Utilization of Kota stone slurry powder and accelerators in concrete

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Abstract. Recent advances in the concrete technology are aiding in minimizing the use of conventional materials by substituting by-products of various industries and energy sources. A large amount of stone waste i.e., dust and slurry form both are being originated during natural stone processing and causing deadily effects on the environment. The disposal problem of stone waste can be resolved effectively by using waste in construction industries. In present work, Kota stone slurry powder, as a substitution of cement was used along with accelerators namely calcium nitrate and triethanolamine as additives, to study their impact on various properties of the concrete mixtures. Kota stone slurry powder (7.5%), calcium nitrate (1%) and triethanolamine (0.05%) were used separately as well in combination in different concrete mixtures. Mechanical Strength, modulus of elasticity and electrical resistivity of concrete specimens of different mix proportions under water curing were studied experimentally. The durability properties in terms of strength and electrical resistivity against sulphate and chloride solution attack at various curing ages were also studied experimentally. Results showed that accelerators and Kota stone slurry powder separately enhanced the mechanical strength and electrical resistivity; but, their combination decreased strength at all curing ages. The durability of concrete specimens was also affected under the exposure to chemical attack too. Kota stone slurry powder found to be the most effective material among all materials. Material characterization was also done to study the microstructural properties.

Keywords: Kota stone slurry powder; accelerators; mechanical strength; electrical resistivity; resistance against chemical attack; cost analysis

1. Introduction

Concrete is one of the most versatile construction material in the world. Concrete is a compound material consisting of Portland cement, aggregates, water and admixtures which has wide applications. Portland cement is commonly used as a binder in concrete. In India, 370 million cubic meter cement is being consumed by the concrete industries per annum and origin of basic raw materials is natural (Paliwal and Maru 2017). A large amount of CO2 harmful greenhouse gases (GHG) is emitted during manufacturing of cement. Around 7% of total world GHG is released due to cement industry alone among all the industries. During cement production, 1 ton of cement releases 1 ton of CO_2 in atmosphere and by the year 2020, CO₂ emission will rise by 50% in comparison to the present level. To reduce GHG and save natural resources during cement production, industrial waste is being used from the last few years (Parveen et al. 2017, Nas and Kurbetci 2018). The rise in cement popularity leads to depletion of natural resources, which seeks a serious solution to this emerging problem. The alternative materials have been found which can be utilizing in the concrete. To increase the technical and economic feasibility of concrete, industrial by-products are used as a fractional substitution of cement. Utilization of supplementary cementitious materials (SCMs) i.e., silica fume (SF), coal fly ash, limestone powder (LP), metakaolin, slag and biomass ash in the production of concrete as a partial substitution to cement has received considerable attention nowadays. The utilization of SCMs significantly lessen the impact of cement and concrete production on environment by providing alternate solution to the disposal problem of SCMs and by reducing CO₂ emission and also enhanced its various properties (Rakhimova and Rakhimov 2014, Sadrmomtazi *et al.* 2017, Opiso *et al.* 2017, Sharma *et al.* 2018, Joshaghani *et al.* 2017a, El-Hassan and Ismail 2017, Singh *et al.* 2019).

Dimension stone is an important material which has main applications in flooring and cladding of monuments, hotels, and temples etc. Nature gifted versatile deposits of stone to India that makes it the third largest country in the world in stone production (Rana et al. 2017). A huge amount of waste is produced during the quarrying and processing of stones, which have a disposal problem due to limited storage or disposal facilities (Manca et al. 2015). During the cutting process, approx. 25% of the stone mass is lost. The stone waste can be sorted into two categories; a) solid waste originated during mining and cutting operations, and b) stone slurry produced during the polishing process of stone. The stone is cut and sawn into different thickness with the help of diamond blades. Wastewater littering from the polishing process unit and in the form of slurry, which has suspended stone dust particles, is disposed off to open land or watercourses. Stone waste is indestructible. Disposal of stone dust on the ground results in repulsive dirty look, land infertility, loss of valuable topsoil due to

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blanketing with dust, contamination of rivers and other surface water bodies. This is a major threat to environment and efforts should be made to find viable engineering applications at the earliest. This menacing problem seeks a solution by utilizing the stone slurry into concrete as a substitution of cement/aggregates to improve its various properties. Use of stone waste in construction industries offers a reduction in concrete production cost, saving of natural resources and energy; and as the safer environment by resolving their disposal problem (Hussain 2011, Rana *et al.* 2017, Devi *et al.* 2019b).

Accelerator is an admixture used in cement paste, mortar and concrete to accelerate setting time and early age strength. It allows concrete placing at low temperature with reduced risk of frost damage. The chemical admixtures usually used as accelerators are of chloride and nonchloride type. Calcium chloride is the least expensive and most commonly used material from an early age but, nowadays it is not recommended due to its corrosive nature. The non-chloride type accelerators i.e., nitrate, formate, nitrite, and amine are being used (Chik et al. 2008). Ethanolamines are generally organic base and triethanolamine (TEA) is prevalent among all. As TEA exhibits both retarding and accelerating properties depending on cement type and dosages rate so, it should be used wisely during handling (Heren and Olmez 1996).

Durability of a concrete structure; subjected to chemical attack, is considerable especially in an urban area due to higher amount of factory waste and high population (Gülşan *et al.* 2018). Deterioration of the concrete structure under various conditions has become the most severe and demanding challenge (Odd E. and Gjorv 2016). During the service life of a structure, it may undergo various distresses due to design defects, low quality of raw materials, overloading and poor construction quality (Joshaghani *et al.* 2017b). The chemical attacks are very noticeable where; a high concentration of salt is present in soil (Zeidan *et al.* 2016).

TEA accelerated C_3A reaction; but retarded the hydration process of C_3S and its effect increased with the increase in TEA quantity. A low dosage of TEA optimized the pore size distribution; but high dosage injured the pore size distribution (Han *et al.* 2015). Addition of TEA (0.03% and 0.1%) increased one day compressive strength of Portland cement paste but, decreased the strength after 3 days (Kong *et al.* 2013). Calcium nitrate (CN) showed a little beneficial effect at later age strength. Combination of CN either with TEA or TIPA decreased the setting time and enhanced the strength (Aggoun *et al.* 2006, Gok and Kilinc 2015). Accelerating-retarding nature of TEA was due to the formation of ettringite of different intensity, which was governed by TEA dosages (Yaphary *et al.* 2017).

Incorporation of stone slurry (5%) as fine aggregate improved the mechanical and durability properties due to filling effect (Almeida *et al.* 2007 a, b). Increase in burnt stone slurry (BSS) decreased consistency, stiffening time and workability of mortar but improved the strength and microstructural properties (Al-Akhras *et al.* 2010). The cement substitution with granite sludge up to 10% could be efficiently used without loss in 28 days compressive strength (Marmol et al. 2010). Diatomite (5% and 10%), waste marble powder (5%) and the combination of diatomite (10%) and WMP (5%) improved strength of concrete (Ergun, 2011). Marble powder upto 20% increased the compressive and split tensile strength afterward it started to decrease (Alyamac and Aydin 2015). Strength decreased with the increase in marble slurry (MS). MS (5-10%) enhanced the resistance of concrete against corrosion (Rana et al. 2015). Replacement of cement by 15% waste marble powder (WMP) decreased the compressive strength of concrete while, replacement of sand by 15% WMP increased the compressive strength of concrete. Sand replacement by WMP (10%) had the maximum split tensile strength. Replacement of cement and sand by WMP (15%) enhanced the quality and durability properties of concrete too (Ashish et al. 2016, Ashish 2018). Increase in Kota stone slurry decreased the compressive and flexural strength of concrete (Jain and Majumder 2016). Use of limestone waste as fine aggregate produced strong and durable concrete structure (Rana et al. 2017). Standard consistency and slump reduced but, setting time increased with the enhancement in MS content. Addition of MS upto 15% increased the mechanical properties for lower water binder ratio (w/b) ratio and same effect was for 10% MS at higher w/b ratio (Singh et al. 2017a, 2017b). Kota stone slurry upto 10% increased the strength properties of mortar afterward it decreased (Chouhan et al. 2017). Increase in GGBS increased the slump values while increase in Kota stone slurry decreased the slump. GGBS (40%) with Kota stone slurry reduced the compressive strength but, in the absence of Kota stone slurry it slightly increased compressive strength (Ali et al. 2018). Kota stone dust improved the early age strength and reduced the permeability of cement mortar (Meena et al. 2018).

Research significance

The acute development of dimensional stone industries yields a large amount of waste which causes damage to the environment. Incorporation of stone slurry waste (powder form) in concrete has a significant contribution to the environment and is economically feasible by solving their disposal as well as storage problems. After strength based optimization of mortar mixes, the optimized quantity of materials was used in the present work. Kota stone slurry powder (7.5%) as a replacement of cement, and accelerators i.e., CN (1%) and TEA (0.05%) as additives were used in various mix proportions of concrete. The objective of this study is to check the suitability of accelerators and stone waste (Kota stone slurry powder (KSSP)) in concrete. To achieve the objectives; workability by flow table test, compressive strength at 7, 28, 56 and 90 days; split tensile strength at 7, 28, 56 and 90 days, electrical resistivity (ER) at 28, 56 and 90 days and elastic modulus at 28 days were studied experimentally. The durability i.e., changes in compressive strength and ER of concrete specimens subjected to sulphate and chloride solution attack at 28 and 62 days was also studied. The microstructural characterizations using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)







Figs. 1 (a) SEM of PC; (b) SEM of KSSP; (c) EDS of PC; (d) EDS of KSSP

techniques were also studied. To investigate the economic feasibility, a cost analysis was also carried out. The prime purpose of adding KSSP in concrete with accelerators was to minimize the cost and make it eco-friendly by saving the natural resources and energy. The utilization of stone waste in concrete also mitigates the risk associated with their direct disposal to land or watercourse.

Table 1 The chemical composition of cement and KSSP (EDS analysis)

Chemical compound (%)	Cement	KSSP
CaO	60.29	49.78
SiO_2	21.42	17.01
Al_2O_3	5.91	2.92
MgO	2.65	0.61
N_2O	0.64	0.88
K ₂ O	1.11	0.42
FeO	4.81	0.14
Loss of Ignition	-	28.24

Table 2 Physical	properties of a	sand and coarse	aggregate
2			

Proportios	Coarso cond	Coarse aggregate Coarse aggregate			
Flopetties	Coarse sand	(10mm)	(20mm)		
Type	Coarse sand	Crushed	Crushed		
Туре	Coarse sand	aggregate	aggregate		
Fineness	3 17	6.05	6.89		
modulus	5.17	0.05			
Specific gravity	2.62	2.66	2.60		
Bulk modulus	1646	1/160	1360		
(Loose, kg/m^3)	1040	1400	1500		
Bulk modulus					
(Compacted,	1824	1650	1500		
kg/m ³)					

2. Materials and methods

2.1 Materials

Various concrete mix proportions using Portland cement, aggregates, CN, TEA, KSSP, and water were produced. Portland cement (PC) of 43 grade with fineness of 3 mm, 27.5% consistency, specific gravity of 3.12 and strength of 44.5 MPa at 28 days complying with IS: 8112-1989; coarse sand of zone II (Devi et al. 2019a) and coarse aggregates (10 mm and 20 mm size) complying with IS: 383-1970 were used in concrete mixtures. The cement, coarse sand and aggregates were procured locally and tap water was used in the casting and curing process during whole experimentation. KSSP was procured from Kota stone (India), which is flaggy low-grade limestone of sedimentary type rock origin and available in a number of colors and textures. The waste is generated in two forms: solid waste and slurry during dimensioning. The stone slurry generates as a semi-liquid substance consisting of fine particles, originated during dimensioning process (Kumar and Lakhani 2017). Before use in concrete mixtures, it was dried under sunlight and then grounded into finer particles (Devi et al. 2019b). KSSP was white in color (specific gravity 2.79 and mean particle size 0.049 µm). Two accelerators i.e., calcium nitrate tetra hydrate purified [Ca(NO₃)₂.4H₂O] and triethanolamine LR [C₆H₁₅NO₃] were used as additives in concrete mixtures. CN was water soluble and in crystalline form (Devi et al. 2018). TEA, as described in FHA (Federal Highway Administration) report, is an oily, water-soluble liquid with a fishy odor. It is very dosage sensitive. The chemical compound of cement and KSSP have been given in Table 1 and their SEM and EDS

Mix No.	Cement, kg/m ³	Sand, kg/m ³	Aggregates, kg/m ³	Water, kg/m ³	CN, kg/m ³	TEA, l/m ³	KSSP, kg/m ³
N1	390	503.1	1088.1	167.7	0	0	0
N2	360.75	503.1	1088.1	167.7	0	0	29.25
N3	390	503.1	1088.1	167.7	0	0.195	0
N4	390	503.1	1088.1	167.7	3.9	0	0
N5	390	503.1	1088.1	167.7	3.9	0.195	0
N6	360.75	503.1	1088.1	167.7	0	0.195	29.25
N7	360.75	503.1	1088.1	167.7	3.9	0	29.25
N8	360.75	503.1	1088.1	167.7	3.9	0.195	29.25

Table 3 Mix proportion of various concrete mixtures

images illustrated in Figs. 1 (a), (b), (c) and (d) respectively. The properties of aggregates have been given in Table 2.

2.2 Mixture proportions

Various mix proportions were prepared with varying percentages of KSSP, CN and TEA. The contents of KSSP, CN and TEA were selected from the optimization of mortar mixes based on compressive strength results and optimized quantities of materials were used in the concrete mixes. Eight different mix proportions were casted and have been given in Table 3. Cement was replaced by 7.5%

KSSP; CN and TEA of accelerating nature were used as additives with dosages of 1% and 0.05% by the weight of cement respectively and the water-cement ratio was kept as constant 0.43. Eight mix proportions were prepared for concrete; the first mix was control mix and other seven mix proportions containing different percentages of CN, TEA and KSSP either individually or in combination. Concrete mix design was done as per IS: 10262-2009. Casting and testing of the different mix proportions were done as per IS: 516-1959.

2.3 Testing procedure

2.3.1 Fresh properties

Workability of the fresh concrete was measured by the flow table test and compaction factor as per IS: 1199-1959.

2.3.2 Compressive and split tensile strength

The compressive and split tensile strength of concrete specimens of different mix proportions was studied. The concrete cubes of size 150 mm×150 mm×150 mm and cylinders of size 150 mm×300 mm were casted for compressive strength test and split tensile strength test respectively. After 24 hours maturing, the specimens were demoulded and kept into curing tank for the required age and tested as per IS: 516-1959.

2.3.3 Elastic modulus

The elastic modulus of cubical concrete specimens (150 mm×150 mm×150 mm) was determined using UPV values (IS: 13311-1992). Dynamic modulus of elasticity, E_d can be computed from *P*-wave velocity using Eq. (1) given below

$$E_{d} = \frac{V_{p}^{2} \rho(1+\nu)(1-2\nu)}{(1-\nu)}$$
(1)

Table 4 Co-relation between electrical resistivity and corrosion rate (Broomfield 2007)

ER (kΩ-cm)	>20	10-20	5-10	<5
Corrosion Intensity	Low	Low to moderate	High	Very High

where V_p =Pulse velocity; ρ =Density of concrete; ν =Poisson's ratio

2.3.4 Electrical resistivity

Electrical resistivity is an ease with which ions can move inside the concrete and measures the diffusion of ions in the concrete. Resistivity can be used to indicate durability, corrosion and also for on-site quality control as it is a non-destructive test. The electrical resistance, R and electrical resistivity, ρ of concrete cubes (150 mm×150 mm X 150 mm) were determined using Eqs. (2) and (3) respectively (Zongjin 2011)

$$R = \frac{V}{I} \tag{2}$$

$$\rho = \frac{RA}{L} \tag{3}$$

where V=potential difference developed between two electrodes; I=alternating current applied; A=cross-sectional area perpendicular to the current; L=height of the concrete specimen.

The recommended values for the correlation between electrical resistivity and corrosion have been given in Table 4.

2.3.5 Chemical attack

To study the durability properties of concrete specimens, the concrete cubes of size 150 mm×150 mm×150 mm were used. After 28 days of water curing, the cubical concrete specimens were taken out from the curing tank and immersed for next 28 and 62 days into 5% MgSO₄ solution; and 5% NaCl solution (ASTM C1012 2012). The compressive strength and ER of concrete of different mix proportions were determined at the $(28^*+28^{\#})$ and $(28^*+62^{\#})$ curing age; where "*" point to specimens under water curing and "#" point to specimens immersed into chemical solution attack.

2.3.6 Microstructural analysis

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used for the microstructural analysis of concrete specimens. After 28



Fig. 2(a) Flow value of concrete of different mix proportions

days of water curing, the fragments of tested concrete specimens were collected followed by acetone wash to mitigate the air content of the sample and then dried. Before scanning; gold plating on samples was done to make them electric conductive. SEM analyzes the morphology of hydration products and EDS determines their elemental composition and confirms the presence of ettringite (Pillai *et al.* 2016). EDS is an analytical technique which is coupled with SEM. EDS spectrum portrays the plot between *X*-ray and energy. The energy peaks correspond to element present in the specimens confirms their existence as well as intensity.

3. Results and discussion

3.1 Workability

The workability of fresh concrete of different mix proportions was measured by the flow table test and compaction factor test. Figs. 2 (a) and (b) shows the effect of CN, TEA and KSSP alone and in their combination on the workability of concrete. Fig. 2(a) showed that workability of concrete decreased for all the mixes in comparison to the control mix. Flow for all the concrete mix proportions varied from 38.70% to 71.47%. Addition of CN and TEA decreased the flow by 38.25% and 18.84% respectively, due to low plasticity maintaining effect. Replacement of KSSP reduced the flow by 46.27% in proportions to control mix may be due to the presence of KSSP particles which, absorb water readily and increased water demand consequently. Combination of accelerators and KSSP decreased the spread from 36.94% to 0.94% with reference to the control mix. Accelerators reduced the workability due to nonplasticizing effect and KSSP reduced the workability due to water absorbing capability of porous KSSP particles. KSSP reduced the workability and results were in good agreement with Almeida et al. 2007a and Ashish, 2018. Addition of CN reduced the flow more in comparison to TEA due to less plasticizing effect.

It has been illustrated from Fig. 2(b) that the value of the compaction factor varied from 0.77 to 0.86. Compaction factor value decreased for all the concrete mix proportions. For mix N2, N3, N4, N5, N6, N7 and N8; the compaction factor value decreased by 5.87%, 9.30%, 10.47%, 1.16%, 3.49%, 4.65% and 1.16% with reference to control mix.

The concrete with low workability can be used in



Fig. 2(b) Compaction factor of concrete of different mix proportions



Fig. 3 Compressive strength of concrete at different curing ages

foundation walls and footings. The superplasticizer can also be used to improve the workability or mitigate the effect of used materials. The concrete produced with these materials were of low workability and can be used in light reinforced sections.

3.2 Compressive strength

Fig. 3 shows the consequence of accelerators and KSSP on the compressive strength of various concrete mixtures. Fig. 3 illustrates that KSSP and CN individually enhanced the compressive strength of concrete; but, TEA alone decreased compressive strength in comparison to control mix at all the curing ages i.e., 7, 28, 56 and 90 days. KSSP increased the compressive strength; may be because of high content of lime which formed additional hydrated calcium silicate gel by reacting with silica that contributed enhancement in strength (Al-Akhras et al. 2010). It may also be due to KSSP's pore filling effect which fills the voids and thus produces a dense matrix (Almeida et al. (2007 a, b) and Ergun, 2011). CN enhanced compressive strength of concrete and similar findings were reported by Rosskopf et al. (1975), Aggoun et al. (2006). CN increased the strength of specimens due to better bonding between constituents of a solid phase (Kumar et al. 2018). Another aspect of increasing compressive strength may be due to the high content of lime as suggested by Neville and Brooks (1997). TEA decreased the strength of concrete in comparison to control mix and similar results were reported by Ramachandran, (1976). TEA reduced early age strength of concrete due to the retarding effect of TEA on C3S



Fig. 4 Split tensile strength of concrete of different mix proportion at different curing ages

hydration process (Han *et al.* 2015, Huang *et al.* 2010). The combination of CN+TEA, CN+KSSP, and KSSP+TEA increased the compressive strength of concrete at all curing ages may be due to the predominant nature of CN and KSSP. The combination of CN+TEA+KSSP reduced the compressive strength of concrete at all ages in proportions to reference mix may be because of the interaction of these materials and TEA was found to be dominant among all the materials. The value of compressive strength of concrete for various mixes varied from 28.24 MPa to 36.40 MPa, 32.88 MPa to 41.18 MPa, 36.26 MPa to 45.89 MPa and 39.41 MPa to 47.04 MPa at 7, 28, 56 and 90 days respectively. From this observation, the mix N2 was found as optimum mix proportion.

For mix N2 and N4; compressive strength of concrete specimens increased by 13.05%, 12.53%, 13.79% and 8.99% at 7, 28, 56 and 90 days respectively; and 4.75%, 4.41%, 5.76% and 3.54% at 7, 28, 56 and 90 days respectively; whereas, TEA decreased the compressive strength by 10.77%, 8.72%, 4.27% and 4.53% at 7, 28, 56 and 90 days respectively in comparison to the control mix. The compressive strength of concrete mix N5, N6 and N7 increased by 2.76%, 8.89%, 14.53%; 2.15%, 3.97%, 11.19%; 4.10%, 4.88%, 10.72% and 0.74%, 4.95% and 8.64% at 7, 28, 56 and 90 days respectively; but, mix N8 decreased the compressive strength by 6.60%, 4.22%, 8.34% and 7.94% at 7, 28, 56 and 90 days respectively with reference to reference mix.

3.3 Split tensile strength

The effect of CN, TEA, and KSSP on the split tensile strength of concrete has been shown in Fig. 4. CN and KSSP increased the split tensile strength individually at all the curing ages. Increase in the split tensile strength of concrete with KSSP may be attributed to its rough or granular surface which exposed as the crack path developed under load and tends to longer during the determination of split tensile strength (Alyamaç and Aydin 2015). The other reason for increasing the split tensile strength of concrete with KSSP may be due to low porosity and good strength between cement paste and interfacial transition zone (Khodabakhshian *et al.* 2018). Increase in split tensile strength of concrete consisting of CN may be attributed due to better bonding of solid constituents of concrete. TEA alone decreased split tensile strength with reference to



Fig. 5 Elastic modulus of concrete of different mix proportion at 28 days

control mix at various curing ages i.e., 7, 28, 56 and 90 days. Combinations of CN+TEA and CN+KSSP increased the split tensile strength because of predominant nature of CN which formed the better bonding in the matrix. The combination of CN and KSSP increased the strength due to better bonding and pore filling effect. The combination of TEA+KSSP and CN+TEA+KSSP reduced the split tensile strength may be because of predominant behavior of TEA. The mix N2 was found as optimized mix proportion in terms of compressive strength.

Split tensile strength of various concrete mixtures varied from 2.97 MPa to 3.78 MPa, 3.14 MPa to 4.69 MPa, 3.56 MPa to 4.98 MPa and 4.05 MPa to 5.47 MPa at 7, 28, 56 and 90 days curing respectively. For mixes N2 and N5; the split tensile strength increased by 13.22%, 10.45%, 5.82%, 8.04% and 5.75%, 8.09%, 2.49%, 1% at 7, 28, 56 and 90 days respectively in comparison to control mix. The split tensile strength decreased for mix N3 by 2.74%, 5.2%, 7.04% and 2.14%; N6 by 5.79%, 9.52%, 12.15% and 1.20%; and N8 by 9.45%, 25.23%, 24.09% and 19.49% at 7, 28, 56 and 90 days respectively in comparison to control mix. For mix N5; the split tensile strength increased by 10.14%, 8.50%, 4.29% and 3.45%; and N7 by 9.14%, 8.69%, 6.39% and 5.09% at 7, 28, 56 and 90 days as compared to control mix.

3.4 Elastic modulus

The influence of CN, TEA, and KSSP on the elastic modulus of different mix proportions of concrete has been studied and depicted in Fig. 5. The elastic modulus of concrete followed the same trend as the compressive strength. Addition of TEA decreased the value of elastic modulus; whereas, CN and KSSP individually increased the elastic modulus. KSSP increased the elastic modulus of concrete (Almeida *et al.* 2007a & b; Khodabakhshian *et al.* 2018). The increase in elastic modulus indicated the lesser deformation for the same stress when loaded (Kabeer and Vyas, 2018). CN increased the elastic modulus of concrete may be because of better bonding in concrete. CN+TEA, TEA+KSSP, and KSSP +CN increased the value of elastic modulus; but, the combination of CN+TEA+KSSP decreased the elastic modulus at 28 days curing.

The elastic modulus of the concrete at 28 days varied from 38.71 GPa to 46.17 GPa for the different mix



Fig. 6 Electrical resistivity of concrete mix proportions at various curing age

proportions. For mix N2, N4, N5, N6, and N7; the elastic modulus increased by 6.04%, 3.71%, 3.08%, 2.30% and 2.47% at 28 days. For mix N3 and N8; the elastic modulus reduced by 5.16% and 10.77% at 28 days respectively. The mix N2 was found to be an optimized mix proportion in term of elastic modulus.

3.5 Electrical resistivity

The variation in ER of different mix proportions of concrete has been given in Fig. 6. Fig. 6 showed that ER of concrete of all mix proportions has been increased except N3 and N8 at all curing ages. Addition of CN and replacement of KSSP separately as well as in combination increased the ER of concrete and this may be attributed to better bonding due to use of former materials and filling effect of KSSP particles. The use of mineral admixtures increased the ER due to improvement in the microstructure of pore structure which restrained the ion movement in the solution that fills the pores. Increase in ER may be because the fraction of internal hydration product increased with the strength gain and these products interrupt the path of movement of ions which ultimately increased the resistivity (Xiao et al. 2007). ER of concrete increased with the increase in the hydration process and adequate curing helped in the development of pore structure which obstructed the ion movement (Silva and Brito 2013). The reduction in ER of concrete for mixes N3 and N8 may be due to less formation of hydration products which increase the porosity consequently. The values of electrical resistivity for different concrete mixtures varied from 23.58 k Ω -cm to 30.03 k Ω -cm, 28.38 k Ω -cm to 36.83 k Ω -cm and 33.55 k Ω -cm to 40.5 k Ω -cm at 28, 56 and 90 days respectively.

It has been observed from Fig. 6 that for mix proportion N2, N4, N5, N6 and N7; ER increased by 16.41%, 15.66%, 13.98%, 0.16% and 12.21% at 28 days; 13.52%, 3.71%, 7.86%, 0.5% and 10.63% at 56 days and 11.73%, 5.86%, 6.16%, 2.0% and 9.42% at 90 days with reference to control mix. For mix proportions N3 and N8; ER reduced by 2.66% and 6.06% at 28 days; 8.07% and 10.89% at 56 days and 6.01% and 6.15% at 90 days respectively. The mix N2 had a higher value of ER; while, N8 had the least value of ER among all mix proportions. The optimized mix proportion was N2 which had higher values of electrical resistivity which correspond to a very low corrosion rate (Broomfield 2007).



Fig. 7 Compressive strength of concrete with and without subjected to chemical attack

3.6 Resistance against chemical attack

The concrete specimens were immersed into magnesium sulphate (MgSO₄) solution and sodium chloride (NaCl) solution for $28^{\#}$ days and $62^{\#}$ days after 28^{*} days of water curing. The impact of chemical solutions on the concrete cubes specimens was calculated in terms of strength loss. The electrical resistivity was also measured along with compressive strength of the concrete.

3.6.1 Compressive strength

The compressive strength of concrete with different mix proportions was studied after immersion in solutions of magnesium sulphate and sodium chloride at 28[#] and 62[#] days and has been illustrated in Fig. 7. Fig. 7 showed that addition of TEA decreased the strength of concrete under the exposure to sulphate attack; whereas, CN had comparable strength to the control mix. KSSP increased the resistance against sulphate attack in comparison to reference mix may be because of filling of voids which restrained the sulphate ion movement into concrete consequently increased the strength. CN+KSSP increased the compressive strength of concrete at 28[#] days and 62[#] days exposure to magnesium attack may be because of the filling effect of KSSP particles. The inclusion of CN and KSSP alone and in combination improved the resistance against the sulphate attack may be because of reduction in porosity due to better bonding of CN and filler effect of KSSP particles which filled the voids and restrained the entry of sulphate ions into concrete. The increase in strength of specimen against sulphate solution attack may be due to ettringite formation which formed more closed pore structure and increased the strength (Alnahhal et al. 2018). TEA+CN, TEA+KSSP, and CN+TEA+KSSP decreased the compressive strength in comparison to the control mix may be because of predominant nature of TEA which formed fewer hydration products consequently increased porosity thus permit more sulphate ions to enter into concrete and deteriorate the concrete structure. The reduction in compressive strength under sulphate attack may be attributed to less cohesion between cement particles and loss of adhesion of cement particles to aggregates surface (Rana et al. 2016). Reduction in compressive strength under the exposure to sulphate solution may be attributed to destruction of cement paste due to formation of magnesium

silicate hydrate (M-S-H). Also, the reaction between magnesium sulphate and calcium hydroxide formed gypsum which deteriorates the matrix of concrete and reduced the strength under the exposure to sulphate attack (Mostofinejad *et al.* 2016). The reduction in compressive strength was found with the increase in exposure period against sulphate attack. The optimum mix proportion was N2 in term of resistance against the sulphate attack.

The mix N2 and N7 had the higher compressive strength i.e. higher resistance to sulphate attack than control mix N1; and N4 had comparable strength to control mix. For mix N3, N5, N6, and N8; compressive strength reduced against the sulphate attack at $28^{\#}$ and $62^{\#}$ days. The compressive strength of concrete specimens against sulphate solution attack varied from 31.14 MPa to 43.67 MPa at 28[#] days, and 27.53 to 39.97 MPa at 62[#] days respectively. For mix N2 and N7; the compressive strength of concrete specimens against sulphate attack increased by 12.7% and 14.8%, and 10.8% and 8.4% at $28^{\#}$ days and $62^{\#}$ days respectively with reference to control mix. For mix N3, N4, N5, N6 and N8; compressive strength of specimens subjected to exposure sulphate attack reduced by 4.1%, 0.57%, 19.7%, 10.3%, and 22.4%; and 6.1%, 0.35%, 29.4%, 14% and 26.6% at 28[#] and 62[#] days respectively in comparison to control mix. For mix N1, N2, N3, N4, N5, N6, N7 and N8; the compressive strength of concrete specimens under the exposure of sulphate attack decreased by 6.1%, 6.8%, 6.4%, 9.7%, 26.4%, 16.9%, 5.5% and 16.4%; and 22.2%, 19%, 19.8%, 23.5%, 41.6%, 32.6%, 19.7% and 26.7% with respect to 56 and 90 days water curing respectively.

In the case of chloride attack, all the mix proportions of concrete decreased the compressive strength in proportions to the control mix as shown in Fig. 7. The reduction in compressive strength against the chloride attack may be due to poor compaction which results into porous structure and discontinuous pore system that increased the permeability of chloride ions thus decrease in strength results (Vijaylaxmi et al. 2013). The reduction in compressive strength under the exposure to the salt solution was also observed by Temiz and Kantarcı (2014). The compressive strength of concrete specimens under the exposure of sodium chloride solution varied from 32.57 MPa to 39.63 MPa and 29.7 MPa to 36.63 MPa at 28[#] days and 62[#] days respectively. The compressive strength also reduced with the increase in exposure time to chloride attack for all the mix proportions. For mix N2, N3, N4, N5, N6, N7 and N8; the compressive strength of concrete specimens subjected to chloride attack reduced by 1.7%, 13.7%, 13.9%, 10.2%, 8.7%, 4.3% and 17.8%; and 12.1%, 22.9%, 26.4%, 24%, 21.3%, 21.5% and 27.6% at 28[#] and 62[#] days respectively with reference to the control mix. For the concrete specimens exposed to sodium chloride solution for 28[#] and 62[#] days; compressive strength of mix N1, N2, N3, N4, N5, N6, N7 and N8 reduced by 4.7%, 19%, 15%, 20.2%, 20%, 15.4%, 22% and 15.3%; and 22.2%, 29.4%, 27%, 37.1%, 36.1%, 32.7%, 35.9% and 25.3% in comparison to water cured specimens at 56 and 90 days respectively.

3.6.2 Electrical resistivity

The influence of addition of accelerators i.e., CN and TEA; and replacement of cement by KSSP in different mix



Fig. 8 Electrical resistivity of concrete with water curing and chemical attack

proportions of concrete specimens under the chemical attack at various ages were studied. It has been observed from Fig. 8 that for mix proportions N2, N4, and N7 increased the ER of concrete while other mix proportions reduced the resistivity of concrete specimens when subjected to magnesium sulphate attack. ER of concrete increased with the use of KSSP and CN individually and in combination both; due to pore filling effect and better bonding of constituents of matrix respectively, which results into a reduction in porosity consequently increase in resistivity of concrete. The reduction in ER of concrete using TEA either alone or in combination with CN, KSSP and both may be attributed to predominant nature of TEA which formed porous structure thus increase in porosity and movement of current ions which results into a reduction in resistivity. The value of ER varied from 21.19 k Ω -cm to 30.02 k Ω -cm and 17.02 k Ω -cm to 26.15 k Ω -cm at 28[#] and 62[#] days under sulphate attack.

For mix N2, N4 and N7; ER of concrete specimens subjected to magnesium sulphate solution increased by 12.8%, 8.7% and 7.8% at $(28^*+28^{\#})$; and 15.2%, 5.9% and 6.6% at $(28^*+62^{\#})$ days respectively with reference to reference mix. For mix N3, N5, N6, and N8; ER of concrete specimens under the exposure of sulphate attack decreased by 1.7%, 17.7%, 11.3% and 20.4%; 0.4%, 17.6%, 9.4% and 25% at $(28^*+28^{\#})$ and $(28^*+62^{\#})$ days respectively with respect to control mix. For the concrete specimens of mix N1, N2, N3, N4, N5, N6, N7 and N8 subjected to sulphate solution for 28[#] and 62[#] days; ER reduced by 16.4%, 18.5%, 10.6%, 12.5%, 36.6%, 26.1%, 19.5% and 25.3%; and 36.5%, 35.4, 32.6, 36.7, 50.9%, 43.6%, 38.7% and 49.3% in comparison to 56 and 90 days water curing respectively.

The variation of ER of concrete consisting of CN, TEA, and KSSP has been illustrated in Fig. 8. From Fig. 8, it has been reported that ER of concrete specimens decreased for all the mix proportions at $(28^*+28^{\#})$ and $(28^*+62^{\#})$ days under the exposure of sodium chloride attack. The reduction in ER may be due to porous microstructure which increased the movement of current ions that results into lower resistivity. The values of ER of concrete specimens immersed into chloride attack varied from 18.75 k Ω -cm to 30.63 k Ω -cm and 16.47 k Ω -cm to 25.25 k Ω -cm. The



(d)

Fig. 9 (a) SEM of control mix of concrete; (b) SEM of KSSP in concrete; (c) SEM of CN in concrete; and (d) SEM of TEA in concrete (where A- CSH ; B- CH; C- Ettringite; D- pores)

maximum value of ER was for mix N2 and minimum values for N8. For mix N2, N3, N4, N5, N6, N7 and N8; ER of concrete specimens subjected to chloride attack decreased by 13.6%, 29.9%, 23%, 26.9%, 15.83%, 38.8% and 25.1% at $28^{\#}$ days; and 10.9, 25.62, 20.4%, 22.1%, 17.1%, 34.77% and 23.9% at $62^{\#}$ days respectively with reference to the control mix. For concrete specimens exposed to sodium chloride solution at $(28*+28^{\#})$ and $(28*+62^{\#})$ days, for mix N1, N2, N3, N4, N5, N6, N7 and N8; ER decreased by 3.8%, 28.1%, 26.7%, 28.8%, 35.3%,

Table 5 Ca/Si and (Al+Fe)/Ca ratio (Mohammed *et al.* 2013)

Hydration product formed	Ca/Si	(Al+Fe)/Ca
CSH	0.8-2.5	≤ 0.2
СН	≥10	≤ 0.04
AFm	≥ 4.0	>0.4

19.7%, 47.4% and 19.1%; and 29.4%, 44.5%, 44.1%, 47.1%, 48.37%, 42.6%, 58.3% and 42.8% in comparison to water cured specimens at 56 and 90 days respectively.

The values of electrical resistivity under the exposure of sulphate attack produced a low corrosion rate; but, increase in exposure time accelerated corrosion rate from low to moderate. The electrical resistivity value of concrete specimens under the chloride solution exposure had not shown a significant trend as sulphate attack produced for corrosion rate. However; the increase in exposure time to chloride attack; decreased the electrical resistivity value which showed acceleration in corrosion rate as suggested by Broomfield (2007).

3.7 Micro-structural analysis

To study the microstructure of concrete specimens, SEM and EDS test was conducted for control mix, KSSP, CN, and TEA and has been illustrated in Figs. 9 (a)-(d) respectively.

It has been observed from Figs. 9 (a)-(d) that the hydration products i.e., CSH, CH, and voids can be seen over the matrix. The CSH gel was present in all the mix proportions and also confirmed from EDS analysis, that responsible for the strength improvement. The voids were also present in the mix proportions especially in control mix of concrete as shown in Fig. 9(a). Fig. 9(b) showed the dense microstructure due to filling effect of KSSP that contributed to increase in strength. Fig. 9(d) showed the presence of CH along with CSH gel in concrete mix containing TEA.

To analyze the hydration phase of CSH, CH, and ettringite, the following criteria were adopted, that suggested by (Mohammed *et al.* 2013) have been given in Table 5.

In the present study, the percentage values of Ca, Si, Al, and Fe were calculated by considering atomic weight. The values of Ca/Si and (Al+Fe)/Ca ratio varied from 0.25 to 18.77 and 0.055 to 2.969 respectively and have been given in Table 6.

3.8 Cost analysis

The cost analysis was carried out to assess the economic aspects of investigated scenario for the different mix proportions of concrete. The Kota stone slurry powder, being waste material from the stone industry, is freely available except freight charges CN and TEA are little costly. The cost of the materials used in concrete production provided by the supplier has been presented in Table 7. The cost of concrete with different mix proportions per cubic meter has been shown in Fig. 10. The cost of concrete is in

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Mix No.	Ca/Si					(Al+Fe)/Ca			Hydration product formed
N1	0.544	0.595	0.75	0.85	0.593	0.420	2.969	-	CSH+AFm
N2	1.112	1.204	1.811	0.936	0.277	0.275	0.198	0.116	CSH+AFm
N3	18.77	3.305	14.65	-	0.055	0.061	-	-	CSH+CH
N4	0.0882	5.269	0.25	0.452	0.222	0.728	2.447	0.577	CSH+AFm

Table 6 Ca/Si and (Al+Fe)/Ca ratio of concrete from EDS analysis

Table 7 Cost of materials used



Fig. 10 Cost analysis of concrete with different mix proportions

INR (Indian Rupee).

Fig. 10 showed that the calculated cost of control mix per cubic meter was 4997 INR. The cost of concrete per cubic meter consisting KSSP and the addition of CN and TEA separately was 4807, 6674 and 5203 INR respectively. For mix N5, N6, N7, and N8; the cost of concrete was 6880, 5013, 6484 and 6690 INR respectively. The replacement of cement by 7.5% KSSP shows the benefits of 4% while the addition of 1% CN and 0.05% TEA incurs the loss of 33% and 4% with reference to control mix. For mix N5-N8 the cost of concrete per cubic meter raised by 0.3% to

37.7% in proportion to control mix. The mix N8 had the highest cost of construction while N2 had minimum cost among all the mix proportions.

Substitution of cement with waste material (KSSP) reduced the cost of concrete, cement content, improved properties and provides a safer environment. It has been concluded that Kota stone slurry powder was the cost-efficient material among all the proportions.

4. Conclusions

The rapid growth in cement industries leads to deterioration of resources and environment. To lessen this, industrial by-products are being exercised in concrete production. The utilization of waste in construction industry reduces their harmful effect and also conserves the natural resources. In the present study, Kota stone slurry powder is used with or without accelerators. Various tests have been conducted on the concrete specimens to examine the effect of addition of calcium nitrate, triethanolamine, and replacement of Kota stone slurry powder with cement. Results showed the addition of admixtures produces concrete mixes of sole character. The following major findings were concluded from this study:

• Workability of concrete decreased for all the mix proportions. Kota stone slurry powder decreased the workability due to its finer particle size. Accelerator reduced the workability may be due to their low plasticity effect.

• Kota stone slurry powder increased strength, elastic modulus, and electrical resistivity due to its filling effect which formed dense microstructure. Kota stone slurry powder increased the resistance against sulphate solution due to dense matrix and filling of voids; but Kota stone slurry powder decreased the resistance against the chloride attack slightly.

• Calcium nitrate increased compressive strength, split tensile strength, elastic modulus and electrical resistivity of concrete at all the curing ages due to better bonding. Addition of triethanolamine diminished mechanical strength and electrical resistivity of concrete at all curing ages may be because of formation of fewer hydration products and porous structure as compared to reference mix.

• The combination of any two materials increased the compressive strength, elastic modulus and electrical resistivity of concrete; but, a combination of these three materials decreased the strength and electrical resistivity at all the curing ages.

• Combination of calcium nitrate either with triethanolamine or Kota stone slurry powder increased the split tensile strength; but, a combination of triethanolamine either with Kota stone slurry powder or both Kota stone slurry powder and calcium nitrate reduced the split tensile strength in comparison to control mix at all curing ages.

• Kota stone slurry powder, calcium nitrate, and their combination increased the resistance against sulphate attack may be because of filling effect and better bonding; while other mix proportions had lower resistance to sulphate attack in comparison to reference mix.

• The compressive strength of concrete specimens subjected to sulphate and chloride solution attack decreased in comparison to that of concrete specimens under water curing at respective curing ages.

• The compressive strength of all the mix proportions diminished in comparison to control mix when exposed to chloride attack and this reduction rate increased with

the increase in exposure time.

• Calcium nitrate, Kota stone slurry powder, and their combination increased the electrical resistivity of concrete specimens under the exposure to sulphate attack for all the curing ages as compared to control mix while triethanolamine either alone or in combination with calcium nitrate and Kota stone slurry powder reduced the electrical resistivity of concrete specimens against sulphate attack.

• The electrical resistivity of concrete specimens increased for all curing ages except triethanolamine individually and in combination with both calcium nitrate and Kota stone slurry powder (i.e. mix N8) as compared to the control mix.

• The electrical resistivity of concrete specimens decreased for all the mix proportion at $(28^*+28^{\#})$ and $(28^*+62^{\#})$ days against chloride attack. The concrete specimens exposed to sulphate and chloride solution for $(28^*+28^{\#})$ and $(28^*+62^{\#})$ day decreased the electrical resistivity of all mix proportions in comparison to 56 and 90 days water curing respectively.

• The corrosion rate was low for water cured specimens in comparison to that of chemical attack which was also indicated by the higher value of electrical resistivity. After prolonged exposure time to chemicals; the corrosion rate accelerated especially in case of chloride solution which replicates fast deterioration of the concrete.

• SEM analysis of concrete mixtures having Kota stone slurry powder showed dense microstructure due to its filling ability which results into increase in strength, electrical resistivity and resistance against chemical attack. The CSH gel was present in the concrete mixtures consisting of calcium nitrate, Kota stone slurry powder, and triethanolamine as observed from EDS analysis.

• After performing a cost analysis of the manufacturing cost of concrete, it has been concluded that only Kota stone slurry powder reduced the cost of concrete.

• Kota stone slurry powder reduced the cement quantity which turned to saving of cement and minimal hazardous effects of Kota stone slurry powder on the environment and also resolves the disposal and storage problems related to Kota stone slurry powder.

Kota stone slurry powder and accelerators were used in various concrete mixtures to study the workability, strength, elastic modulus, electrical resistivity, and resistance against sulphate attack at different curing ages. The addition of triethanolamine diminished the strength and durability properties of concrete. The use of calcium nitrate, Kota stone slurry powder alone and in combination improved the strength and durability properties of concrete. Also, utilization of Kota stone slurry powder in concrete reduced the cement quantity and consequently, cost of concrete, problems associated with it to certain extent and also resolve disposal problems and thereby produced ecofriendly end product. Kota stone slurry powder, calcium nitrate, and their combination can be used in various field applications.

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