

Geotechnical Evaluation of Limestones from Cape Monze and Adjoining Areas, Karachi, Pakistan for Their Utilization as Road Aggregate

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Abstract: Limestone samples ($n = 19$) were collected from outcrops of Nari and Gaj formations for the determination of physicochemical and mechanical characteristics. Compressive strength of Nari and Gaj formations varied in the range of 29-63 and 94-32 MPA with mean of 44 and 58 MPA respectively. Density of Gaj Formation (range: 2364-3264; mean: 2893 Kg/m³) is relatively higher than Nari Formation (range: 2321-3284; mean: 2565 Kg/m³). Mean specific gravity of both Nari and Gaj formations is 2.5. Absorption of Nari Formation (mean: 2.64) is higher than the Gaj Formation (mean: 1.78). Mean Sulphate soundness of Nari Formation (8.7%) is slightly higher than Gaj Formation (8.5%). Abrasion values of both formations are within the AASHTO reference range ($< 40\%$) where mean value of Loss Angles for Nari Formation is 34% and Gaj Formation is 26%. Crushing values of both Nari (10-50%) and Gaj (10-25%) formations where mean of Nari (27%) is double the mean of Gaj (13%) Formation. Mean water-soluble sulphate and chloride of both formations is same (0.1% and 0.04% respectively). Both formations have alkaline pH ($8.1 \pm$). Mean TOC content of Nari and Gaj formations is 0.4%. Carbonate% of Nari and Gaj formations is $< 46\%$. Clay lumps and friable particles in both formations are highly variable but the mean values are within permissible range ($< 1\%$). Elongation Index of both formations is double (30) the standard EI value (15%) set by National Highway Authority, Pakistan. Mean Flakiness value of both formations is 20%.

Keywords: Limestones, aggregate, geotechnical properties, Cape Monze, Karachi.

Introduction

Limestone contributes about 71% of the total aggregates production in the world (Teprodal, 1993). While sandstone share in aggregate industry is $< 3\%$. Aggregates are mainly used in concrete mix as an extender (70-80%) and asphalt mixes in pavements or road construction. Quality of concrete is a function of physicochemical and geotechnical properties of limestone deposits (Maville, 2000). With ever increasing population and rapid industrial and economic development, construction activities are also increasing. As a result, market demand for aggregate is continuously increasing in recent years. Hence, there is a dire need to identify and evaluate new deposits of construction raw materials for road and cement mix concrete in and around Karachi. Limestone is being exploited on a large scale from Cape Monze-Hub River road area over many decades for using as aggregate in asphalt and cement concrete. However, no work has been carried out in detail on physicochemical and geotechnical characteristics of such these limestone deposits. Thus, present study is aimed at studying the physicochemical and mineralogical characteristics of limestones from study area and to estimate reserves of limestones for using in construction industry.

Materials and Methods

Study area

In present study, nineteen representative rock samples were collected from bed rocks exposed in different

localities like Cape Monze, Goth Mubarak, Goth Muhammad Siddiqui of Allah Bano, Sona Pass, Lal Bakhar, Kochani and Raees Goths on Hub river road, as per ASTM D-75 for detailed geotechnical study. Physical and chemical characteristics were determined in terms of clay lumps, percent finer than 0.075mm, shaped test; flakiness and elongation indices, unconfined compressive strength, aggregate crushing value, and ten percent fine value. The chemical properties determined to evaluate the behavior of crushed stone as aggregate are total organic content, soundness, potential alkali-silica reactivity, carbonate, chloride, sulphate and the pH.

Results and Discussion

Physical Characters

In study area, limestone is important lithology which is well exposed as escarpment and ridges, along Hub river. These limestone units were selected as the major rock used as aggregates by construction industry. Main objective to determine the physical properties of limestones is to evaluate in terms of aggregate quality and durability for road and concrete (Table 1). Following parameters have been discussed separately to elaborate the influence of individuals on aggregate quality.

Flakiness Index (FI) and Elongation Index (EI)

Flakiness Index (FI) and Elongation Index (EI) values varied between 26.76-33.75 and 18.67-22.75% respectively for Gaj Formation. Similarly, 27.46-33.37

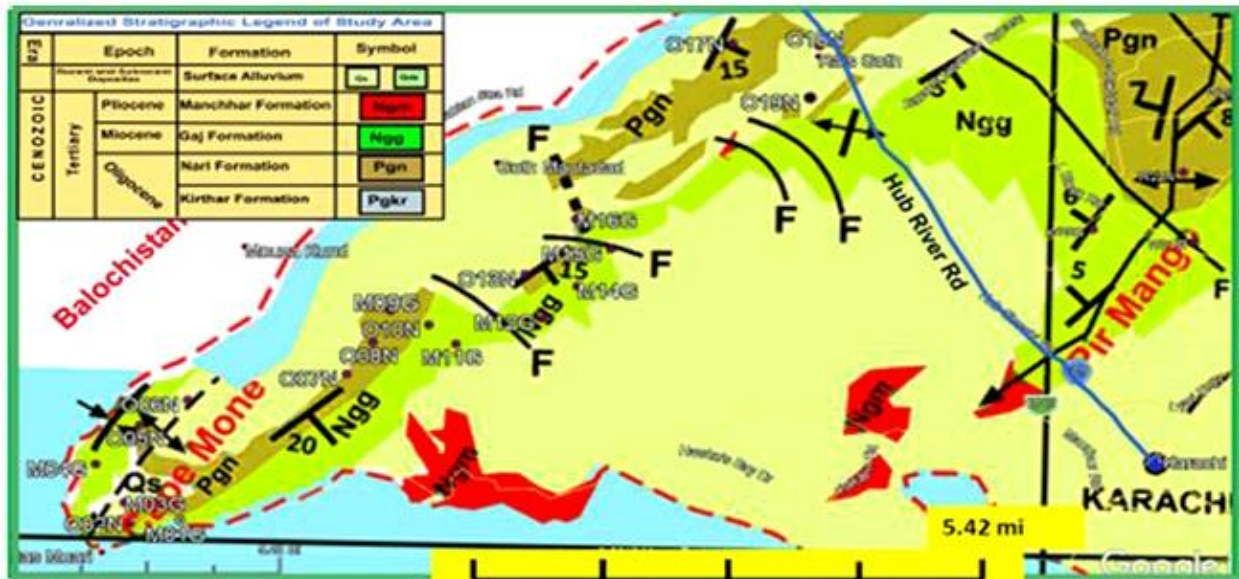


Fig. 1 Geological map of study area.

and 18.06-22.38% ranges are reported for FI and EI values for Nari Formation respectively. These results have shown that flakiness and elongation indices of collected samples are within the corresponding permissible limits (25%) of ASTM (Table 1). The consistency in the values of EI and FI of both the formations is attributed to the same environment of deposition and subsequent lithification processes. EI and FI translate the dimensions of particles i.e. cubic or flaky. Cubic and angular particles provide strength to the bituminous mixtures. On the other hand, workability of concrete is function of smooth and rounded grains which provide better bond characteristics (Shetty, 2010).

Clay Lumps and Friable Particles

The fraction of clay lumps (CL) and friable particles (FP) altogether varied between 0.1-1.02 and 0.62-2.54 for Gaj and Nari formations respectively (Table 1). It is observed that all the values of clay lumps and friable particles are within the reference range (2%) of ASTM C-33. Clay lumps resemble with aggregate or gravels which are basically small balls made up of soil and disperse in water rapidly. Friable particles are granular in nature which crumbles in water. The presence of such particles in aggregate affects density, durability and strength of mix.

Material Finer than 0.075mm

For this test, coarse aggregate was obtained from intact outcrops of both formations. Material finer than 0.075mm ranges between 0.7-3.0 and 0.5-1.5 for Gaj and Nari formations respectively. These values are within the permissible limit (<3%) of ASTM C-33 designation. Finer material generally sticks on the surface and cavities of the coarse aggregate which affects bond between aggregate and cement or asphalt.

On the other hand, such fine material increases water demand, which results in low strength of concrete.

Unconfined Compressive Strength (UCS)

Unconfined Compressive Strength (UCS) values range between 32.02-94.31 for Gaj Formation and 31.22-63.25 for Nari Formation. Relatively higher values of UCS for Gaj Formations are attributed to relatively less clastic influx during deposition as compared to Nari Formation. This high range of UCS makes Gaj Formation limestone of good quality for aggregate. According to Deer and Miller (1996) UCS values between 28 and 110 MPa are recommended for using as aggregates. Hence, limestone of both the formations are suitable for asphalt and cement concrete. About half (11) of the total collected samples (19) from the study area are categorized as medium to low strength limestones (Fig .2).

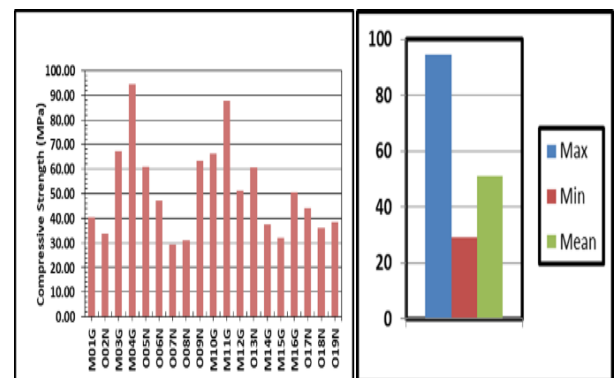


Fig. 2 Showing Unconfined Compressive Strength.

Density

Density of collected samples from Gaj and Nari formations is almost similar which varied between 2364-3264 and 2321-3284 kg/m³. The limestone

having density less than 1700 kg/cm³ is considered as soft and susceptible to weathering while density above 2500 kg/cm³ is considered as hard to work and weathering resistant. About half of the total collected samples from both Nari and Gaj formations are showing density more than the limiting value (2500 kg/cm³). These sites are strongly recommended for aggregate quarry. Out of these high-density limestone sites, mostly belongs to Gaj Formation (Fig.3).

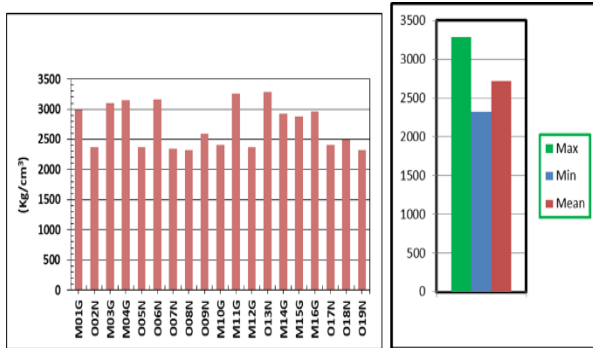


Fig. 3 Showing unconfined density.

Specific Gravity

Specific gravity of both Nari and Gaj formations varies in the range of 2.2-2.71 and 2.49-2.7 respectively. Slight deviation in the specific gravity of limestone from both formations is attributed to the heterogeneity of the sediment influx at the time of deposition which is also manifested in some other characteristics of Nari and Gaj formations. The specific gravity of all the samples is within the recommended values (2-3) of ASTM and suitable for aggregate purpose (Fig. 4).

The study area is located in the south east of lower Sindh and lies between latitudes from 24° 50' 1.74" to 24° 58' 9.60"N and longitude from 66° 38' 45.09" to 66° 56' 8.80"E. The study area comprises longitudinal ridges composed mainly of Gaj and Nari formations of Oligocene and Miocene ages respectively. Lithic character of the rocks exposed in study area varies from limestone and sandstone followed by siltstone and shale with subordinate conglomerate (Fig. 1). Out of these rocks, limestone forms the major ridges in study area.

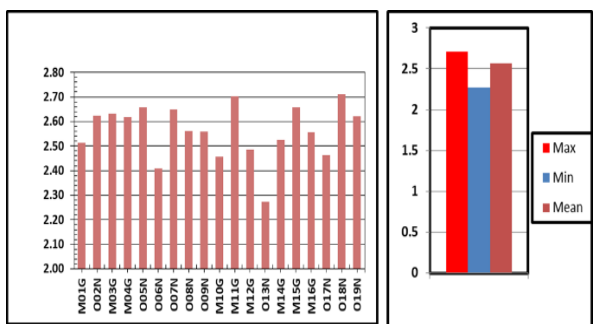


Fig. 4 Showing specific gravity.

Water Absorption

Water absorption in collected samples span between 0.5-2.34 and 0.6-6.54% for Gaj and Nari formations respectively (Table 1). Only two samples from Gaj Formation show absorption values > 2% while half of the collected samples from Nari Formation have absorption > 2% (Fig. 5). In this context, Gaj Formation is more suitable for concrete and asphalt work as compared to Nari Formation. However, water absorption was found well within 3% in most of the limestone samples collected from study area.

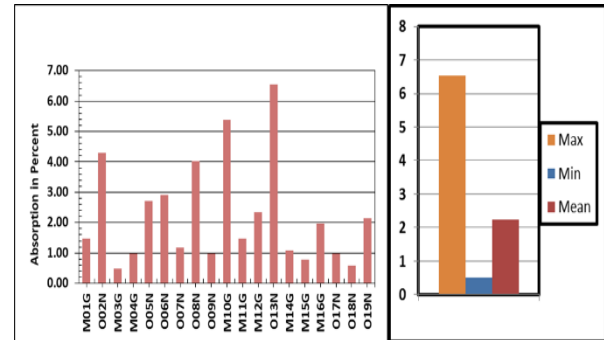


Fig. 5 Showing absorption percentage.

Los Angeles Abrasion Value

Los Angeles (LA) abrasion values of these limestones range between 18.88-32 and 18-58% respectively (Table 1). Four samples (O7N, O13N, O17N and O19N) of Nari Formation have LA values more than 35% while all the samples of Gaj Formation qualify ASTM-C131 designation (Fig. 6). LA abrasion values high in one third of collected samples from Nari Formation are attributed to heterogeneity in limestone composition which is due to more clastic influx at the time of Nari beds deposition. Relatively high amount of fine clastic influx increases the entropy of the beds leading to reduce the abrasion strength.

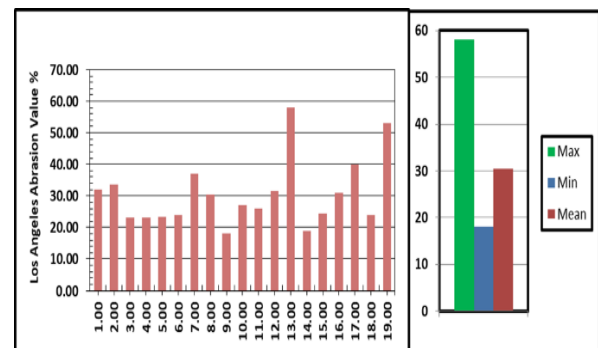


Fig. 6 Showing Los Angeles value percentage.

Aggregate Crushing Value

Aggregate Crushing value (ACV) of Nari and Gaj formations show wide variations, which ranges between 10.48-50.81 and 10.23-25.31 respectively. All limestone of Gaj Formation has ACV within the

permissible limit while four samples (O6N, O7N, O17N and O19N) of Nari Formation showed ACV values > 30% (Fig. 7).

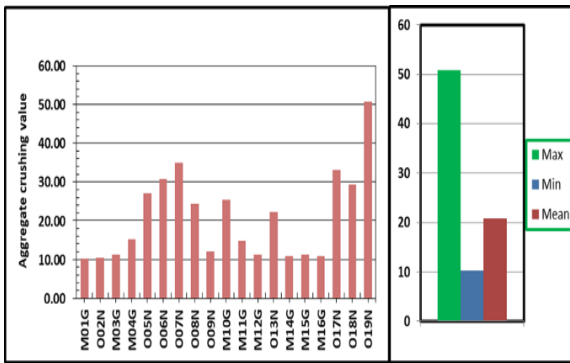


Fig.7 Aggregate crushing value.

Ten Percent Fines Value (TFV)

Resistance of aggregates against crushing is measured by TFV test. This test was carried out only on four samples of limestone (O06N, O7N, O17N and O19N) having ACV values > 30% and it is found that TFV values of these samples are more than 150 kN (ASTM C-33). (Table 1). For weak aggregates, TVF of 10% is preferred due the fact that these fines overcome the cushioning effect.

Chemical Characteristics

Chemical characteristics of limestone suggest varying conditions of weathering which is required for proper utilization of limestone as aggregate. Among chemical parameters, percentage of sodium sulphate soundness, sulfate, chloride, TDS, total organic content (TOC), carbonate and pH were determined in the collected samples of limestone from various localities under study.

Sodium Sulphate Soundness Test

Sodium sulphate soundness test reveals the variation range of 6.79-9.96 and 4.94-15.52% for Gaj and Nari formations. This test determines strength of aggregates to weathering. ASTM D-692 specifies 5 cycles and a maximum loss of 12% when the sodium sulfate is used. Only one sample (O13N) from Nari Formation showed soundness value above ASTM guideline value (12%) whereas remaining samples showed soundness value within the reference range (Fig. 8).

Sulphate

Sulphate content varies in the range of 0.03-0.23 and 0.03-0.31% for Gaj and Nari formations respectively (Fig. 9). Slightly high content of sulphate in Nari Formation is attributed to the occurrence of gypsiferous layers in shales and limestone beds.

Corrosion of construction material is influenced by sulphur bearing compounds (Reid et al., 2001). Sulphur or sulphate minerals are natural sources in aggregate material. Amount of soluble sulphate present in aggregate is responsible for sulphate attack on concrete (Longworth, 2008). If sulphate content in an aggregate is found above 5% of Portland cement, it is not used in concrete (AS-2758, 2009). Sulphate content is < 1% in all collected samples from both formations, which is consistent with the findings of Tam and Tam, (2007). Hence the limestone sources are suitable for using as aggregate material.

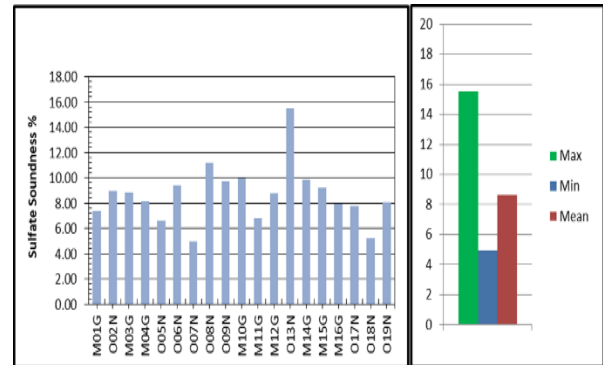


Fig. 8 Showing sulphate soundness percentage.

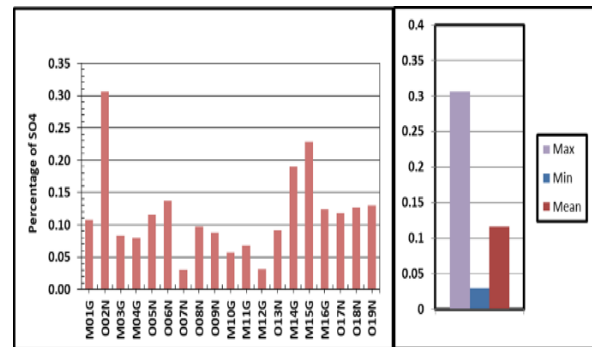


Fig. 9 Showing percentage of sulphate.

Chloride

For present study, water soluble chloride is evaluated as per ASTM C-1218, (2015). Chloride content in the limestones of Nari and Gaj formations ranges between 0.03-0.11 and 0.01-0.1% respectively. Chloride content is used to determine the corrosion risk factor (Pargar et al., 2017). Chloride may naturally get mixed in concrete as contaminant or in association with aggregates from admixtures and through mixing water (Dehwah et al., 2002; Al-Saleh, 2015). Presence of water-soluble sulphate in substantial amount creates or accelerates the corrosion of metals. Determination of water-soluble chloride varies with parameters like fineness of sample, quantity of water added, time and temperature (Silva et al., 2013). Chloride content in all the limestone samples of Nari and Gaj formations is <1% which is consistent with the BS and ACI specifications and thus these rocks can be used as aggregate for construction purpose (Fig.10)

Table 1 Physicochemical and mechanical characteristics of limestone samples from Nari and Gaj formations, Karachi.

S. No.	Symbol	Formation	Latitude	Longitude	1. Compressive Strength MPA	2. Tensile Strength (Brazilian Test) MPA	3. Shear Strength MPA	4. Density = $W/V = \text{Kg/m}^3$	5. Specific Gravity	6. Absorption in Percent	7. Sulfate Soundness %	8. Loss Angeles Abrasion Value	9. Aggregate crushing value	10. Percentage of SO_4	11. Percentage of Cl_2 Mass	12. TDS	13. pH	14. Total Organic Contain	15. Loss on Ignition (LOI) %	16. Carbonate Percentage
1	W01G	Gaj	24°54'53.30"N	66°45'52.31"E	40.42	10.10	161.68	2.99	2.51	1.48	7.39	32.00	10.23	0.11	0.04	5.00	8.07	0.64	40.88	40.56
2	W03G	Gaj	24°51'6.93"N	66°40'41.28"E	67.36	16.84	269.46	3.11	2.63	0.50	8.86	23.00	11.34	0.08	0.04	3.00	8.16	0.72	12.37	50.43
3	W04G	Gaj	24°50'35.61"N	66°40'19.19"E	94.31	23.58	377.24	3.14	2.62	0.99	8.13	23.00	15.32	0.08	0.03	5.00	8.45	0.20	40.84	56.39
4	W10G	Gaj	24°54'55.80"N	66°45'57.80"E	66.42	16.60	265.67	2.41	2.46	5.39	9.96	27.00	25.31	0.06	0.03	2.50	8.13	0.23	41.05	54.39
5	W11G	Gaj	24°54'1.46"N	66°47'24.56"E	87.57	21.89	350.30	3.26	2.70	1.48	6.79	26.00	14.85	0.07	0.03	3.70	8.01	0.30	39.90	49.00
6	W12G	Gaj	24°53'50.08"N	66°48'24.97"E	51.33	12.83	205.30	2.36	2.49	2.34	8.80	31.50	11.26	0.03	0.06	2.10	8.14	0.07	43.07	40.90
7	W14G	Gaj	24°55'5.84"N	66°49'28.19"E	37.58	9.39	150.31	2.92	2.53	1.09	9.86	18.88	10.95	0.19	0.05	2.35	8.21	0.68	42.57	33.58
8	W15G	Gaj	24°55'49.25"N	66°49'36.69"E	32.02	8.00	128.06	2.88	2.66	0.79	9.19	24.50	11.35	0.23	0.11	2.35	8.17	0.23	41.05	45.43
9	W16G	Gaj	24°56'19.03"N	66°48'60.00"E	50.46	12.61	201.82	2.97	2.56	1.96	7.93	31.00	10.76	0.12	0.04	2.35	8.07	0.64	40.88	42.50
10	W02N	Nari	24°50'9.88"N	66°40'26.45"E	33.61	8.40	134.42	2.36	2.62	4.31	8.97	33.54	10.48	0.31	0.05	2.50	8.21	0.64	40.88	45.48
11	W05N	Nari	24°51'56.90"N	66°41'6.50"E	60.98	15.24	243.92	2.36	2.66	2.72	6.63	23.50	27.00	0.12	0.03	3.50	8.05	0.42	39.56	48.68
12	W06N	Nari	24°54'43.6"N	66°45'59.4"E	47.16	11.79	188.62	3.16	2.41	2.91	9.43	24.00	30.84	0.14	0.10	4.30	7.83	0.62	27.53	36.10
13	W07N	Nari	24°54'0.32"N	66°45'2.71"E	29.29	7.32	117.15	2.35	2.65	1.19	4.94	37.00	34.94	0.03	0.04	1.70	8.14	0.05	37.93	40.40
14	W08N	Nari	24°54'3.97"N	66°45'2.89"E	31.22	7.80	124.86	2.32	2.56	4.03	11.18	30.50	24.44	0.10	0.04	2.35	8.06	0.14	34.81	38.90
15	W09N	Nari	24°50'15.34"N	66°41'25.03"E	63.25	13.84	253.01	2.59	2.56	0.99	9.71	18.00	12.05	0.09	0.04	6.00	8.18	0.57	41.35	43.70
16	W13N	Nari	24°52'48.41"N	66°41'40.50"E	60.63	15.16	242.51	3.28	2.27	6.54	15.52	58.00	22.35	0.09	0.04	4.30	7.83	0.32	41.22	42.72
17	W17N	Nari	25° 0'23.80"N	66°52'46.50"E	43.99	11.00	175.97	2.41	2.46	0.99	7.78	40.00	33.00	0.12	0.05	3.00	8.42	0.56	14.64	46.82
18	W18N	Nari	25° 0'28.20"N	66°53'1.80"E	36.11	9.03	144.44	2.49	2.71	0.60	5.23	24.00	29.44	0.13	0.03	3.00	8.21	1.15	72.01	33.10
19	W19N	Nari	24°58'52.00"N	66°54'25.50"E	38.49	9.62	153.98	2.32	2.62	2.15	8.04	53.00	50.81	0.13	0.01	1.95	8.19	0.37	27.46	34.50

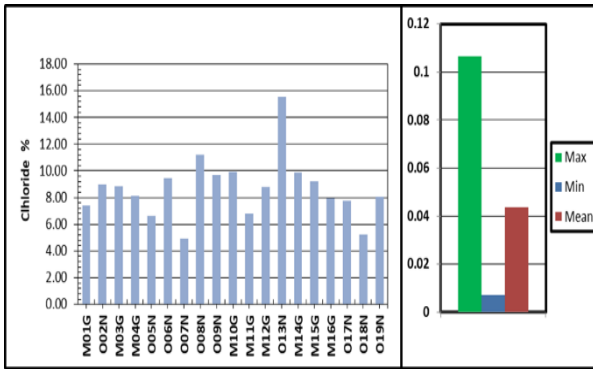


Fig. 10 Showing chloride percentage.

The pH of Limestone

ASTM (C-25 to 06, 2006) procedure given for chemical analysis of limestone quicklime, and hydrated lime was adopted to analyze the pH of studied samples. Data revealed that the pH is alkaline and it varied between 8.01-8.45 and 7.83-8.45 for Gaj and Nari formations respectively (Fig. 11). The pH of limestone rock samples was evaluated for its utilization in concrete and cement manufacturing. The permissible range of aggregate pH is 9-11, which should not exceed 9 in case of concrete floor surface as it damages the adhesives used for fixing the tiles (Grubb et al. 2007). Since the pH of all collected samples is found to be < 8.5 , these rocks can be used for aggregate production.

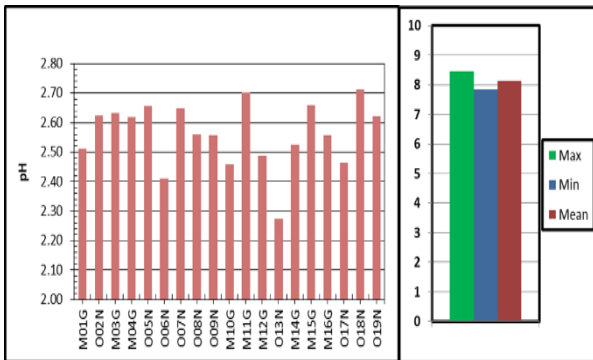


Fig. 11 Showing pH.

Organic Impurities

Loss on ignition (LOI) method was used to determine organic impurities in Gaj and Nari formations as proposed by Dean Jr. (1974). Organic impurities varied in the range of 0.07-0.72 and 0.05-1.15% for Gaj and Nari formations respectively. Except one sample (O18N) all the collected limestone samples from both formations have LOI $> 1\%$ which make these sources suitable for aggregate production and use in concrete and asphalt work (Fig. 12). Possible sources of organic impurities in a natural aggregate are decayed vegetation, remains of animals (Parkhe et al., 2016). Organic matter in aggregate weakens the strength of concrete and mortar by interfering with hydration process leading to hindrance in setting and hardening

of concrete. Moreover, dimensional instability in concrete is also caused by the occurrence of organic impurity in coarse aggregate (Olonade et al., 2018).

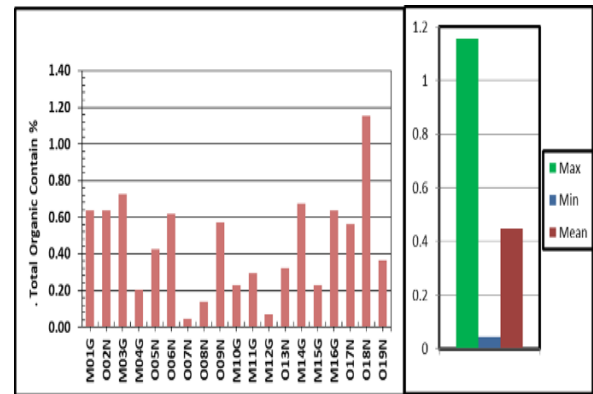


Fig. 12 Showing total organic content.

Carbonate

Carbonate content in Gaj and Nari formations varies in the range of 33.58-56.39 and 33.1-48.68% respectively (Fig. 13). The highest value of carbonate is 56.39%, whereas the lowest is 33.10%. One sample of Gaj and four of Nari Formation showed carbonate $< 40\%$ (Table 1). Very low content of carbonate in limestone is attributed to environment of deposition. Generally high carbonate limestone occurs in deep marine environment where clastic influx is rare. Conversely, low carbonate limestones are formed in shallow marine environment where siliciclastic influx is more pronounced resulting in low content of carbonates. Carbonate percentage in limestones play a very important role in terms of its durability and strength i.e. greater the carbonate percentage greater will be the strength. Samples showing higher values of UCS, ACV and LAV have also higher values of carbonate percentage.

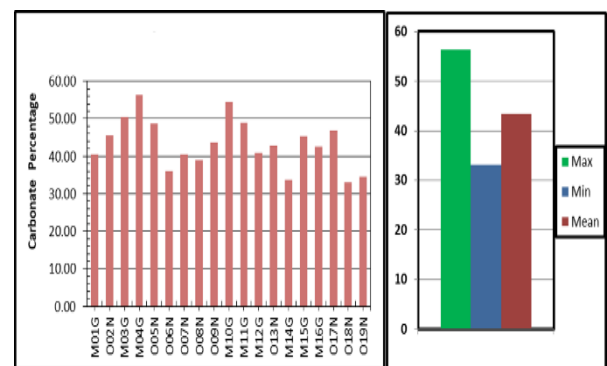


Fig. 13 Showing carbonate percentage.

Conclusion

The values of all engineering parameters are comparable with standard values of ASTM which refer the limestone of Nari and Gaj formations as excellent aggregate source. It is concluded from physical and chemical properties of these limestone rocks that these

areas suitable for serving as subbase, base, asphalt concrete and cement concrete work. The limestone of Gaj Formation is relatively better than Nari Formation for using as aggregate. The studied sites are logistically accessible through metaled road and the rocks may be crushed into raw material by blasting method and can be transported to the nearby crushing facility.

References

- Al-Saleh, (2015). Analysis of total chloride content in concrete: Case studies in construction materials, **3**, 78-82, Nigeria.
- Deere, D.U., Miller, R.P., (1966). Engineering Classification and Index Properties for intact rock. Rept. for 1 Feb 1964-1 Apr 1966 Illinois Univ. at Urbana Dept. of Civil Engineering, USA.
- Farhad, P., Kolevaorcid, D.A., Breugel, K.V, (2017). Determination of chloride content in cementitious materials: from fundamental aspects to application of Ag/AgCl chloride sensors. Faculty of Civil Engineering and Geosciences, Department Materials and Environment, Delft University of Technology.
- Farshori, M. Z. (1972). The Geology of Sindh. Mimigraphed edition. Department. of Geology, University of Sindh, Jamshoro, 81. sections and maps.
- Grubb J.A., Limaye H.S., Kakade, A.M. (2004). The information in this article was originally presented at the ACI fall convention, San Francisco.
- Ian Longworth (2008). Sulfate damage to concrete floors on sulfate-bearing hardcore Identification and remediation, Department for communities and local government, London. *Int. J. Econ. Environ. Geol.*, **8** (1), 14-19.
- Iqbal, M. W. A., Khan, M. Y. (1980). Records of the Geological Survey of Pakistan, 82, *Geological Survey of Pakistan*.
- Kahraman, (2010) "Predicting Los Angeles abrasion of rocks from some physical and mechanical properties", Yilmaz Ozcelik, Department of Mining Engineering, Hacettepe University, Turkey.
- Kandhal, P. B., Parker, Jr. F. (1998). Report 405, Aggregate tests related to asphalt concrete performance in pavements, National Academy Press, Washington, D.C.
- Khan (2000). Study of the geology of Kirana group, central Punjab and Evaluation of its utilization and economic potential as aggregate, University of Punjab, Lahore, Pakistan.
- Khan, M.A. (1988). Characteristics of building stones of Sindh, Department of Geology, University of Karachi, Pakistan.
- López Buendíaav A.M. (2006). Lithological influence of aggregate in the alkali carbonate reaction, *Cement and Concrete Research*, **36**(8), 1490-1500.
- Meininger, R. (2004). Micro-Deval vs. L. A. Abrasion" Rock Products, **107** (4), 33-35.
- Neville, A. M. (2000). Properties of concrete. Fifth edition Pearson Education limited Edinburgh Gate Harlow Essex CM20 2JE England.
- Olonade, et al., (2018). Case studies in construction materials: case study performance evaluation of concrete made with sands from selected locations in Osun State, Nigeria, *Case Studies in Construction Materials*, **8**, 160-171.
- Parkhe, D.D., Shrigriwar, R.V., Panse, R.V. (2016). Study of Sand having more organic impurities, *International Journal of Advances in Science Engineering and Technology*, Maharashtra Engineering Research Institute, Dindori Road, Nashik, Maharashtra.
- Reid and Chandler, (2001). Data on the use of various recycled materials in 1999, presented by Testing pH of concrete need for a standard procedure, Oxfordshire, South-east of England.
- Sensogut, C. Duzyol, S., Cinar, I. (2017). Evaluation of resistance to los Angeles abrasion and physical factors with grindability properties of some aggregate materials,
- Shah, S. M. I. (1977). Stratigraphy of Pakistan, Memoir Geological Survey of Pakistan, Ministry of Petroleum and Natural Resources, *Geological Survey of Pakistan*, **22**,.
- Shetty, M.S. (2010). Concrete technology, theory and practice. (revised edition) S. Chand & Company Pvt. Ltd. Ram Nagar, New Delhi.
- Silva, N. (2013). Chloride induced corrosion of reinforcement steel in concrete threshold values and ion distributions at the concrete-steel interface, Department of Civil and Environmental Engineering Chalmers University of Technology, Gothenburg, Sweden.
- Tam V.W.Y., Wang, K., Tam, C.M., (Year). Ways to facilitate the use of recycled aggregate concrete, Proceedings of the ICE – Waste and Resource Management, **160**(3), 125-129

Tutti, K. (1982). Corrosion of steel in concrete, Swedish Cement and Concrete Research Institute, Stockholm, Sweden.

W.E. Dean Jr. (1974) Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition comparison with other methods, *Journal of Sedimentary Petrology*, **44**, 242-248.