# Physiochemical and Compositional Analysis of Two Different Aggregates Supplied by LGED, Jessore

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LABORATORY OF NANO-BIO AND ADVANCED MATERIALS ENGINEERING

Dept. of Chemical Engineering
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9th April 2017, Sunday

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# Certification

This is to certify that the work embodied in the accompanying report entitled "Physiochemical and Compositional Analysis of Two Different Aggregates Supplied by LGED, Jessore" has been carried out entirely by the Laboratory of Nano-bio and Advanced Materials Engineering (NAME) at the Dept. of Chemical Engineering (ChE) of Jessore University of Science and Technology (JUST), Jessore, Bangladesh.

Supervisor
Dr. Md. Zaved H Khan, Dept. of ChE, JUST

NAME
Laboratory of Nano-Bio &
Advanced Materials Engineering

Co-supervisors
Md. Zahid Hossain Khan, Senior Assistant Engineer, LGED, Jessore.
Md. Rafiul Hasan, Lecturer, Dept. of ChE, JUST

Research Assistants
Mr. Md. Arifur Rahman, Student, Dept. of ChE, JUST
Mr. Md. Abu Naser Shatez, Student, Dept. of ChE, JUST

# Abstract

Aggregate is a material vastly used in the construction industry related to concrete structures, asphalt bases and pavement. To achieve required dimensional stability, durability and strength of structures, aggregate characteristics and related engineering properties is one of the main issues needed to be addressed. The Local Government Engineering Department (LGED), Bangladesh is receiving massive quantities of aggregates supplied by several sources present within and along its periphery, however, no concerted effort has been witnessed to document aggregate chemical characteristics, leading to all sort of durability problems and threatening service life of structures. There is a dire need to develop a data-base that contributes to the suitability of material in asphalt and concrete mix. Aggregate characterization technique is a forefront vision to enhance the quality of concrete alongside being a pioneering move to select construction materials. It focuses on quality and performance in roads, bridges and buildings and determines suitability of their use in Hot Mix Asphalt and Concrete Mix Design, thus addressing issues related to applicability in given situation, strength, durability and maintenance and monitoring and rehabilitation.

This project report aims to present a methodology for aggregate chemical characterization based on their physiochemical properties, petrography examination and engineering properties. Based on experimental design formulated to evaluate the chemical properties and behaviour of rocks and crushed rock respectively, statistical techniques have been applied to ascertain significance of relationships between various properties governing aggregate characterization. Conclusions are drawn regarding suitability of characterization of aggregates in relation to their construction application and ability to address construction related problems. The aggregate characterization model thus developed has the capacity and potential to be utilized and extended for various scenarios.

# 1. Introduction

Understanding construction material and its behaviour in asphalt and cement applications has always been a challenge to construction industry. It is of utmost importance to assess and evaluate the properties at material level and as part of the mix for durability and monitoring point of view. The importance of using the right type and quality of aggregates cannot be overemphasized. The fine and coarse aggregates generally occupy 60% to 75% of the concrete volume (70% to 85% by mass) and strongly influence the concrete's freshly mixed and hardened properties, mixture proportions, and economy. Aggregate characterization is the first step needed to facilitate construction industry which focuses on quality and performance issues related to their application in cement concrete, asphalt and other construction. Being a high seat of learning, LGED, Bangladesh has assumed the responsibility to take up the task of developing a comprehensive mechanism of aggregate characterization which would cover all aspects of variation in aggregate. These variations include aggregate physical and engineering properties as well as their chemical and reactivity considerations. All this calls for attempting aggregate characterization based on source rock, inherent variation, crushing plants limitations and brought down to laboratory testing of various properties.

Naturally occurring concrete aggregates are a mixture of rocks and minerals. A mineral is a naturally occurring solid substance with an orderly internal structure and a chemical composition that ranges within narrow limits. Rocks, which are classified as igneous, sedimentary, or metamorphic, depending on origin, are generally composed of several minerals. For example, granite contains quartz, feldspar, mica, and a few other minerals; most limestone consist of calcite, dolomite, and minor amounts of quartz, feldspar, and clay. Weathering and erosion of rocks produce particles of stone, gravel, sand, silt, and clay. Bringing all this into one framework is the major objective of the research reported in this paper. It aims to provide a methodology for chemical characterization of aggregates which can encompass various construction issues pertaining to Bangladesh.

In the present study an effort is made to characterize two types of aggregate materials: widely used black colour aggregates imported from India (hereafter referred as S-1) and white coloured aggregates imported from abroad by contractor (hereafter referred as S-2). These materials have undergone physiochemical characterization and compositional analysis.

Different acid values, salt contents, water absorption behaviour etc. were determined in wet chemistry laboratory. UV visible spectroscopy (UV-vis), X-Ray Fluorescence (ED-XRF) and X-Ray Diffraction (XRD) analyses were used for chemical and mineralogical characterization, respectively. Physical properties such as surface morphology, particle density, heat resistance were determined by using scanning electron microscopy (SEM) and DT/TGA instruments.

**References:**

1. Akbulut, H., and Gu¨ rer, C. (2006). "Use of Aggregates Produced from Marble Quarry Waste in Asphalt Pavements". Building and Environment, Vol. 42, pp 1921-1930.
2. Ali, M.S., Khan, A.M., and Zaidi S.M. (2008), "Sampling Techniques for the Characterization of Hub River Aggregates, Sindh, Balochistan Area, Pakistan". 1st International Conference of Transportation and Infrastructure, Beijing, China.
3. Baker, D., and Hendy, B. (2005). "Planning for Sustainable Construction Aggregate Resources in Australia". The Queensland University of Technology Research Week International Conference, Brisbane, Australia.
4. Brandes, H.G., and Robinson C.E. (2006). "Correlation of Aggregate Test Parameters to Hot Mix Asphalt Pavement Performance in HAWAII". Journal of Transportation Engineering ASCE, Vol. 132, pp 86-95.
5. Dhir, R. K., Ramasy, D. M., & Balfour, N. (1971). "A Study of the Aggregate Impact and Crushing Value Tests". Journal of the Institute of Highway Engineers, pp 17-27.
6. Division of Mines and Geology (2000). "Guidelines for Classification and Designation of Mineral Lands". California Surface Mining and Reclamation Policies and Procedures, Special Report 51, California, US.
7. French, W.J. (1991). "Concrete Petrography". Quarterly Journal of Engineering Geology, Vol. 3, pp 17- 48.
8. Kohler, S. (2006). "Aggregate Availability in California". Department of Conservation, California Geological Survey.
9. Langer, W.H., Green G.N., Knepper, D.H., Lindsey, J.D.A., Moore, D.W., Nealy, L.D., and Reed, J.C. (1997). "Distribution and Quality of Potential Sources of Aggregate Infrastructure Resources Project Area, Colorado-Wyoming".
10. Liu, H., Kou, S., and Arne, P. (2004). "Microscope Rock Texture Characterization and Simulation of Rock Aggregate Properties". SGU Project 60-1362.
11. Lopez-Buendia, A.M., Climent, V., Verdu, P. (2006). "Lithological Influence of Aggregate in the Alkali- Carbonate Reaction". Cement and Concrete Research, Elsevier Ltd. Valencia, Spain, Vol. 36.
12. Pan, T., Tutumluer, E., and Carpenter, S.H. (2006). "Effect of Coarse Aggregate Morphology on Permanent Deformation Behaviour of Hot Mix Asphalt". Journal of Transportation Engineering ASCE, pp 580-589
13. Rafeeqi, S.F.A. (2007). "Proceedings of International Workshop on Cement Based Materials and Civil Infrastructure". Karachi Pakistan, pp 91-102.
14. West, G., & Dumbleton, M.J. (1970). "The Mineralogy of Tropical Weathering Illustrated by Some West Malaysian Soils". Quarterly Journal of Engineering Geology, Vol. 3, pp 25-40.

# 2. Materials and methods

## 2.1 Sampling

Two types of aggregates were collected to perform comparative study of physio chemical property and its chemical composition analyses. One was black aggregates which were imported from India and other was white aggregates which was imported from abroad for the first time.

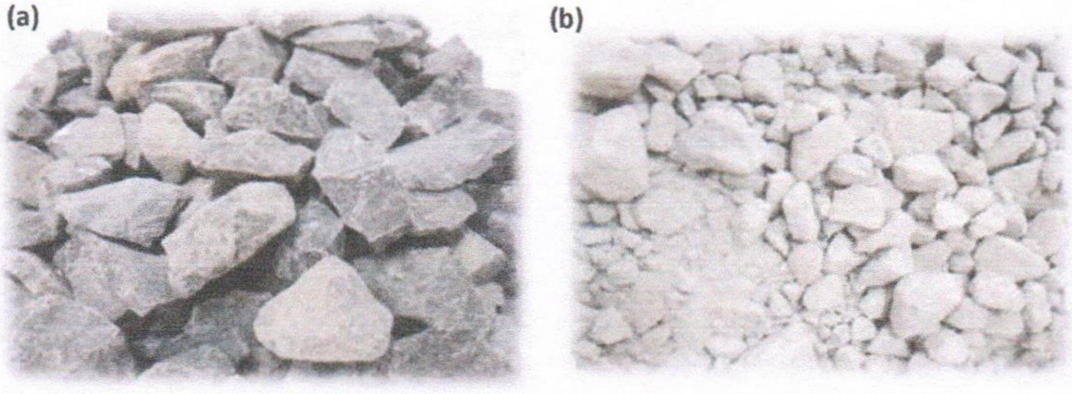


Figure 2.1: Photo images of, (a) Black aggregate rocks (origin: India); (b) White aggregate rocks (origin: undefined)

To carry out all experiment, four types of sample were prepared each time; which were coarse aggregates, fine aggregates, powdered sample and aqueous stock solution.

### 2.1.1 Coarse aggregates

As requirement of ASTM standard procedure, coarse aggregates were collected in different size and shape. Coarse aggregates were collected from different part of raw material store place. Conventional method was applied to separate desire size of aggregate by sieve. Coarse aggregate samples were used for physio chemical experiment.

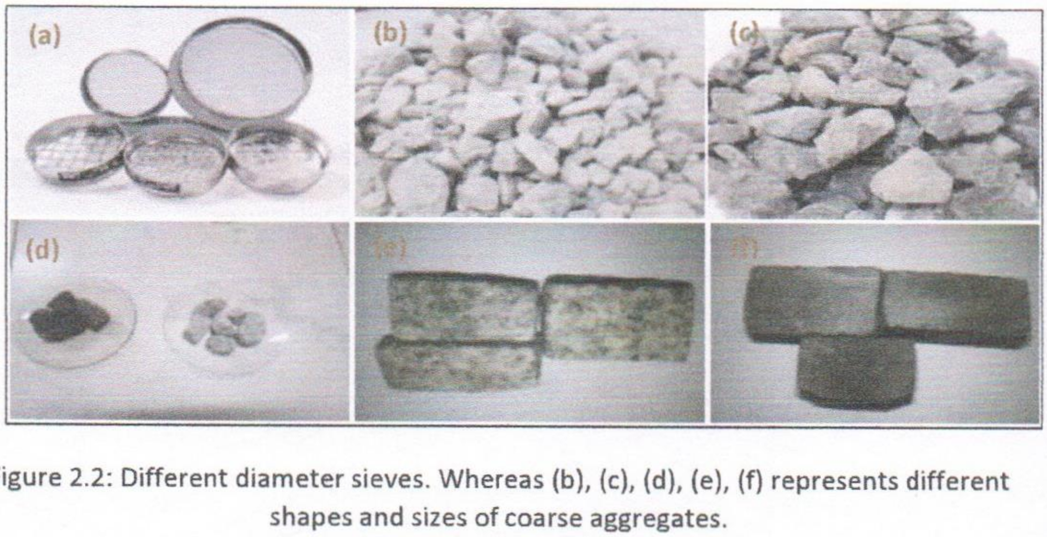


Figure 2.2: Different diameter sieves. Whereas (b), (c), (d), (e), (f) represents different shapes and sizes of coarse aggregates.

### 2.1.2 Powdered sample

Powdered sample was prepared by conventional grinding process. A hammer and 75 $\mu m$ (sieve-200) was used to collect powder sample. Powder samples were performed EDXRF, XRD, SEM and TGA analysis.

### 2.1.3 Aqueous stock solution

Aqueous stock solution was prepared for wet chemical analysis. Sample was prepared by ASTM standard method. 50 gm sample was weighted and transferred to the 500 ml volumetric flask. Volumetric flask filled up with distilled water. Kept the volumetric flask for 15hr on magnetic stirrer for digestion and temperature maintained up to 60°C. 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.

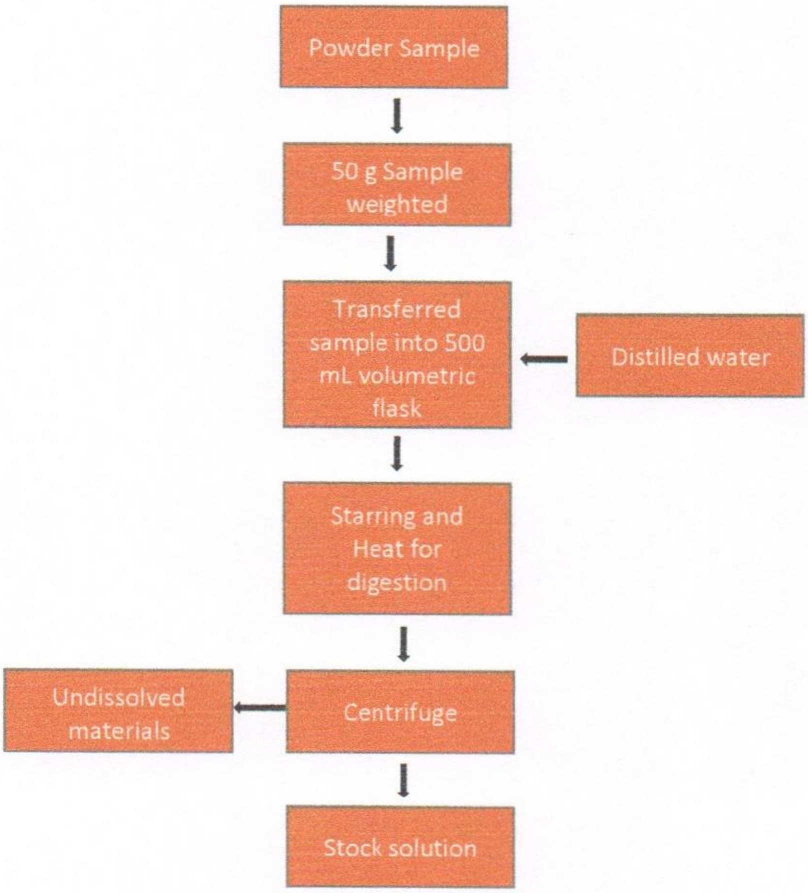


Figure 2.3: Block diagram presentation for aqueous stock solution preparation technic.

## 2.2 Physiochemical Analysis

### 2.2.1 Acid Test

According to ASTM standard testing procedure, a sample of stone weighing about 100 gm is taken. It is placed in a solution of hydrophobic acid (HCl) having strength of 1% and is kept there for seven days. Solution is agitated at intervals.

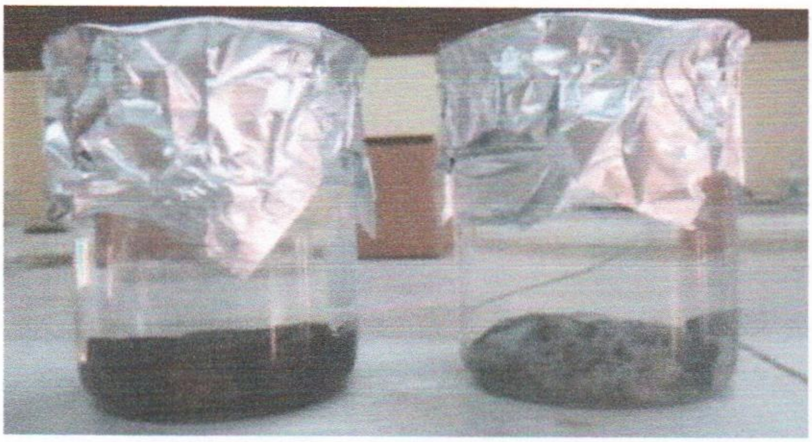


Figure 2.4: Photo images of Acid tests for Sample-1 and Sample-2

### 2.2.2 Crystallinity Test

Following ASTM standard testing procedure, three cubes of stone with a size of 20mm was taken. They are dried for 72 hrs and weighed. They are then immersed in 14% solution of $Na_2SO_4$ for 2 hours. They were dried at 100 °C and weighed. Difference in weight was noted. This procedure of drying, weighing, immersion and reweighing is repeated at least 5 times. Each time, change in weight was noted but two type of stone showed negligible weight change. Crystallization of $CaSO_4$ in pores of stone causes decay of stone due to weathering. But as $CaSO_4$ has low solubility in water, it is not adopted in this test.

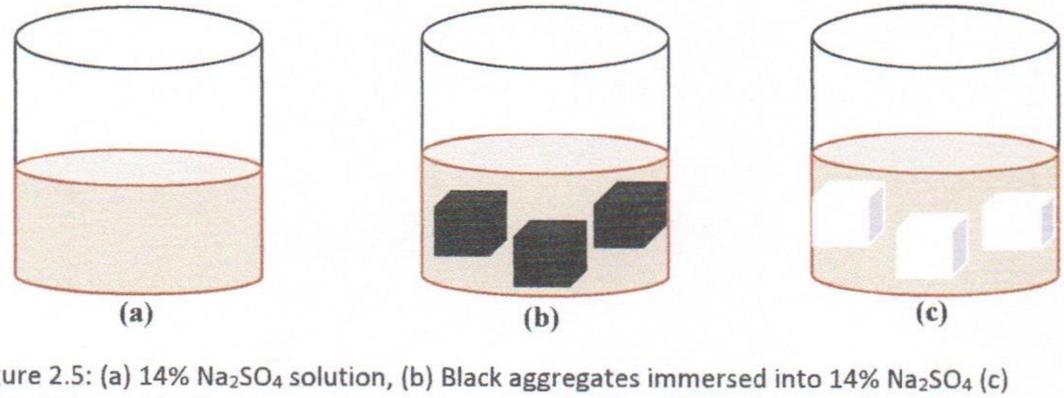


Figure 2.5: (a) 14% $Na_2SO_4$ solution, (b) Black aggregates immersed into 14% $Na_2SO_4$ (c) White aggregates immersed into 14% $Na_2SO_4$ solution.

## 2.3 Physical Properties Test

### 2.3.1 Procedure

- Dry Weight,
- Dry the test specimens to constant weight by heating to 220 to 230°F (105 to 110°C) and determine the dry weight, D, in grams to the nearest 0.1 g.
- The drying procedure may be omitted only when the test specimens are known to be dry, as may be the case with samples taken directly from kilns.
- The drying of the specimens to constant weight and the determination of their dry weight may be done either before or after the saturation operation. Usually, the dry weight is determined before saturation. However, if the specimens are friable or evidence indicates that particles have broken loose during the saturating operation, dry and weigh the specimens after the suspended weight, S, and the saturated weight, W, have been determined, as described in Sections 3.4.3 and 3.4.4 Use this second dry weight in all appropriate calculations.

### 2.3.2 Saturation

- Place the test specimens in water and boil for 2 h. During the boiling period, keep them entirely covered with water, and allow no contact with the heated bottom of the container.
- After the boiling period, cool the test specimens to room temperature while still completely covered with water. After boiling keep the specimens immersed in water for a minimum of 12 h before weighing.

### 2.3.3 Suspended Weight, S

- Determine the weight, S, of each test specimen after boiling and while suspended in water in grams to the nearest 0.1 g.
- This weighing is usually accomplished by suspending the specimen in a loop or halter of AWG Gage 22 (0.643-mm) copper wire hung from one arm of the balance. The balance shall be previously counter-balanced with the wire in place and immersed in water to the same depth as is used when the refractory specimens are in place.

### 2.3.4 Saturated Weight, W—

- After determining the suspended weight, blot each specimen lightly with a moistened smooth linen or cotton cloth to remove all drops of water from the surface and determine the saturated weight, W, in grams by weighing in air to the nearest 0.1 g. Perform the blotting operation by rolling the specimen lightly on the wet cloth, which has previously been saturated with water, and then press only enough to remove such water as will drip from the cloth. Excessive blotting will induce error by withdrawing water from the pores of the specimen.

### 2.3.5 Calculation

- **Exterior Volume, V**—Obtain the volume, V, of the test specimens in cubic centimetres by subtracting the suspended weight from the saturated weight, both in grams, as follows: V. This assume that 1 $cm^3$ of water weighs 1 g. This is true within about 3 parts in 1000 for water at room temperature.
- **Volumes of Open Pores and Impervious Portions**— Calculate the volume of open pores and the volume of the impervious portions of the specimen as follows:

  Volume of open pores, $cm^3$=W-D

  Volume of impervious portion, $cm^3$ =D-S
- **Apparent Porosity, P**—The apparent porosity expresses as a percentage the relationship of the volume of the open pores in the specimen to its exterior volume. Calculate P as follows:

  $P (\%)=[(W-D)/V)]x100\%$
- **Water Absorption, A**—The water absorption, A, expresses as a percentage the relationship of the weight of water absorbed to the weight of the dry specimen. Calculate A as follows:

  $A (\%)=[(D-W)/D]x100\%$
- **Apparent Specific Gravity, T**—Calculate the apparent specific gravity, T, of that portion of the test specimen which is impervious to boiling water as follows:

  $T=D/(D-S)$
- **Bulk Density, B**- The bulk density, B, of a specimen in grams per cubic centimetre is the quotient of its dry weight divided by the exterior volume, including pores. Calculate B as follows:

  B, $(g/cm^3)$ = D/V

### 2.3.6 Silt and Clay test:

Fill 1% solution of common salt and water in the measuring cylinder up to 50 ml mark. Now add fine aggregates to be tested to this solution till the level of the salt solution shows 100 ml mark. The aggregates sizes were determined with literature reference (6). Top up the level of salt solution up to 150 ml mark. Shake the mixture of aggregates and salt solution well and keep it undisturbed for about 3 hours. The silt being of finer particles than aggregates, will settle above in a form of layer. Measure the thickness of this silt layer.

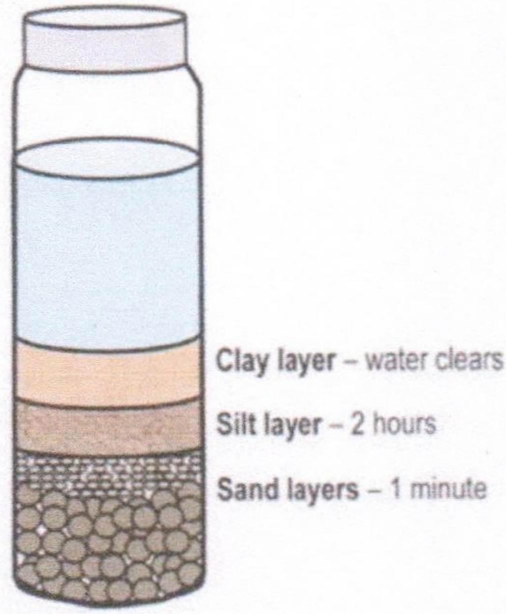


Figure 2.6: Procedure for Silt content test in fine aggregates

## 2.4 Wet Chemical Analysis

### 2.4.1 Qualitative analysis

All identification of ions was completed by Test method ASTM C1218/C1218M.

**Nitrate ion identification**: Nitrate test, known as the **brown ring test** can be performed by adding iron(II) sulphate to the prepared sample solution of a nitrate, then slowly adding concentrated sulphuric acid such that the acid forms a layer below the aqueous solution. A brown ring will form at the junction of the two layers, indicating the presence of the nitrate ion.

The overall reaction is the reduction of the nitrate ion by iron(II) which is oxidized to iron(III) and formation of a nitrosonium complex where nitric oxide is oxidized to $NO^+$.

$$2HNO_3 + 3H_2SO_4 + 6FeSO_4 \text{--->>} 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$[Fe\,(H_2O)_6]SO_4 + NO = [Fe(H_2O)_5(NO)]SO_4+$$

**Sulphate ion identification:** Firstly, take 10 mL sample solution into a beaker. Add 2 mL concentrated HCl acid to the sample. Heat the sample on a hot plate near boiling point. Add 5 ml barium chloride solution and continue to heat the solution for 10 min. Remove the sample from hot plate. Allow to cool at room temperature and white precipitate obtained.

$$Ba^{2+}{}_{(aq)} + SO_3{}^{2-}{}_{(aq)} \text{==>} BaSO_{3(s)}$$

$$BaSO_{3(s)} + 2HCl_{(aq)} \text{==>} BaCl_{2(aq)} + H_2O_{(l)} + SO_{2(aq}$$

**Chloride ion identification:** Take 10 mL solution and adjust pH 8-9. Add one drop potassium chromate solution color turned into yellow. Add silver nitrate dropwise into the sample solution till solution color change into brick red color. After all the chloride has been precipitated as white silver chloride, the first excess of titrant results in the formation of a silver chromate precipitate, which signals the end point. The reactions are:

$$Ag^+ + Cl^- = AgCl(s)$$

$$2\ Ag^+ + CrO^{2-} = Ag\ CrO\ (s)$$

**Phosphate ions identification:** When a solution containing phosphate ions is heated with a solution of ammonium molybdate [(NH4)2MoO4] and dilute nitric acid a bright yellow precipitate of ammonium phosphomolybdate [$(NH_4)_3PO_4 .12MoO_4$] is formed. The yellow precipitate is extremely insoluble in nitric acid.

$$PO_4^{3-} + 12(NH_4)_2MoO_4 + 21HNO_3 + 3H^+ \rightarrow (NH_4)_3PO_4{\cdot}12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$$

## 2.5 Quantitative analysis

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

## 2.6 Characterization of sample

For characterization of sample various instruments were used. Scanning electron microscope (SEM) used for morphology analysis, stability measurement and helps to analyse the behaviour of 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 Discussion

## 3.1 Physiochemical Analysis

### 3.1.1 Acid Test:

Acid test is performed to check the insoluble matter content and insoluble residues in aggregates. Acid test also gives the weather stability assumption. A good aggregate maintains its sharp edges and keeps its surface free from powder at the end of acid test. If the edges are broken and powder is formed on the surface, it indicates such an aggregates will have poor weathering quality.

***Observation:*** *In our acid test experiment both Sample-1 and Sample-2 shows unbroken edges and produced little amount of powder and changed its colour, which is acceptable.*

Figure 3.1: Photo images of before (left) and after (right) acid tests for both samples.

Standard method applied: ASTM D3042 and BS 812-119:1985

### 3.1.2 Crystallinity Test:

Crystallinity test is performed for stability test of aggregates. It is well known that the degree of crystallinity of silica aggregate is one of the major factors influencing alkali reactivity. Poorly-crystallized polymorphs of silica have higher Gibbs free energies and are thus thermodynamically less stable than well-crystallized species, which means that reactivity decreases over the range from amorphous to well-crystallized species of silica.

***Observation:*** *This has been confirmed by results obtained by our experiment that both sample shows good crystalline stability.*

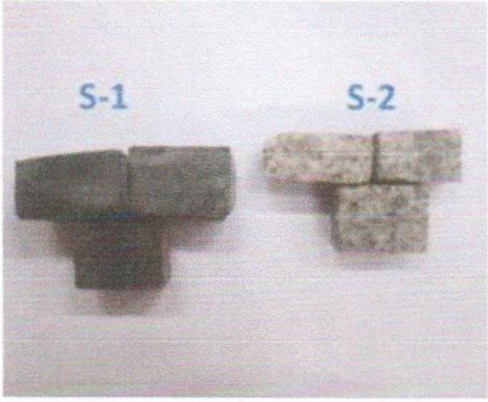


Figure 3.2: Photo images after crystallinity test. Standard method applied: ASTM C1260.

### 3.1.2 Silt and Clay Test:

This test is generally conducted in order to determine the volumetric percentage of silt in fine aggregates for percentage up to 4%, otherwise more detailed test as prescribed by standard code are required to be conducted. In this test we have used mixed aggregates choose from different part of aggregates stock. To classify fine aggregates, we have used 4.75 mm sieve and followed literature reference [15]. BS 882 method was followed for this measurement.

***Observation**: Based on the two samples tested, the maximum silt content was ~ 15.2% for Sample-2 compared with the minimum ~ 2.3% for Sample-1. BS 882 and ASTM C40 recommends that no more than a maximum of 6% silt content for fines aggregates be used in concrete structure [16]. Previous studies indicate that silt fine content has an effect on concrete's durability, especially when silt fine content in concrete is more than 5% [16]. It was also reported that concrete exhibits higher chloride ion penetrability when silt fine content is more than 5%.*

### 3.1.3 Physical Properties Test:

The moisture content of an aggregate is an important factor when developing the proper water/cementitious material ratio. All aggregates contain some moisture based on the porosity of the particles and the moisture condition of the storage area. Aggregate can be found in four different moisture states that include oven-dry (OD), air-dry (AD), saturated-surface dry (SSD) and wet. Of these four states, only OD and SSD correspond to a specific moisture state and can be used as reference states for calculating moisture content. In order to calculate the quantity of water that aggregate will either add or subtract to the paste, the following three quantities must be calculated: absorption capacity, effective absorption, and surface moisture.

The density of the aggregates is required in mixture proportioning to establish weight-volume relationships. Specific gravity is easily calculated by determining the densities by the displacement of water. All aggregates contain some porosity, and the specific gravity value depends on whether these pores are included in the measurement. There are two terms that are used to distinguish this measurement; absolute specific gravity and bulk specific gravity. Absolute specific gravity (ASG) refers to the solid material excluding the pores, and bulk specific gravity (BSG), sometimes called apparent specific gravity, includes the volume of the pores. For the purpose of mixture proportioning, it is important to know the space occupied by the aggregate particles, including the pores within the particles.

Table 1: Tests and permissible limits for physical properties of coarse aggregates for concrete as stipulated by QCS (2010).

| Test type | S-1 | S-2 | Permissible/Standard limit | Testing method |
|---|---|---|---|---|
| Moisture content (%) | 1.65 | 0.112 | 1-2% | ASTM C70 |
| Water absorption (%) | 0.50 | 0.21 | Max 2% | ASTM C127 |
| Density (kg/m$^3$) | 2858.02 | 2650 | 2400 | ASTM C29 |
| Specific gravity | 2.85 | 2.65 | 2.6-2.9 | ASTM C127 |
| Porosity (%) | 38.7 | 12.6 | - | ASTM C29 |
| pH | 7.89 | 7.56 | 7.5-9.5 | ASTM C33 |

***Observation**: Sample-1 shows higher moisture content as well as water absorption rate. When absorption is concerned, it will effect water demand with in concrete and should be adjusted for water/cement ratio while proportioning mix design. The density and specific gravity of Sample-2 is lower than that of Sample-1. Very high porosity observed for Sample-1. It is obvious that a porous aggregate produce concrete of unit weight, as that of light weight aggregates. Bond between aggregates and surrounding hydrates paste of cement strongly depends on porosity.*

## 3.2 Wet Chemical Analysis

Wet Chemistry, also called wet chemical analysis, generally refers to chemistry performed on samples in the liquid phase. Since wet chemical analysis is performed on liquid samples, this type of element analysis can often be performed on samples too small for other instrumental methods.

There are two types of wet chemical analysis method:

1. Qualitative &
2. Quantitative

## 3.2.1 Qualitative analysis

### 3.2.1.1 Different Ions identification

Water-extractable chloride, when present in sufficient amount, has a potential to initiate or accelerate corrosion of metals, such as steel, embedded in or contacting a cementitious system, such as mortar, grout, or concrete. This test method is applicable when aggregates contain a high background of naturally occurring chloride. Test method ASTM C1218/C1218M determines water-soluble chloride.

Excessive amounts of mobile sulphate, derived from aggregates or other constituents in concrete, can cause disruption due to expansion. However, specifications for many constituent materials (aggregates, cement etc.) place limits on the sulphate content. Also, in the UK, sulphate problems caused by naturally occurring aggregates are rare [17]. Where a new source or material is to be considered or is suspected of containing sulphate, it should be assessed before being used.

Table 2: Observation of different water soluble ion presence in aggregates

| Observations | S-1 | S-2 | Comments |
|---|---|---|---|
| Brick red color | + | + | Chloride ion ($Cl^{-1}$) present |
| White precipitate | + | + | Sulphate ion ($SO_3^{2-}$) present |
| Yellow precipitate | + | + | Phosphate ion ($PO_4^{3-}$) present |
| Brown ring obtained | + | + | Nitrate ion ($NO^{-3}$) present |

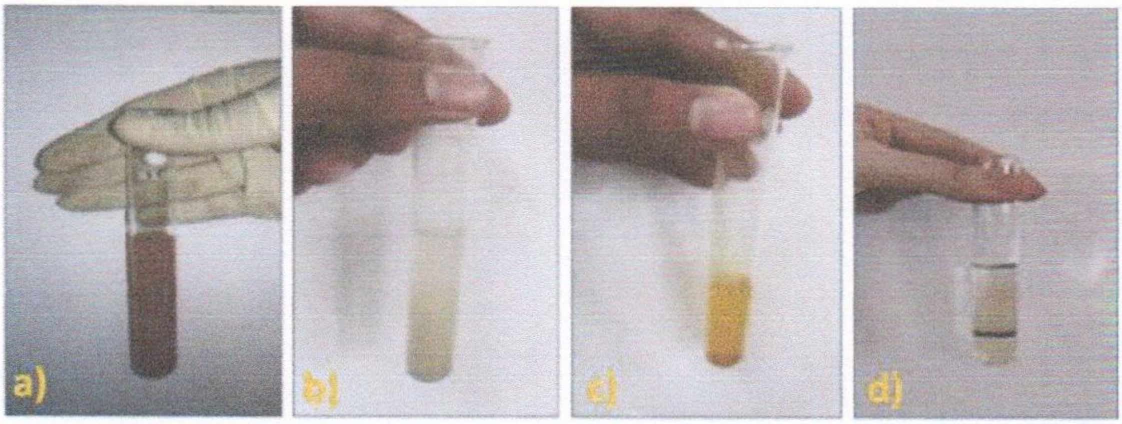


Figure 3.3: Photo images of the confirmation of different soluble ion presence in aggregates solutions; a) Chloride, b) Sulphate, c) Phosphate, and d) Nitrate.

### 3.2.2 Quantitative analysis

In analytical chemistry, *Quantitative analysis* is the determination of the absolute or relative abundance (often expressed as a concentration) of one, several or all particular substance(s) present in a sample.

By Ultraviolet Visible Spectrophotometer (UV-vis) we have measured the exact concentration of different ion present in aggregates solution and the obtained results are given bellow-

Table 3: Water soluble ion content amount present in aggregates

| **Ion name** | **S-1 (mg ion /kg sample)** | **S-2 (mg ion/kg sample)** | **Standard Limit** | **References** |
|---|---|---|---|---|
| Nitrate ($NO_3^-$) | 0.8 | 1.5 | Max. 3% | [18] |
| Chlorine ($Cl^-$) | 0.12 | 0.33 | Max. 0.1 % by mass | ASTM C1218, [19], [20] |
| Phosphate ($PO_4^{2-}$) | 0.54 | 0.21 | No data | No data |
| Sulfate ($SO_3^{2-}$ ) | 44.98 | 27.48 | 15-55 | ASTM C1580, [22], [23] |

***Observation:*** *Sample-1 and Sample-2 both contains permeable amount of dissolve ions. Although Sample-2 contains higher amount of $Cl^{-1}$ ion compare to Sample-1, but the amount is within standard range. According to literature, high amount of water soluble Chloride ion, which might have negative impact on concrete structure [19-20]. A particular feature of Chloride attack which distinguishes it from other mechanisms of deterioration of reinforced concrete is that the primary action of Chlorides is to cause corrosion of steel reinforcement and it is only a consequence of this corrosion that the surrounding concrete is damaged [21]. The other ion concentrations are within standard range.*

## 3.3 Chemical Compositions Analysis

### 3.3.1 Scanning Electron Microscopy (SEM):

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition.

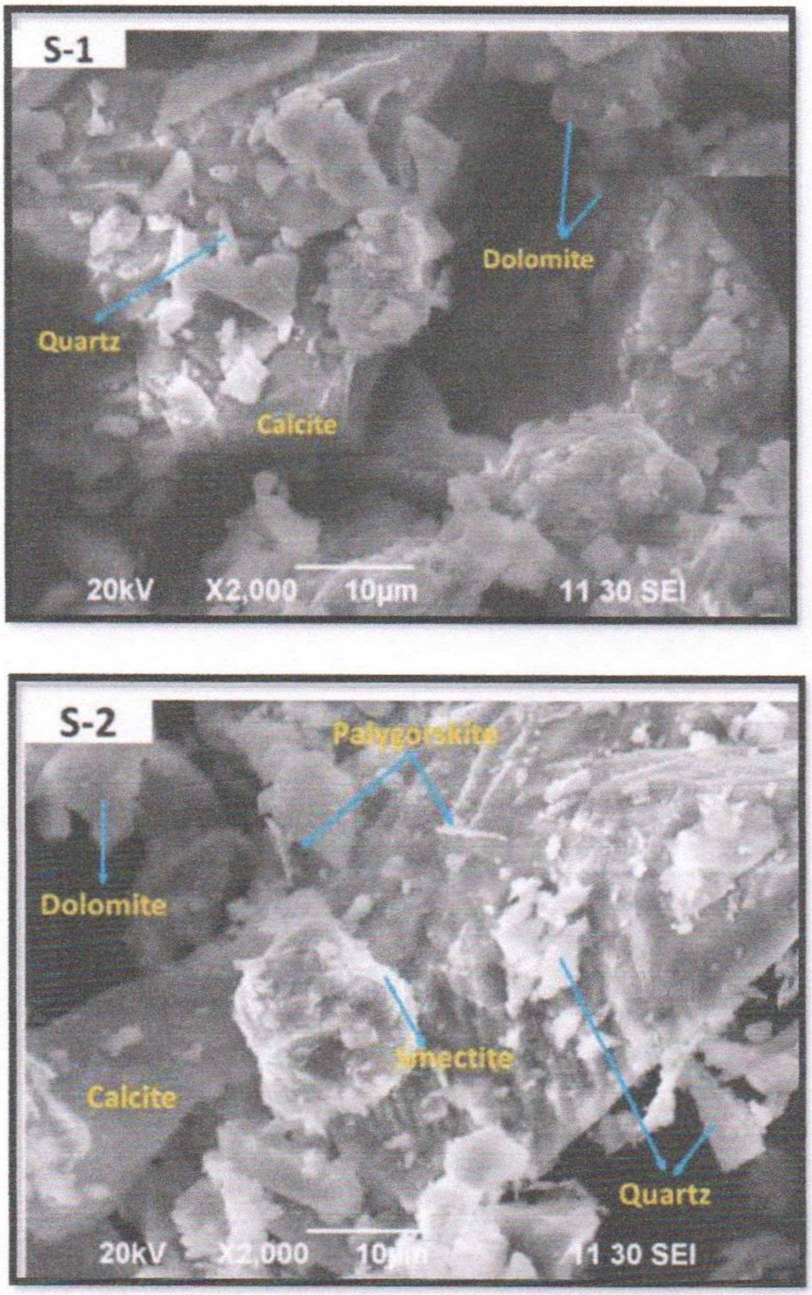


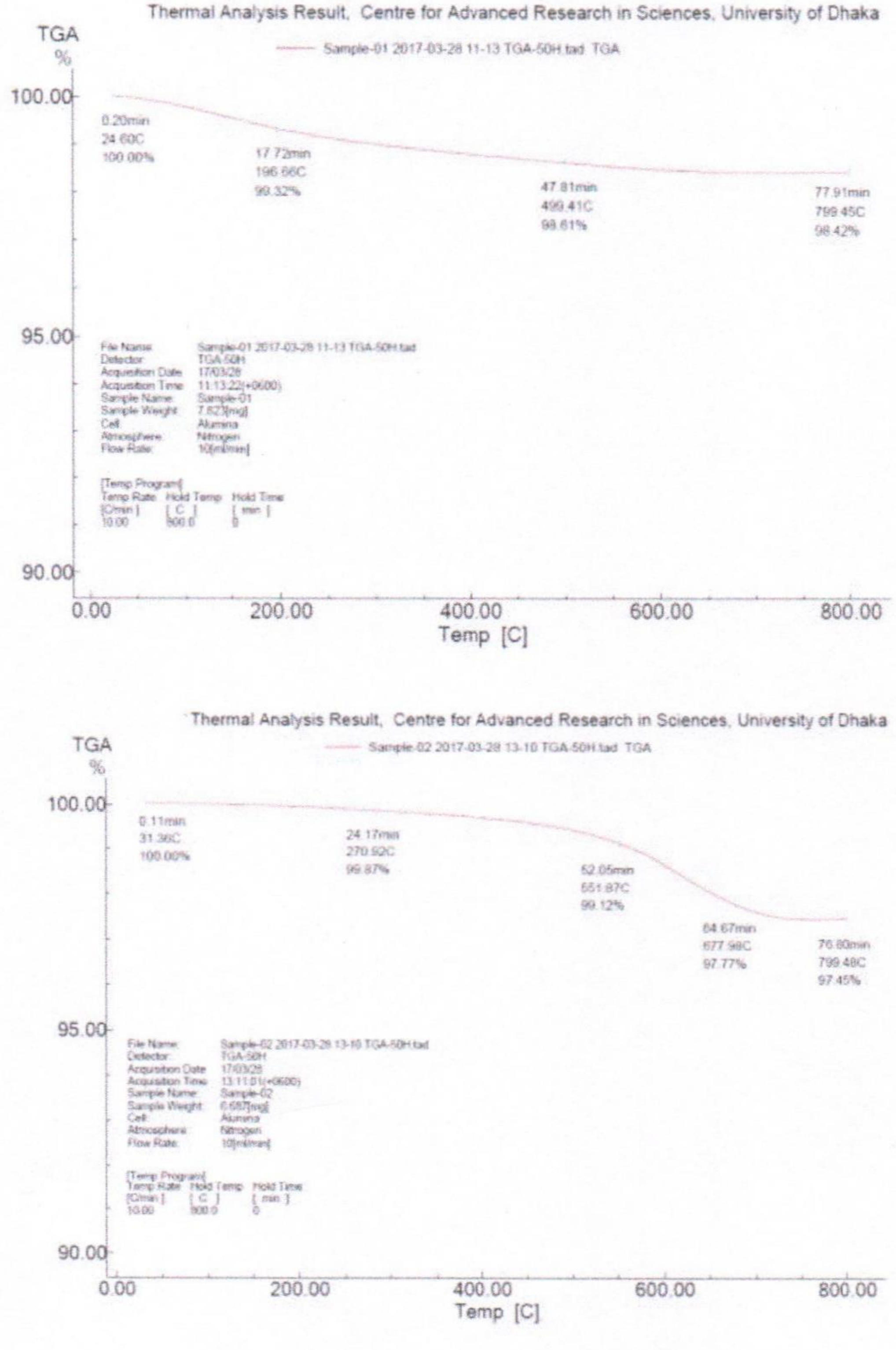
Figure 3.4: SEM images of Sample-1 and Sample-2. SEM was done in BUET, Dhaka.

***Observation:*** *Figure 3.4 shows the SEM images. From the image of Sample-1, presence of calcite, dolomite and some quartz are identified. On the other hand, below figure represents the development of palygorskite* $(Mg,Al)2Si_4O10(OH)\cdot 4(H_2O)$ *fibers between calcite crystals near smectite flakes. Elongate palygorskite fibers developed as cement between calcite crystals, and as fiber and fan-shaped bundles at the edge of smectite are clearly observed for Sample-2.*

### 3.3.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). TGA test results combined with XRF, XRD and pore index test results can give a rapid evaluation of carbonate aggregate intended for use in concrete structure. The slopes of the weight loss plot prior to the dolomite and calcite transitions does correlate with field performance. The noncarbonate fraction, which correlates to the acid insolubles, can be determined by TGA for most calcites and some dolomites. TGA has provided information that can be used to help predict the quality of aggregate.

***Observation:*** *From TGA curve, it has been clearly observed that weight loss due to adsorbed water occurs around <120*$^0$*C, when there are not particular hydrated salts. The loss of chemical water bound to the several calcium aluminum silicate hydrates (CSH, CAH, CASH) occurs around 200-600*$^0$*C. The loss of* $CO_2$ *due to decomposition of carbonates takes place at >600*$^0$*C. For Sample-1, the weight loss gradually increased with increasing temperature and time. Finally, around 800*$^0$*C about 1.58% weight loss was observed which is very similar to other aggregates. Whereas, for Sample-2, a dramatically decreased in weight loss observed after 500*$^0$*C until 800*$^0$*C and finally a weight loss of 2.55% was achieved. This can be explained as the loss of Dolomite, that is an anhydrous carbonate mineral composed of calcium magnesium carbonate, ideally* $CaMg(CO_3)$*. Further details study is necessary to established and to explain TGA study. Prior study shows excellent research output for TGA study [24].*



File Name: Sample-01 2017-03-28 11-13 TGA-50H.tad
Detector: TGA-50H
Acquisition Date: 17/03/28
Acquisition Time: 11:13:22(+0600)
Sample Name: Sample-01
Sample Weight: 7.623[mg]
Cell: Alumina
Atmosphere: Nitrogen
Flow Rate: 10[ml/min]

[Temp Program]
Temp Rate [C/min] 10.00 | Hold Temp [ C ] 800.0 | Hold Time [ min ] 0

File Name: Sample-02 2017-03-28 13-10 TGA-50H.tad
Detector: TGA-50H
Acquisition Date: 17/03/28
Acquisition Time: 13:11:01(+0600)
Sample Name: Sample-02
Sample Weight: 6.687[mg]
Cell: Alumina
Atmosphere: Nitrogen
Flow Rate: 10[ml/min]

[Temp Program]
Temp Rate [C/min] 10.00 | Hold Temp [ C ] 800.0 | Hold Time [ min ] 0

Figure 3.5: TGA analysis curve for Sample-1 (above) and Sample-2 (below). TGA analysis was done in University of Dhaka.

### 3.3.2 EDXRF Analysis:

EDXRF is one of the compositional analysis which was done for the both samples to compare their elemental composition. All the EDXRF analyses were performed in BCSIR laboratories.

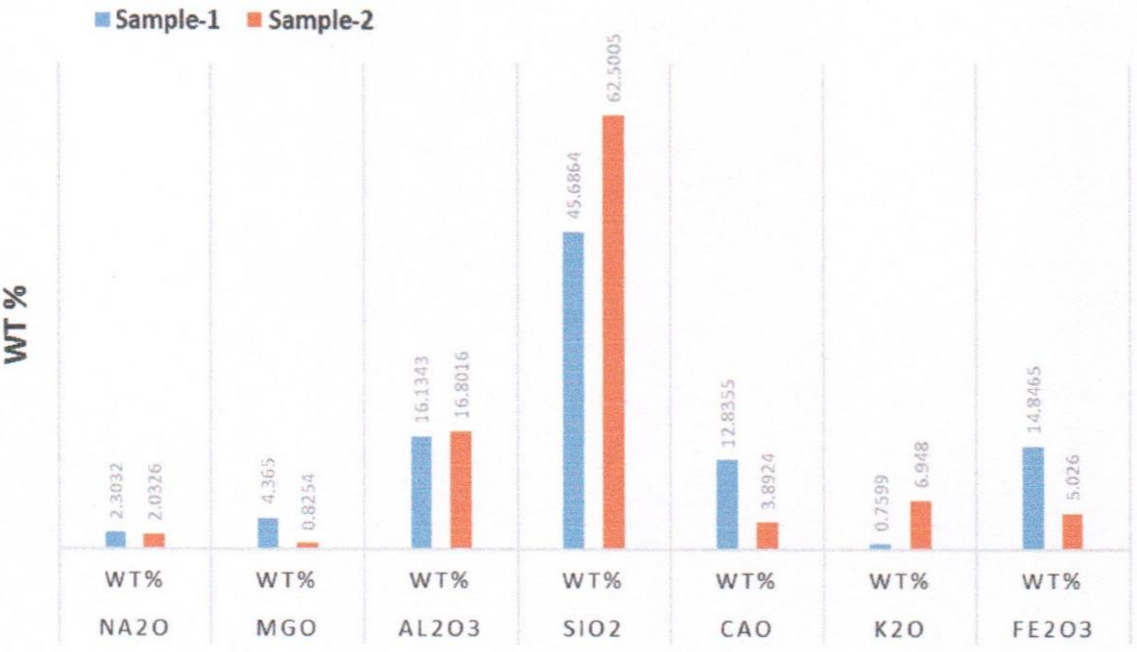


Figure 3.6: Weight % of different elements exists in Sample-1 and Sample-2 measured by EDXRF. Here Sample-1 referes to Black aggregates and Sample-2 referes to White aggregates.

Table 4: Major elements presented in Sample-1 and Sample-2

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | CaO | $K_2O$ | $Fe_2O_3$ |
|---|---|---|---|---|---|---|---|
| | wt% | wt% | wt% | wt% | wt% | wt% | wt% |
| Sample-1 | 2.3032 | 4.365 | 16.1343 | 45.6864 | 12.8355 | 0.7599 | 14.8465 |
| Sample-2 | 2.0326 | 0.8254 | 16.8016 | 62.5005 | 3.8924 | 6.945 | 5.026 |

***Observation**: In gesture, EDXRF analysis report shows clear compositional differences between Sample-1 and Sample-2. The bar chart for each sample is shown in Figure-3.6 in terms of wt%. The given chart resembling that Sample-1 is enriching in MgO, CaO, and $Fe_2O_3$; whereas $SiO_2$ and $K_2O$ are predominating in Sample-2. High amount of Silica content in Sample-2 is a big concern. Alkali-silica reaction may occur when aggregates containing glassy, high-silica minerals are used as concrete aggregate. The alkalis in the cement react with certain silica in the aggregate forming a gel around the aggregate. This gel has an increased volume and causes deterioration of the concrete [26-27].*

During the collection of Sample-2 (recently imported white aggregates), it was noticed that, all coarse aggregates are covered with powder materials and also lot of fine/powder materials exists as residues. To confirm the components of that fine/powder materials, we have done EDXRF analyses for three types of Sample-2. Hereafter refered as Sample-2.1, Sample 2.2, and Sample 2.3 as Pure white aggregates without fine materials, white aggregates with fine materials, and only fine materials respectively.

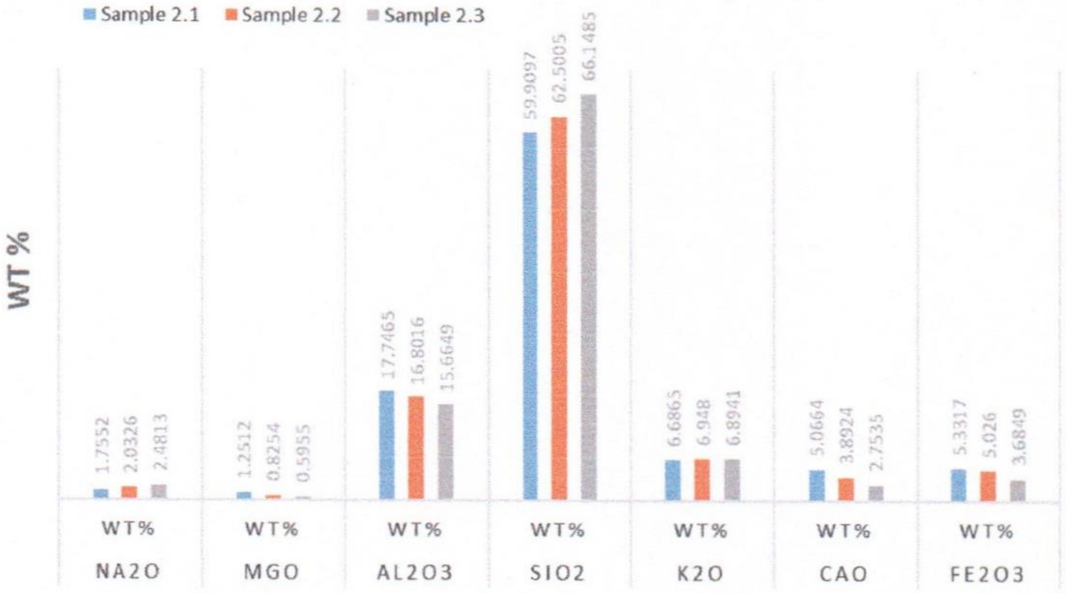


Figure 3.7: Wright % of major components for Sample-2. Here Sample 2.1- aggregates without any fine materials; Sample 2.2- aggregates with fine materials; and Sample 2.3 – only fine materials.

Table 5: Major elements in all three types of Sample-2

| | Condition | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $K_2O$ | CaO | $Fe_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| | | wt% | wt% | wt% | wt% | wt% | wt% | wt% |
| Sample 2.1 | Washed Coarse | 1.7552 | 1.2512 | 17.7465 | 59.9097 | 6.6865 | 5.0664 | 5.3317 |
| Sample 2.2 | With fine materials | 2.0326 | 0.8254 | 16.8016 | 62.5005 | 6.948 | 3.8924 | 5.026 |
| Sample 2.3 | Only fine materials | 2.4813 | 0.5955 | 15.6649 | 66.1485 | 6.8941 | 2.7535 | 3.6849 |

***Observation:*** *It is clearly observed that all three types of Sample-2 has similar components but different wt%. Specially the fine materials that are visible as powder substances on the aggregates and also presented as a residual material are high in Silica (66%). Usually recycled concrete aggregates contains high amount of silica and responsible for alkali-silica reaction as reported by others.*

### 3.3.3 XRD Analysis:

X-ray diffraction was used to identify the crystalline phases and the corresponding intensities of various compounds of the aggregates.

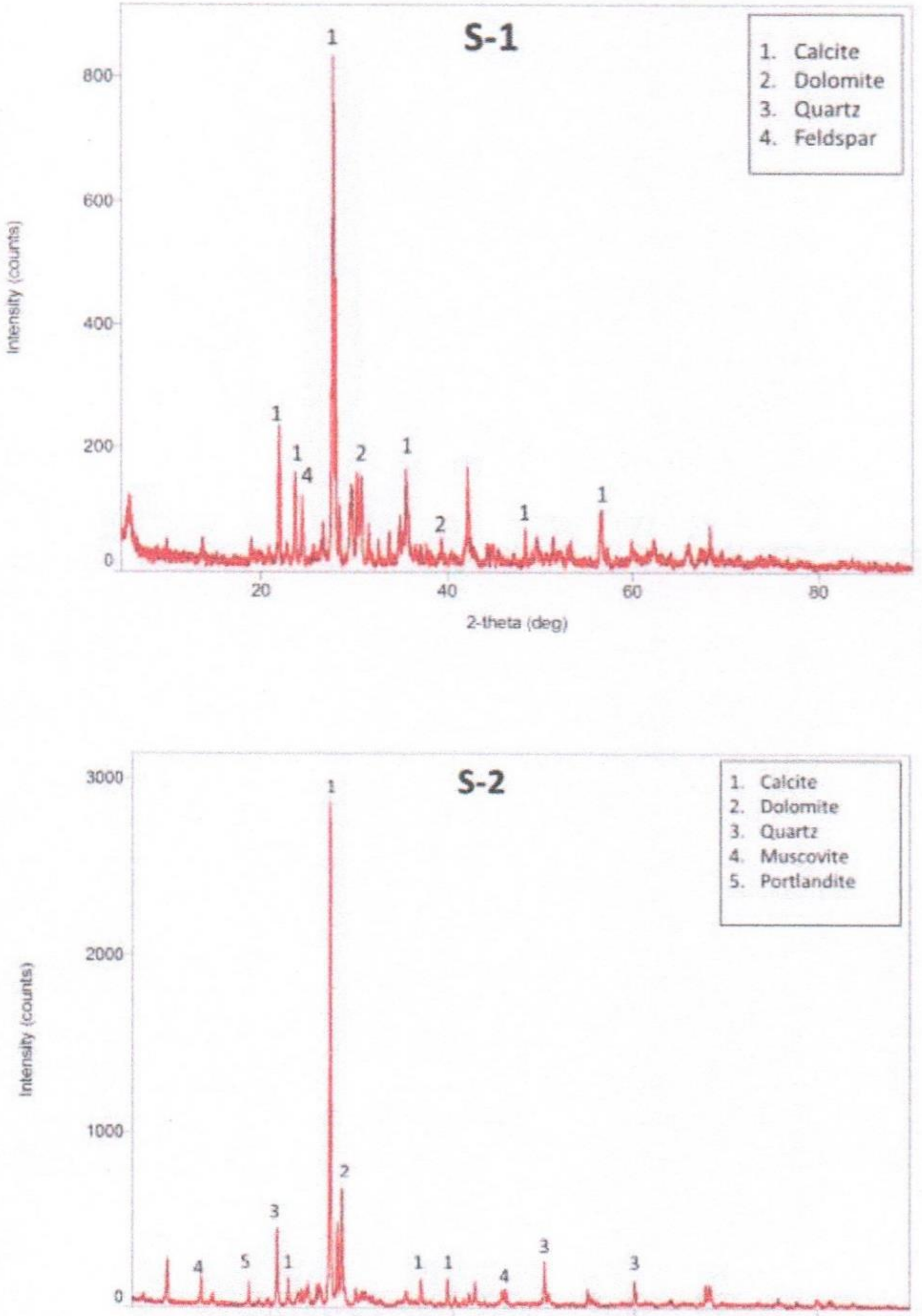


Figure 3.8: XRD spectra of Sample-1 and Sample-2. XRD was done in BUET, Dhaka.

***Observation**: The existence of calcite and dolomite in aggregates can be clearly observed for both samples. However, the intensity and peak region for quartz shows higher for Sample-2 compared with Sample-1 due to the existence of more Silica in Sample-2 confirmed by EDXRF experiment. Moreover, clear existence of Muscovite and Portlandite in Sample-2 observed. The Muscovite peak comes from the hydrated phyllosilicate mineral of aluminium and potassium. EDXRF data clearly shows the existence of higher amount of potassium (K) in Sample-2. Quartz and feldspar are more likely to have a solid origin. However higher amount of Quartz usually observed for recycled concrete aggregates [25].*

## References:

[15] http://civilblog.org/2014/07/07/how-to-classify-aggregates-according-to-size/

[16] 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).

[17] http://www.concrete.org.uk/fingertips-nuggets.asp?cmd=display&id=836

[18] Wolfram Franke et al., THE FATE OF NITRATE IONS IN CONCRETE UNDER THE FOCUS OF CORROSION INHIBITION. Published in the proceedings of the 2nd International Congress on Durability of Concrete as paper No. 9; 4.-6.12.2014, New Delhi, India.

[19] World Academy of Science, Engineering and Technology International Journal of Civil, Environmental, Structural, Construction and Architectural Engineering Vol:8, No:9, 2014

[20] http://projects.bre.co.uk/aggregate/Cltest/Clprecsn.htm

[21] Adam N. (1995). Materials and Structures, 28, page 63-70.

[22] http://www.concreteconstruction.net/how-to/permissible-levels-of-chlorides-and-sulfates-in-aggregate_o

[23] https://www.bca.gov.sg/ImportersLicensing/others/test_requirements.pdf

[25] Materials **2015**, 8, 8804–8816; doi:10.3390/ma8125493

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

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

[28] N. P. F. Madero et al., Characterization and testing of rock aggregates of the Santa Marta Batholith, (Colombia). REVISTA ION, Vol. 27, núm. 2 (2014).

## 4. Conclusion and Remarks

There are several concerns with using Sample-1 (black aggregates imported from India) and Sample-2 (white aggregates that was recently imported) as a concrete material, especially in regards to the excess fines, high amount of silica content, residual silt content and microcrystalline quartz materials. The overall findings are given below-

- *The physical properties of the Sample-1 and Sample-2 such as the unit weight, specific gravity, and percent voids have been evaluated. It was observed that Sample-2 aggregates are different in sizes and contains huge amount of fine materials, whereas Sample-1 seems to be cleaned and in uniform size. It was reported in literature that the most effective method to remove fine particles that can attribute to geotextile clogging is the agitation and pressure washing. Several researchers reported about excess fine particles (somewhere it was noted as dust/silica) in aggregates and they suggest to wash the aggregates prior to use in structural concrete. As Sample-2 contains powdered materials on its surface and residues, it is suggested to wash before using in concrete.*

- *Sample-2 contains huge amount of Silt materials and the experimental value is about 15%, whereas, the permissible world standard is maximum 4-6%. So, it is a big concern and need to treat before using in concrete structure. On the other hand, Sample-1 contains standard amount of Silt materials (2.3%).*

- *From EDXRF, it is clear that Sample-1 contains high amount of Iron. An aggregate with a high unbound iron content may result in oxidation, discoloration, softening, and loss of the mineral over time. On the other hand, Sample-2 contains high amount of Silica and Potassium. High amount of Potassium can make aggregates more reactive. Moreover, the alkali-silica reactivity of aggregates (due to high Silica content) is a critical parameter with regard to the concrete durability, and which affects its structural weakening and shortens its useful life. This finding is in good agreement with the XRD results.*

- *From XRD, it was revealed that Sample-2 comprised high proportion of quartz. High amount of Quartz may contain alkali reactive silicate which is harmful building structure as described in many literatures.*

- *From SEM, it was revealed that Palygorskite and Smectite materials clearly exist in Sample-2 and an extensive study is needed to make a structural difference conclusion.*

## 5. Future recommendations

1. Details study is necessary to examine the chemical compositions with wet chemical analysis and their effects on concrete structure. Due to the shortage of time, it was not possible to do several ion tests. It requires enough time to do wet chemistry lab works.
2. It is also recommending to study the effect of different major elements and their percentage on structural properties of aggregates.
3. Continuous structural chemical composition monitoring is recommended in case of physiochemical effect.
4. In abroad, several chemistry laboratories are closely working with Civil Engineering Departments regarding aggregate and concrete characterization, compositional analyses etc. So, we are suggesting to make a collaboration with foreign laboratories for this type of research work. We already have collaboration with several international laboratories and we are interested in future research with LGED.

NAME
Laboratory of Nano-Bio &
Advanced Materials Engineering

# End of Report