

Replacement of Coarse Aggregate with Marble Waste for The Preparation of Alkali Activated Concrete

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ABSTRACT

Concrete is the most widely used man-made construction material from ages due to its versatility and cost effectiveness. Ordinary Portland Cement (OPC) has been conventionally used as the primary binder to produce concrete. One ton production of Portland cement emits approximately about 0.8 to 1 ton of carbon dioxide into the atmosphere, including for burning of the fuel fossils and for process of production using raw materials. This enormous liberation of carbon dioxide from the cement industries is one of the major issues for the cause of ecological imbalance, resulting in greenhouse effect. Hence several efforts have been in progress to reduce the global warming issue. To reduce these carbon dioxide emissions, one of the possible alternatives is the use of alkali activated binders using industrial by-products containing alumino-silicate materials such as Ground Granulated Blast furnace Slag (GGBS), fly ash etc. GGBS is obtained from a blast furnace in water or steam by quenching molten iron slag (a by-product of iron and steel-making), to produce a glassy, granular product which is then dried and ground into a fine powder. Fly-ash & GGBS is considered as a sole binder in the production of Alkali Activated Concrete (AAC) by activating with sodium hydroxide and sodium silicate solutions. The present project work, the molarity of sodium hydroxide 10M and 60% Fly-ash and 40% GGBS as cementitious material (cement replacement) with various percentages of coarse aggregate replacing with marble waste i.e. 10%, 20%, 30% 40% and 50%. A comparative study was conducted on the performance of mechanical properties of oven (600C) and ambient cured (7, 28 days) marble waste-based alkali activated concrete. It was observed that higher compressive strength (28 days ambient curing) was attained for the eco-friendly concrete (AAC) up to 30% replacement of coarse aggregate with marble waste.

Keywords: AAC (alkali activated concrete), GGBS (Ground Granulated Blast furnace Slag), Fly ash, Molarity, NaOH

1. INTRODUCTION

Concrete is the most versatile material used worldwide for construction purposes in Civil Engineering works because of its mouldability, strength, durability and low cost. Portland cement is the major constituent of concrete. In the developing world, demand for cement is growing rapidly which causes an urgent need for alternative binders to meet the infrastructure and housing needs of billions of people, without further compromising the carbon dioxide (CO₂) levels of Earth's atmosphere (Taylor et al. 2006). The production of cement requires decomposition of limestone i.e., calcium carbonate (CaCO₃) at high temperatures to generate reactive calcium silicate and aluminate phases. Ordinary Portland Cement (OPC) is normally made by heating a mixture of raw materials in a rotary kiln to about 1,450°C, cooling this semi-molten material to form a solid clinker, then inter grinding with calcium sulfate to generate a fine powder. The major raw material used is limestone i.e., calcium carbonate (CaCO₃), which is blended with materials such as shales or clays to provide the necessary alumina and silica. The clinker is predominantly calcium silicate, which is rapidly cooled to stabilize a

mixture of tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$) and dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$), with minor (but important) CaO-rich aluminate and aluminoferrite phases. The production of the clinker or Portland cement is an energy-intensive process and consumes 4 GJ per ton of cement. The manufacture of one ton of Portland cement clinker releases 0.8 to 1 ton of CO_2 into the atmosphere.

2. LITERATURE SURVEY

In this section a critical review of existing literature on development of alkali activated slag mortar and concrete and behaviour of alkali activated slag concrete is presented. It covers past to recent understanding of mechanical and microstructural properties, durability aspects related to acid attack and sulphate attack of alkali activated slag concrete.

Bakharev et al. (1999) investigated the alkali activation of Australian slag using sodium silicate, sodium hydroxide, sodium carbonate, sodium phosphate and combinations of these activators. Compressive strengths for the pastes were achieved in the range from 20 to 40 Mpa. The liquid sodium silicate was used as a most effective activator. The effect of curing at 60°C , modulus of sodium silicate solution and concentration of alkalis on the compressive strength and setting times were studied with this activator. In the present investigation, sodium silicate solution with comparatively lower Na content and modulus of 0.75 was recommended for formulation of alkali activation of Australian slag concrete. Puertas et al. (2000) studied the activation of fly ash / slag pastes with the help of NaOH solutions. In this process different parameters were studied such as activator concentration (NaOH – 2M and 10M), curing temperature (25°C and 65°C), and fly ash / slag ratios (100/0, 70/30, 50/50, 30/70, and 0/100). The models describe the mechanical behaviour of the alkali – activated fly ash / slag pastes. Compared to the other two factors, curing temperature in the development of the strength of the pastes was found out to be less. For the development of compressive strength to increase the NaOH concentration and higher strengths can be obtained when activator concentration of 10M was used. As the slag content in the pastes increases, it was studied that the compressive strengths increase. The main reaction product in 50% fly ash/50% slag activated with 10M NaOH solution of pastes is a Hydrated Calcium Silicate, like that of C-S-H gel, with high amounts of tetra coordinated Al and inter layer Na ions in its structure.

Collins et al. (2001) investigated the level of micro cracking that occurs in alkali activated slag concrete subjected to various types of curing regimes. Without the use of Portland cement the AASC was obtained by activating GGBS with alkalis. The compressive strength development of alkali activated slag concrete were monitored. The level of micro cracking was measured using three divergent tests: (i) frequency and size of surface cracks using crack-detection microscope (ii) water sorptivity tests measuring absorption of water by capillary attraction and (iii) mercury intrusion porosimetry tests which measured the pore size distribution of alkali activated slag concrete and alkali activated slag pastes. The results obtained show that due to the lack of moist curing of AASC not only enhanced the level of micro cracking but also reduced the strength development of alkali activated slag concrete.

Zuda et al. (2006) carried out a study on the properties of alkali activated aluminosilicate material based on alkali activated slag. i.e., porosity, bulk density, compressive strength, thermal conductivity and specific heat capacity of the material were determined at the room temperature conditions under a thermal load ranging up to 1200°C prior to the measurements and is compared to the reference material data. This shows that if it exceeds 1200°C reference material is not exposed to any thermal load. By the help of water vacuum saturation measurements, bulk density and porosity were determined. The porosity of the material ascended significantly after it is pre-heated up to a

temperature of about 1200°C. In case of tunnels, this makes it suitable for replacing the traditional cement based as fire protection materials or utilizing it in the form of protective layers. By using mercury porosimetry measurements, the global characteristics of porous space, pore distribution curves were measured. The compressive strength was determined as the most characteristic for alumino-silicates. The thermal conductivity was measured in laboratory conditions using Isomet, a commercial device. These results were determined by using material characterization experiments, such as X-ray diffraction analysis and scanning electron microscopy.

Bougara et al. (2007) investigated the activation of Algerian slag mortars, which exhibit low reactivity due to its lower CaO/SiO₂ ratio and it was mechanically activated by grinding the slag to 250, 360 and 420 m²/kg Blaine surface area, thermally by curing mortar specimens at 20, 40 and 60°C, and chemically by mixing the slag with two alkalis, NaOH and KOH at varying concentrations. The compressive strength was determined at the age of 1, 3, 7, 28 and 90 days respectively. It was observed that all the three methods augmented the reactivity of the slag. It was observed from the results that the slag was highly reactive to the rise in temperature whereas the increase in the fineness was observed along with increased strength development. Alkali activation of the slag resulted in the enhanced strength development, yet the strength was lesser than that of the controlled mortar.

Huang et al. (2009) investigated a cementitious material by utilizing two industrial wastes, Phospho Gypsum (PG) and Steel Slag (SS), combined with another industrial byproduct ground granulated blast-furnace slag and Limestone (LS). The 28 days compressive strength of a mixture of 45% PG, 10% SS, 35% GGBS and 10% LS exceeded 40 Mpa. X-ray diffraction analysis and scanning electron microscopy analyses revealed that the formation of ettringite and C-S-H gel. Where a part of the PG reacted with GGBS and SS to develop into ettringite. It was observed that SS present in the cement acted as alkalinity activator and the extra dosage of SS might cause unsoundness of the cement.

Rovnanik et al. (2013) studied the micro – structural changes in the alkali activated granulated blast furnace slag exposed to high temperatures. By using SEM, HT-XRD analysis and FTIR and MASS, NMR spectroscopy it was determined that the micro structural changes caused due to heat. Only partial dehydration and decomposition of C-A-S-H phase can be observed up to a temperature of about 600°C. This significant change in micro structure is responsible for an increase in compressive strength that reaches 180% of the reference value, and also for the considerable shrinkage of the AAS material. When the dehydration of C-A-S-H phase is complete and new phases start to crystallize, among which akermanite is dominant, the principle changes in the microstructure of alkali activated slag occur between 600°C and 800°C.

Aydm et al. (2014) investigated the effects of various activators on the properties of alkali – activated slag mortars by the developing the workability, setting times, mechanical properties, drying shrinkage, water absorption characteristics and microstructure of alkali activated slag cement binders to establish the modulus ratios and Na₂O contents of the solutions. According to the investigation it was found out that by the activation of slag without heat curing, Portland cement free high-performance composite with compressive strength values ranging up to 100 Mpa can be easily obtained and in case of activation by optimum modulus ratio, sodium silicate alkali activated slag mortars present higher compressive strength, lower water absorption, higher workability, lower porosity and a wide range of setting times in comparison with NaOH activated slag mortars and Portland cement mortars. Alkali activated slag mortars may be used as a binder for the production of high performance composites. Reduced values of capillary water absorption, total water absorption

and volume of permeable voids of alkali activated slag mortars were observed for the mixture modulus of 0.8 at 6 % Na₂O content.

Adam et al. (2015) conducted studies and compared the strength of the alkali activated slag and fly ash based geopolymer mortar. Mortars were prepared with slag activated by a low dosage of alkaline solution and fly ash activated by high alkaline solution. The mix was prepared with a 5-liter Hobart mixer, after which it was poured into 5 cm cubic moulds and vibrated for 1 minute. Two sets of specimens AAS and geopolymer with 1 set being left for 24 hours at room temperature and the other set was cured in 20°C water bath for 6 days before being demoulded and tested. It was observed that the compressive strength obtained for the heat cured specimens at 3 days was relatively equal to the 28 days compressive strength. Although the alkali activated binders along with slag and fly ash are not eco-friendly, they are capable of obtaining high compressive strengths at an early curing age.

Zhang et al. (2016) investigated the mineralogical and elemental compositions in six alkali-activated cements which were prepared by sodium silicate-activated ternary systems of fly ash, slag and silica fume under ambient conditions. The dominant reaction products were C-(N)-A-S-H which were derived from the hydration of slag and N-I-A-S-H derived from activation of fly ash. It was observed that the Alkali activated cements were poorly crystalline and extremely heterogeneous in nature of the reaction products at 1 year by using XRD and SEM coupled with EDX. There was no clear compositional boundary to separate the two hybrid gels and by comparison with the composition of the gel, the porosity and pore structure were observed to be more relative and determining to the compressive strength development of the alkali-activated cements.

3. OBJECTIVE AND METHODOLOGY

3.1 Objective

The aim and objectives of the project to evaluate the performance and suitability of AAC (G30) as an alternative to the usage of Cement concrete using OPC. The main objectives of the present project work are as follows.

- To study the compressive strength development of ambient and oven cured alkali activated concrete by replacing 10, 20, 30, 40, 50% coarse aggregate by marble waste (MW).
- To compare the mechanical properties of the MW based AAC cured under oven and in ambient conditions.

3.2 Methodology

- Collect the Marble waste and sieved from IS Sieve 20mm – 4.75mm. The passed from IS Sieve 20mm waste marble was collected and used for this project work as replacement of coarse aggregate.
- The design mix methodology of OPC – M30 mix design as per IS 10262-2019. The same mix design converted in to M30 to G30 by fully replacing cement with fly-ash, GGBS and alkali solution additionally added to improve the binder properties in fly-ash and GGBS.
- The fly-ash (class F), GGBS, Marble waste prepared at laboratory with manual splitting process, Locally available river sand (ZONE – II) and coarse aggregates (NMAS 20) was used for this investigation.
- The GPC was cured with oven (600C) and ambient cured 7,28days.
- Compare all mixes and find out the optimum dosage of marble waste replacing as coarse aggregate in AAC.

4. EXPERIMENTAL WORK

This section presents the preliminary investigations that have been carried out for developing the mix proportions of alkali activated slag concrete. Mix design for conventional concrete of M30 grade has been carried out according to IS: 10262-2019 and the same proportions of ingredients have been adopted for alkali activated concrete. A total of 6 AAC mixes have been developed with three varying parameters such as coarse aggregate replacing with marble waste by 0%, 10%, 20%, 30%, 40 and 50%. In these AAC mixes, fly ash to GGBS ratio fixed as 3:2 - K.K. Ramagiri 2021[1], with NaOH solution of molarity 10M. Concrete specimens of size 150 mm have been cast and cured under two curing regimes namely ambient curing and heat curing. The specimens under ambient curing are kept at sunlight (packed with over) temperature whereas the specimens under heat curing are kept at a temperature of 60°C for a period of 24 h. The effect of dosage and marble waste replacement on the compressive strength of AAC under ambient curing and heat curing at different ages of 7, 28 days have been studied. The compressive strength of AAC has been compared with under ambient curing and heat curing at different ages of 7, 28 days.

Alkaline Activating Solution: The alkaline activating solution causes the dissolution of the raw materials. The alkaline activating solution must be carefully selected because their composition has different impacts on the development of the mechanical properties in the hardened concrete. The alkaline activators used in the present study are sodium hydroxide and sodium silicate as they have successfully demonstrated their activation capabilities with GGBS, producing the high strength (Ravikumar and Neithalath, 2012). In terms of the alkali activators, it is widely accepted that a mixture of silicates and caustic alkalis ($M_2O \cdot nSiO_2 + MOH$, where M commonly refers to Na or K) results in the best mechanical properties and lowest porosity (Puertas et al. 2014) compared to other types of activators, and the most commonly used cation is Na due to its relatively low cost and availability. This mixed activator benefits the reaction process by offering alkaline conditions in a moderate and continuous manner. Therefore, in this present study sodium hydroxide and sodium silicate solutions are used as alkaline activators.

Curing conditions: Curing conditions have a significant effect on the properties of alkali activated slag concrete. The compressive strength of AAC can be controlled by judiciously choosing the curing conditions. The temperature is another factor in hydration which may act as an accelerator during the hydration process (Gebregziabiher et al. 2016). Heat curing is effective to promote early strength, while the strength at later ages will be reduced, when the curing temperature exceeds 80°C (Bakharev et al. 1999 and 57 Altan et al. 2012). Therefore, in this study specimens are cured under room temperature 27 ± 2 °C (ambient curing) and at 60°C for 24 h (heat curing).

Grade of the concrete: The grade of concrete for Reinforced Cement Concrete (RCC) structures for mild exposure is M30 according to IS: 456-2000. Therefore, in this study has been initiated with M30 grade concrete. As there is no codal provision for mix design of alkali activated concrete, a mix design of M30 grade conventional concrete has been designed and same proportions of ingredients have been adopted for AAC.

Compressive strength: The compressive strength test is conducted for AAC (6 mixes) in the preliminary investigation. The main design index for concrete as a structural material is the compressive strength at an age of 28 days. There are several reasons for choosing compressive strength as the representative index. Firstly, concrete used in a structure is mainly to resist the compression force. Secondly, the measurement of compressive strength is relatively easier. Finally, it

is thought that other properties of concrete can be related to its compressive strength through the microstructure.



Fig. 1: GGBS.

4.1 Properties of ingredients

Ground granulated blast furnace slag (GGBS)

Ground granulated blast furnace slag (GGBS) conforming to BS: 6699-1992 is used as a complete replacement of cement in the manufacture of alkali activated concrete. Its specific gravity is 2.9 with particle size less than 45 microns.



Fig. 2: marble waste.

4.2 Alkaline activating solution

The alkaline activating solution is the combination of sodium hydroxide and sodium silicate solutions. Sodium hydroxide with purity 98% available in solid forms by means of flakes has been used for the present investigation. Sodium hydroxide flakes are obtained from a local dealer. Sodium silicate is also known as water glass or liquid glass, available in liquid (gel) form. The solution preparation and concentration was discussed in mix design.



Fig. 3: Sodium silicate.



Fig. 4: Sodium hydroxide flakes.

4.3 Fly ash

In the present study, one of the source materials used in making geopolymer concrete was Class F fly ash. It was collected from locally available source NTPC Ramagundam, Telangana, India. The specific gravity of GGBS was 2.3 and fineness modulus was 2%.

S. No.	Oxide	Mass (%)	S. No.	Oxide	Mass (%)
1	SiO ₂	58.132	16	Co	0.007
2	Al ₂ O ₃	32.546	17	Ni	0.009
3	Fe ₂ O ₃	4.044	18	Cu	0.012
4	CaO	1.41	19	Zn	0.013
5	Na ₂ O	0.17	20	Ga	0.006
6	K ₂ O	0.96	21	Ge	0.001
7	TiO ₂	1.156	22	Rb	0.007
8	MgO	0.714	23	Sr	0.023
9	P ₂ O ₅	0.474	24	Y	0.006
10	SO ₃	0.125	25	Nb	0.004
11	Zr	0.046	26	Ba	0.035
12	Cr	0.015	27	Nd	0.021
13	Cl	0.021	28	Tl	0.001
14	Ti	1.156	29	Pb	0.008
15	Mn	0.029	30	Th	0.006

Fig. 5: Chemical composition of fly ash by XRF (mass %).

4.4 Fine aggregate

Locally available river sand is used as fine aggregate. The sand is free from clay, silt and organic impurities. The specific gravity and fineness modulus of sand are 2.61 and 2.2 respectively. According to IS: 383-1970 the sand is conforming to grading Zone III. The sand is made saturated surface dry before using to avoid any water absorption.



Fig. 6: Fine aggregate.

4.5 Coarse aggregate

Coarse aggregates of two different fractions of size 20 mm and 10 mm are used. The specific gravity, and fineness modulus of the coarse aggregate are 2.83 and 7.72 respectively.

Mix design

Mix design calculations for M30:

Following are the site considerations used for the mix design for nominal concrete in our experimental work

Concrete Grade	: M30
Type of Cement	: OPC 53
Type of aggregate	: 20mm Sub rounded
Exposure Condition	: Severe
Specific Gravity Of Cement	: 3.14
Specific Gravity Of Fine Aggregate	: 2.61
Specific Gravity Of Coarse Aggregate	: 2.83
Zone Provision	: Zone II
Workability	: 75 mm (slump)

Material	Quantity
Cement (grade 53)	400Kg/m ³
Water	152 liters
Fine aggregate	705.92 kg/m ³
Coarse aggregate	1303.29 Kg/m ³
Sp	4 <u>litre</u>

Fig. 7: Quantities of materials in cement concrete (M30).

Mix design calculations for G30:

For 1 cube:

Volume of the cube = $(0.15)^3 \times 1.1 = 0.0037125 \text{ m}^3$

Weight of water = 564.3 ml

Weight of cementitious material = 1.485 kg

Weight of coarse aggregates = 4.838 kg

Weight of fine aggregates = 2.62 kg

Weight of super plasticizer = 0.0148 lit

Liquid calculations:

1) Fixing NaOH = 10M

NAOH molecular weight = 40

Molarity (M) = $(\text{weight} / \text{molecular weight}) \times (1000 / \text{volume of water})$

$(\text{Weight} / 40) \times (1000 / 1000) = 10$

Weight of NAOH = $10 \times 40 = 400 \text{ gms}$

Alkaline liquids = flyash (0.3 to 0.5) Adopted -0.31

= $1485 \times 0.31 = 461 \text{ ml}$

Na₂SiO₃ to NAOH ratio - 2.0 Na₂SiO₃ = 307ml

NaOH = 154ml

For 1 cube = 564.3 ml water required , then $564.3 - 461 = 103.3 = 104 \text{ ml}$

Material	Quantity
Cementitious material	1.485 kg
Fine aggregate	2.62 kg
Coarse aggregate	4.838 kg
Sp	14.8 ml
Water	104 ml
NaOH	154 ml (61.6 gms to be added for 154ml of water)
Na ₂ SiO ₃	307 ml

Fig. 8: Quantities of materials for 1cube with G30.

In this study, the cementitious material using as 40% GGBS + 60% Fly ash [K. K. Ramagiri 2021]. The coarse aggregate are replacing with marble waste with 10, 20, 30, 40, 50%. The mix proportions for single cube mentioned below:

Mix	Fly ash (gm)	GGBS (gm)	Fine aggregate (gm)	Coarse aggregate (gm)	Marble waste (gm)	NaOH (gm)	Na ₂ SiO ₃ (gm)	Water (ml)	Super plasticizer (ml)
0%	891	594	2620	4838	0	154	307 ml	104	14.8
10%				4354.2	483.8	ml		ml	ml
20%				3870.4	967.6				
30%				3386.6	1451.4				
40%				2902.8	1935.2				
50%				2419	2419				

Fig. 9: Quantities of materials for 1cube with G30 with marble as coarse aggregate replacement.

4.6 Mixing, casting, curing of alkali activated concrete

For mixing, method used for making conventional concrete has been adopted to prepare alkali activated concrete. The solid constituents viz. aggregates, fly ash, marble waste and GGBS are mixed in dry form for about 1 – 2 minutes. At the end of this mixing, the alkaline activating solution with extra water has been added to the solids and the mixing is continued for another 3 – 4 minutes. The workability of the fresh concrete is measured by means of the conventional slump test. Then the fresh

concrete has been placed into the 150 mm cast iron cube moulds and allowed to compact on 3 layers each layer with more than 35 blows. Finally, surface finishing is done carefully to obtain a uniform smooth surface.



Fig. 10: Cube casting with AAC.

Two curing conditions have been adopted in the present study namely ambient curing and heat curing. After casting, one set of specimens are allowed to set for 24 hours. Then the specimens are demoulded and left at room temperature (ambient curing) until the specified period before testing. Another set of specimens are allowed to set for 24 hours. Then the specimens are demoulded and heat cured in an oven at a temperature of 60oC for 24 hours. The specimens subsequently are cured under sun light temperature until the specified period before testing.



Fig. 11: ambient curing.

4.7 Testing

Workability

The workability of all AAC mixes are measured by slump cone according to IS 1199-1959. The slump values for AASC mixes



Fig. 12: Slump test.

Compressive strength

The AAC specimens (150 mm x 150 mm x 150 mm) are tested for compressive strength using 3000 Kn capacity compression testing machine with a loading rate of 140 kg/sq.cm/minute. The compressive strength tests are conducted at different ages of 7, 28days for ambient curing and 1day at oven curing. Specimens at each age are tested in a compression testing machine in accordance with IS: 516-1959 and average strength of these specimens are reported as the compressive strength.



Fig. 13: Compressive strength testing of cubes.

5. RESULTS AND DISCUSSIONS

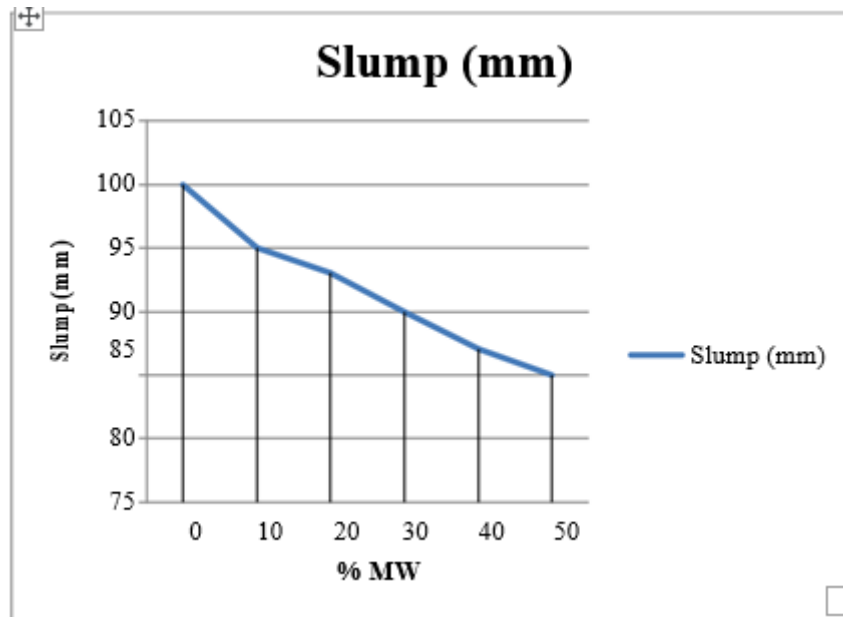


Fig. 14: Slump values.

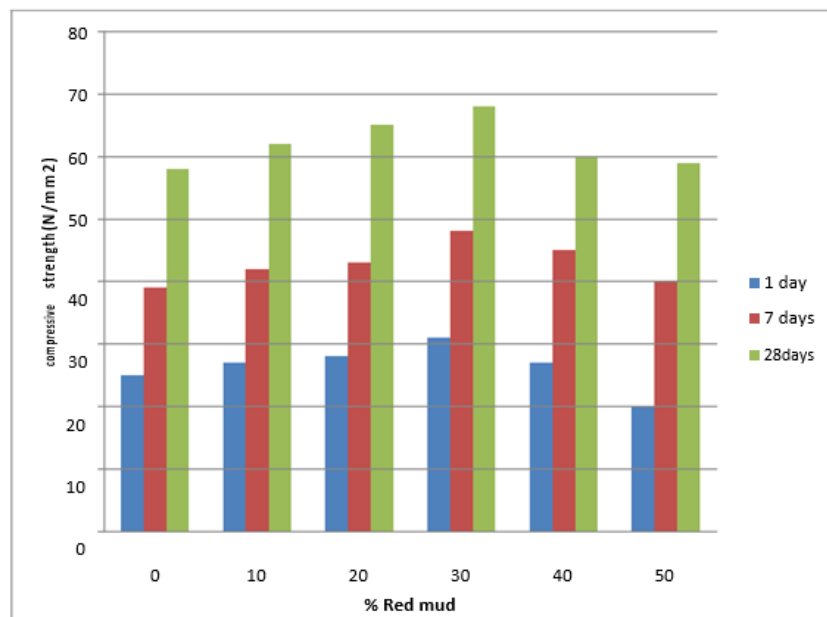


Fig. 15: Compressive strength graphs.

6. CONCLUSIONS

Based on the preliminary investigations on alkali activated concrete under ambient curing and heat curing with coarse aggregate replacement with marble waste, the following conclusions are drawn

Alkali activated concrete specimens exhibited relatively more compressive strength for ambient cured sample at 28days as compared to oven cured sample. The maximum compressive strengths of about 58 MPa at 28days curing of AAC.

By the replacement of coarse aggregate by marble waste in AAC, 30% showed higher compressive strength 68Mpa at 28days ambient curing. The compressive strength increments by 17.24% as compare to the 0% replacement of marble waste in alkali activated concrete.

Within the range of parametric values of the laboratory tests presented, it can be concluded that marble waste based AAC behaves better than conventional AAC. Hence Marble waste can become a suitable alternative to coarse aggregate by reducing the natural granite based coarse aggregate. 100% replacement of cement with flyash and GGBS based AAC, can become a suitable alternative to CC by reducing the emission of CO₂ gases into the atmosphere. Due to low-energy and low CO₂ emissions, alkali activated concrete has a great potential in future sustainable development of concrete. This may be a good addition to the available information regarding the behaviour of AAC.

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