in aggregates on concrete durability, Cement and Concrete Research 25 (1995) 1264-1272.

13. [13] C. Ayora, S. Chinchon, A. Aguado, F. Guirada, Weathering of iron sulfides and concrete alteration, Cement and Concrete Research 28 (4) (1998) 1223-1235.

14. Braga M, de Brito J, Veiga R. Incorporation of fine concrete aggregates in mortars. Constr Build Mater 2012;36:960–8.

15. Smith BJ, Roberts LR, Funkhouser GP, Gupta V, Chmelka BF. Reactions and surface interactions of saccharides in cement slurries. Langmuir 2012;28:14202–17.

16. Pereira P, Evangelista L, de Brito J. The effect of superplasticisers on the workability and compressive strength of concrete made with fine recycled concrete aggregates. Constr Build Mater 2012;28:722–9.

17. T.Y. Lo, W.C. Tang, H.Z. Cui. The effect of aggregate absorption on pore area at interfacial zone of lightweight concrete, Construction and Building Materials, 2008, 22, 623-628.

18. T. Y. Lo, H.Z. Cui, W.C. Tang, W.M. Leung. The effects of aggregate properties on lightweight concrete, Building and Environment, 2007, 42, 3025–3029.

19. D. Fragoulis, M.G. Stamatakis, E. Chaniotakis, G. Columbus. Characterization of lightweight aggregates produced with clayey diatomite rocks originating from Greece, Materials Characterization, 2004, 53, 307–316.

20. İ.B. Topçu, T.U. Lu. Effect of aggregate type on properties of hardened self-consolidating lightweight concrete (SCLC), Construction and Building Materials, 2010, 24, 1286-1295.

21. B. Ruggero, S. Filippozzi, E. Princi, C. Schenone, S. Vicini, Acoustic and mechanical properties of expanded clay granulate consolidated by epoxy resin, Applied Clay Science, 2010,48, 460–465.

22. Shih-Wei Cho. Effect of Silt Fines on the Durability Properties of Concrete. Journal of Applied Science and Engineering, Vol. 16, No. 4, pp. 425-430 (2013).

23. Lerch, William, 1955, Chemical reaction of concrete aggregate: American Society for Testing and Materials Special Technical Publication 169, p. 334- 345.

24. F. Okonta, A. Derrick The Effect of Iron Oxide on the Strength of Soil/Concrete Interface, Proceedings of the 15th African Regional Conference on Soil Mechanics and Geotechnical Engineering, P. 355 – 359 DOI10.3233/978-1-60750-778-9-355

25. Neville, A. M., 1973, Properties of concrete: New York, NY, John Wiley and Sons, 686 p.