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Experimental Investigation of Engineering Properties of Iron-Based Binary and Ternary Pozzolanic Supplementary Cementitious Materials

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Abstract

The characteristic global warming potential of ordinary Portland cement (OPC) makes it a huge challenge for researchers to weigh its enormous use with potentially feasible engineering properties versus the environmental impacts. The formulation of sustainable, economical, and greener supplementary cementitious materials (SCMs) is an ongoing phenomenon, attracting the large-scale attention of industry/ academia. The formulation of ferrock by David Stone with low embodied energy, lower consumption of natural resources and minimal global warming potential has paved the way for the use of novel material comprising iron powder, pozzolans (pulverised fly ash (PFA) and metakaolin (MK) and lime exhibiting at par performance with OPC. However, a gap has been identified in its formulation, raising a further research question on how it will perform if PFA and MK are replaced by ground granulated blast furnace slag (GGBS) or other pozzolans like silica fume (SF) etc., with different mix ratios. Therefore, an endeavour has been made in this study to identify the engineering properties with sustainable use of modified binary and ternary pozzolans/ GGBS in place of 20% PFA in conventional ferrock.

The conventional ferrock contains 8% MK and 20% PFA (as binary pozzolans), 60% iron powder, 12% lime and 2% oxalic acid (set 1). An effort has been made to formulate the different mixes of 10,20,30,40 and 50% by keeping 60% iron powder, 12% lime, 8% MK and 2% oxalic acid constant but replacing 20% PFA with 20% GGBS (set 2), with 10%PFA+10%GGBS (set 3) and with 10%PFA+10%SF (set 4). A target compressive strength of C32/40 or M40 concrete was selected for this study to achieve and compare results with the control mix (0% ferrock) and conventional ferrock during the experimental investigation of modified novel materials. 10-20% ratios of modified mixes exhibited the best performance and achieved the threshold strength of 60 MPa of high-strength cement concrete. Maximum compressive strength of 65 MPa was achieved by the 10% mix of set 2 (20% GGBS), followed by 20% mix ratios of set 3 (10%PFA+10%GGBS) and set 4 (10%PFA+10%SF), achieving 64 MPa. Whereas the 10% mix of the conventional ferrock (set1) reached 63 MPa strength, and the control mix with no ferrock gained 57 MPa strength at 56 days of curing. Overall, an increase of 2-13% compressive strength was observed with10-30% mixes of all the SCMs; however, a decrease of 3-27% was observed with 40-50% use of SCMs. The use of iron powder increased the ductility of ferrock-based SCMs mixes and exhibited more flexural strength. Set 3 performed the best in exhibiting up to 5.8 MPa flexural strength, followed by set 4, set 2 and lastly, set 1 of conventional ferrock. 20% and 30% mix ratios exhibited flexural strength of more than 5% MPa, better than 10% and 40/ 50% mixes. The study supports the use of 10-20% ferrock-based SCMs for high-strength concrete and 10-50% for concrete mixes with a target strength of C32/40 or M40 to decrease the CO_2 footprints of the construction industry significantly.

Keywords : Conventional ferrock, modified ferrock, pozzolans, engineering properties, global warming potential.

Introduction

The invention of ordinary Portland cement (OPC) has paved the way for the modern construction industry due to its sound engineering properties and method of delivery employing insitu casting, precast or modular construction (Nadir & Ahmed, 2021). Concrete is considered the second most widely used material on earth after water; however, embodied CO_2 emitted during manufacturing and use of cement concrete is estimated to be one ton of CO_2 per ton of OPC, ranging to around 10% of global emissions, making it the second highest emitter in the world, with almost 400 billion tons annually (Joshua et al., 2021; Gagg, 2014; Chatham House, 2021; Ahmed et al., 2019; Mineral Products Association (MPA), 2007). This large-scale environmental impact of OPC has encouraged researchers to continuously explore the full/ partial replacement materials to substitute the cement sustainably with enhanced mechanical properties of supplementary cementitious materials (Nadir & Ahmed, 2022). The researchers have endeavoured to use naturally occurring pozzolanic materials like metakaolin (MK) or zeolite or waste materials derived from industrial/ agricultural fields having good aluminous and siliceous constituents demonstrating OPC-like properties, e.g., iron carbonate ($FeCO_3$), ground granulated blast furnace slag (GGBS, an established OPC replacement material), pozzolans like silica fume (SF), pulverised fly ash (PFA), palm ash (PA) and rice husk ash (RHA) etc. (Nadir & Ahmed, 2021; Joshua et al., 2021; Ahmed et al., 2019; Mineral Products Association (MPA), 2007; Nadir & Ahmed, 2022; Vijayan et al., 2019). These materials are considered to enhance the engineering properties of concrete, increase durability and produce considerably fewer CO_2 emissions, especially the materials containing Fe, rather result in negative CO_2 balance by absorbing the CO_2 from the environment to produce $FeCO_3$ (Vijayan et al., 2019). David Stone (Vijayan et al., 2019) conducted a failed test during the formulation of material based on Fe and threw the discarded mix in the bin. The next day while disposing it off, he observed that the discarded material gained strength after the initial setting, like cement concrete. Then, he used this material as a concrete alternative naming it 'iron shell' and later 'ferrock', a greener SCM containing 60% Fe, 20% PFA, 12% MK and 8% $CaCO_3$. The atomic absorption spectroscopy analysis concluded that this material absorbs 8-11% of environment CO_2 during curing while converting Fe into $FeCO_3$, making it a better eco-friendly material than cement concrete which emits 8-10% CO_2 during manufacturing/curing, as explained by the following chemical equation (Vijayan et al., 2019; Arabani & Mirabdolazimi, 2011; Prashanth et al., 2019).

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \uparrow$$

The Ferrock can be used as a partial SCM and can result in plausibly better, greener strong material if an ideal environment of 100% CO_2 curing is provided, which is not feasible. Therefore, contemporary researchers have used it partially with OPC to formulate better-performing eco-friendly material at par OPC. It can be used in the marine environment where corrosion due to saltish sea water accelerates the formation of $FeCO_3$ by providing more Fe^{++} for the chemical reaction with CO_2, increasing production of Ferrock and adding more strength to the structure and preventing further corrosion (Vijayan et al., 2019; Arabani & Mirabdolazimi, 2011; Prashanth et al., 2019). The Ferrock-based concrete can be identified by its characteristic iron colour and is used in pavement tiles and facade work (Vijayan et al., 2019). Oxalic acid can also be used as an accelerator catalyst and a de-scaler/ cleaning agent to minimise the colouring/ scaling effect and to accelerate the ionisation of Fe^{++} to convert insoluble iron to soluble iron carbonate (Prashanth et al., 2019; The Uptide, 2021; Concrete Question, 2022). Vijayan et al. (2019), in an evaluation study on ferrock-based concrete as a greener material, elucidated the engineering properties of the composites by mixing 4%,8% and 12% ferrock with OPC and compared the compressive and split tensile strength with 0% control mix. It was observed that the ferrock-concrete composite with 8% exhibited the best performance in comparison to the control mix and other composites (Vijayan et al., 2019). In a study on eco-friendly ferrock-based cement mortar, cubes of 5, 10, 15, 20% ferrock-cement composites were cast and tested for compressive/ flexural strength on 7, 14 and 28 days strength, and 10% ferrock/ cement mortar composite exhibited the best performance in all mechanical properties' indicators. The cubes were immersed in a 5% Na_2SO_4 concentrated solution for 91 days, and again 10% composite was found to perform better in durability studies against sulphate attack (Karthika et al., 2021). A study was conducted on ferrock-cement composites with variation in the quantity of oxalic acid to elucidate the strength performance and setting time with 4, 6, 8, 10 and 12 moles of oxalic acid and 10 moles of oxalic acid performed the best but increased the cost of composite considerably thus determining that 2% oxalic acid use with ferrock-cement composite is the most feasible combination basing on cost-benefit analysis (Prashanth et al., 2019). The conventional ferrock formulated by David Stone is composed of 60% iron powder, 20% PFA, 12% MK and 8% $CaCO_3$, incorporating a binary pozzolanic formulation containing 20% PFA and 12% MK. There has been a research gap found in the existing experimental studies to ascertain how ferrock-based concrete composites will perform if 20% PFA in ferrock in addition to 8% MK is replaced by 20% GGBS as binary pozzolanic SCM or 20% PFA is partially replaced by 10% PFA+10% GGBS or 10% PFA+10%SF as ternary pozzolanic SCMs. This study has been conducted by using conventional ferrock-based cement composites (60% Fe, 20% PFA, 12% MK and 8% $CaCO_3$ with 2% oxalic acid as the accelerating catalyst), formulation of modified ferrock SCMs with partial substitution of 10, 20, 30, 40 and 50% of the binder (OPC) and entirely replacing the PFA with GGBS as binary pozzolanic composites and partially replacing 20% PFA with 10%PFA+10%GGBS and 10%PFA+10% SF as ternary pozzolanic composites with 60% iron powder. The study aimed to elucidate the best mixes containing iron-based binary and ternary pozzolanic composites to ascertain the workability, compressive strength on 7, 28 and 56 days, and flexural testing on 91 days, in comparison to conventional ferrock mixes and control mix (100% OPC without ferrock).

Materials

Cement

The CEM1 52.5 Snowcrete, white Portland cement, has been used for each mix, which conforms to BS EN 197-1 (BS EN 197-1:2011, 2011). The ingredient composition of CEM1, assessed through elemental analysis using x-ray diffraction/ refractometry, is given in table 1. CEM1 exhibits 53 N/ m^2 compressive strength on 28 days of curing. It is rich in CaO (67.1%), SiO_2 (25.2%) and Al_2O_3 (3.18%), which react chemically on hydration to produce calcium-silicate-hydrates (C-S-H gel) responsible for the strength of cement concrete as shown in the equation below (Nadir & Ahmed, 2021; Nadir & Ahmed, 2022).

$2(3CaO.SiO_2) + 6H_2O \longrightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$ + Heat (Nadir & Ahmed, 2022)

Coarse Aggregate and Fine Aggregate (Sand)

The angular, crushed and cleaned coarse aggregate passing a 20mm sieve and fine aggregate (river sand) passing a 4mm sieve have been used in conformance with BS EN 12620/2013 (BS EN 12620:2013, 2013). The use of aggregates in concrete result in the economical use of cement and provide intra-ingredient bonding, exhibiting more strength without any chemical reaction with cement ingredients. Fine aggregate performs as filler material and controls the creation of voids by filling gaps and increasing intra-ingredients bonding between cement particles and angular coarse aggregate (Nadir & Ahmed, 2021; Vijayan et al., 2019).

Iron Powder (Fe)

Iron powder is the waste product from steel mills during scrap steel processing from other industries through shot blasting. It is finely grained powder having a particle size ranging from 19-45 µm, having a specific density of 2.8 g/cm3, containing Fe metallic particles to the extent of 93%. The iron powder/ dust is hazardous and harmful to the environment, can cause an explosion and is generally disposed off in landfilling, costing huge disposal costs to steel mills; however, its use as an alternative to cement can give some environmental benefits though making slightly lesser cost-effective/ economical in comparison to OPC (García et al., 2017; Karuppasamy et al., 2011; Iron Powder, 2023).

Pulverised Fly Ash (PFA)

Fly ash is a waste product of coal-burnt power plants and is considered one of the significant pozzolanic materials used as SCM in cement concrete to impart economic/ environmental/ strength benefits due to containing a high quantity of SiO_2 (56.2%), Al_2O_3 (23.7%) and Fe_2O_3 (8.88%) as shown in table 1. Class F fly ash is rich in silica and widely used in the construction industry, followed by class C, having a comparatively lower percentage of silica. Their particles are spherical in shape and range in size from 0.5-300 µm. PFA converts to suspended solids on moisture absorption and gets hardened like concrete after the pozzolanic reaction. Therefore, its use in high-performance concrete or partial cement replacement is an established fact in conformance to ASTM C 618/ C125-19 that a pozzolanic material giving the combined sum of silica, alumina and other metals oxide of more than 60% is considered an excellent pozzolanic material and can be used as cement alternative (Thomas, 2007; Wesche, 2014; Snellings et al., 2012; Fly Ask, 2018; Annu, 2019). All the pozzolans contain SiO_2, which reacts with $Ca(OH)_2$ during cement hydration and produce additional C-S-H gel giving increased strength to pozzolan-based SCMs as shown in the following equation (Nadir & Ahmed, 2022). However, if the quantity of pozzolan is increased to a specific limit, they start to produce $Si(OH)_4$ gel with swelling properties and begin decreasing the strength of composites (Nadir & Ahmed, 2022).

$2SiO_2 + 3Ca(OH)_2 \longrightarrow 3CaO.2SiO_2.3H_2O$ (Nadir & Ahmed, 2022)

Metakaolin (MK)

"Metakaolin is obtained by calcinating naturally occurring Kaolinite clay mineral under 450-650 Celsius. It is dehydroxylated aluminium silicate ($Al2O_3.2SiO_2.2H_2O$) which is formed by a weaker but more reactive structure after losing hydrate ion during calcination" (Nadir & Ahmed, 2021). It is an amorphous crystalline material and readily reacts with around 15% residual $Ca(OH)_2$ in the cement hydration process to form an additional quantity of C-S-H gel to enhance the strength of SCM-based concrete (Nadir & Ahmed, 2022). As given in table 1, it contains SiO2 (52.1%) and Al_2O_3 (45.1%), making it a suitable material to use as SCM as per ASTM C 618/ C125-19 (Annu, 2019); however, an increased quantity of MK can result in the production of $SI(OH)_4$ and can result in the development of cracks due to swelling properties of $Si(OH)_4$ gel (Nadir & Ahmed, 2022; Aiswarya et al., 2013).

Ground Granulated Blast Furnace Slag (GGBS)

GGBS is obtained from iron industries as a waste product of blast furnace slag containing almost similar quantities of CaO (44.7%), SiO_2(39.4%) and Al_2O_3 (11.1%) (table 1) at par with the ingredients of OPC. It is a steel industry waste and is considered a direct cement replacement in the construction industry. Its OPC-based composites with up to 70% to 80% replacement with lime have exhibited excellent strength performance and engineering properties, making it an established cement alternative (Neville, 2011; Hewlett, 2017; Oner & Akyuz, 2007; Prasanna et al., 2019; Sakai et al., 2013; Samad et al., 2017; Cunliffe et al., 2021). It is available in off-white colour powder with a specific gravity of 2.9 and vibrated bulk density of 1100-1300 kg/m^3, and fineness of $350m^2/g$ (CSMA. (n.d.)).

Silica Fume (SF)

SF is an amorphous crystalline industrial waste material produced during the reaction of quartz with coal in an arc furnace to manufacture silicon or ferrosilicon alloys (Karthika et al., 2021). It contains 99.1% silica making it the most SiO_2-rich pozzolanic material obtained as a by-product/ waste from the silicon industry. It comes as nano silica and micro silica particles (Chrest, 1994; Ferroglobe, 2020). The excess of silica makes it a good pozzolanic SCM, but its excess quantity of more than 5% can cause swelling and cracks due to the production of $Si(OH)_4$ gel during the hydration process (Torichigai et al., 2021; Nadir & Ahmed, 2022; Thomas, 2007).

Limestone ($CaCO_3$)

Limestone powder is the ground form of calcite containing 96.8% $CaCO_3$, with a particle size of 4µm and bulk density of 900 kg/m^3 (loose) to 1100 kg/m^3 (vibrated). On hydration, it is converted into hydrated/ slaked lime $Ca(OH)_2$ and provides Ca^{++} ion to form C-S-H gel after reacting with silica from pozzolanic material in the aqueous solution (Nadir & Ahmed, 2022; Oates, 2020).

Water and Plasticiser

Regular tap water was used for mixing the ingredients in conformance to BS EN 1008:2002 using a water cement w/c ratio of 0.4. 0.2%-0.25% (of the binder weight) carboxylate polymer-based plasticiser with a specific gravity of 1.06 g/ cm^3 and ph of 6.5 was used to achieve the self-compacting consistency of the mixture (BSI - BS EN 1008:2002, 2002; Oscrete, 2014).

Oxalic Acid

Oxalic acid is a weak organic alpha, omega-dicarboxylic acid having formula $C_2H_2O_4$ or $(COOH)_2$. It is broadly used as a cleaning agent, like weak acid, e.g. vinegar, to remove stains from different surfaces. Its use in ferrock-based concrete as a catalyst increases the reaction for increased formation of $FeCO_3$. The research has elucidated the use of oxalic acid in the range of 10 moles/m^3 of concrete. However, cost-benefit analysis versus strength achievement suggests using oxalic acid in the range of 2% of binder quantity (Prashanth et al., 2019; National Center for Biotechnology Information (NCBI), 2023).

Experimental

The control mix with 100% OPC using 1:2:3 cement, sand and the aggregate ratio has been incorporated as per the prescribed British standards for materials/ mixing concrete as mentioned in the preceding sections targeting C32/40 or M40 concrete. The conventional ferrock formulated by David Stone (60% iron powder, 20% PFA, 12% MK and 8% $CaCO_3$) has been used to mix in a 1:2:3 ratio by partially replacing ferrock as 10,20,30,40 and 50% of OPC as set 1 in table 2. The modified ferrock-based SCMs have been formulated using a 1:2:3 ratio, by complete replacement of 20% PFA with 20% GGBS (set 2) and ternary replacement of 20% PFA with 10% PFA+10% GGBS (set 3) and lastly ternary replacement of 20% PFA with 10% PFA+10% SF (set 4) table 2. The water-cement ratio of 0.4 and the concrete ratio of 1:2:3 have been used to mix the ingredients to cast 100 mm cubes to test on 7, 28 and 56 days of curing for compressive strength as per BS EN 12390-2:2019 on the compressive testing machine shown in figure 1 (BSI - BS EN 12390-2, 2000). The prisms of 500x100x100 mm for testing of flexural strength on 91 days of curing were cast in conformance with BS EN 12350-1 and were tested on a flexural testing machine with gradual hydraulic three-point loading and taking readings in the attached laptop as shown in figure 2 (BS EN 12350-1:2019, 2019). The consistency was ascertained using slump testing using standard cone and rod apparatus (figure 3) with target S1 slump as per BS EN 8500 (BSI - BS EN 8500:206-2019, 2019; Nadir, 2022). Generally, 0.2-0.25% plasticiser was used with the mixes to get an excellent compactable consistency/ workability.

Ingredients	CEM1 52.5 (%)	GGBS (%)	SF (%)	MK (%)	Fe Powder (%)	PFA (%)
Fe_2O_3	0.32	0.31	0.43	0.45	93 Fe	8.88
SiO_2	25.2	39.4	99.1	52.1		56.2
TiO_2	0.18	0.47	<0.1	0.88		0.83
CaO	67.1	44.7	<0.1	0.31		3.46
K_20	0.30	0.43	<0.1	0.17		0.66
Al_2O_3	3.18	11.1	<0.1	45.1		23.7
Mg0	1.33	1.46	<0.1	0.20		3.28
Na_20	<0.1	0.11	<0.1	0.25		1.93
P_2O_5	<0.11	<0.1	<0.1	<0.1		<0.31
C1	<0.23	<0.1	<0.1	<0.1		<0.1
SO_3	<1.57	<1.49	<0.1	<0.1		0.25
O_2					6	

Table 1: Elemental/ ingredient composition analysis by XRD/Refractometry of different materials

Material	Set1 (%)	Set2 (%)	Set3 (%)	Set4 (%)
Iron powder	60	60	60	60
Fly Ash	20	-	10	10
GGBS	-	20	10	-
Silica Fume	-	-	-	10
Limestone	10	10	10	10
Metakaolin	8	8	8	8
Oxalic Acid	2	2	2	2

Table 2: Composition of conventional/ modified ferrock-based binary/ ternary pozzolanic SCMs with 10-50% Ferrock Replacement

Results and Discussion

Workability

The workability was ascertained using slump testing using standard cone and rod apparatus (figure 3) with target S1 slump as per BS EN 8500 (BSI - BS EN 8500:206-2019, 2019; Nadir, 2022). A 0.4 w/c ratio generally demonstrated lower workability of ferrock-based SCMs compared to the control mix. The slump testing resulted in a 0-10 cm true slump, necessitating the use of plasticiser from 0.2-0.25% of the binder weight to achieve a compactable consistency/ workability. Generally, the higher percentages of ferrock mixes resulted in decreased workability and increased use of plasticisers up to 0.25%.

Figure 1: Compressive testing machine for testing of 100 mm cubes (BSI - BS EN 12390-2, 2000)

Figure 2: 3-point loading flexural testing machine for 500x100x100 mm prisms/ beams [44]

Figure 3: Slump testing [45,46]

Compressive Strength

100 mm cubes were tested on 7, 28 and 56 days of water curing for compressive strength as per BS EN 12390-2:2019 on the compressive testing machine shown in figure 1 (BSI - BS EN 12390-2, 2000). A target characteristic compressive strength of C32/40 or M40 concrete was set for all the mixes and was successfully achieved by all the mixes at 28/ 56 days of curing. Generally, the 10-20% ferrock-based SCMs exhibited 10-13% more compressive strength than the control mix (without ferrock mixing) (figures 4-10). The performance of the control mix was observed better in the first seven days of curing except for the 10% ferrock mix of all SCMs (figure 4), as the pozzolanic reaction is delayed and starts after the initial setting/ hydration of OPC (Nadir & Ahmed, 2022; Nadir & Ahmed, 2022). All ferrock SCMs, especially 30-50% partially replaced mixes of sets 3 and 4, exhibited better compressive strength after 28 and 56 days of curing (figure 4, 5). The 10% modified ferrock SCM of set 2 exhibited the maximum compressive strength of 65.3 MPa (13% increase) on 56 days of curing, followed by the 20% ferrock mix of set 4 with 64.4 MPa (12% increase), then 20% ferrock mix of set 3 with 64 MPa (11% increase) and lastly the 10% conventional ferrock SCM (set 1) containing with 63.3 MPa (10% increase), as shown in figure 4, 5. SCMs containing 30-50% ferrock exhibited a gradually decreasing trend of 2-27% in compressive strength with increased use of ferrock percentages, as shown in figure 5. The maximum decrease in compressive strength of 27% was observed in 50% conventional ferrock SCM, followed by a 21% decrease in 50% modified ferrock with GGBS. However, 40-50% ternary ferrock mixes of set 3 (10%PFA+10%GGBS) and set 4 (10%PFA+10%SF) exhibited a lesser decrease in strength compared to control and other 10-30% mixes on 56 days of curing (figure 5). Generally, the results obtained in this study align with the existing literature where different researchers studied 4, 8, 12% and 5, 10, 15, 20, 25% conventional ferrock SCMs and suggested 8-10% exhibiting increased compressive strength and more than 20% ferrock SCMs indicating a decreasing trend in compressive strength (Vijayan et al., 2019; Prashanth et al., 2019; Torichigai et al., 2021; Rajesh et al., 2018; Karthika et al., 2021; García et al., 2017; Karuppasamy et al., 2011). An anomaly has been observed in this study where 50% modified ferrock with 10%PFA+10%SF mix is exhibiting more compressive strength than 40% mix, but the result has not been excluded from the study, being within 10% variation.

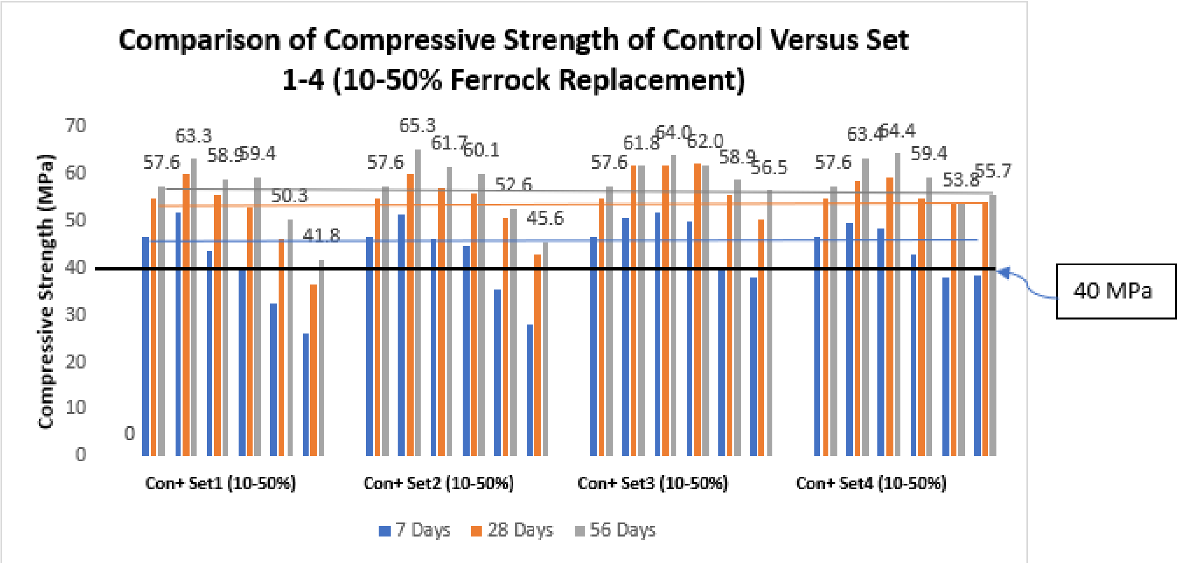

Figure 4: Compressive strength of control versus set 1-4 (from left-right Control and 10-50% ferrock replacements)

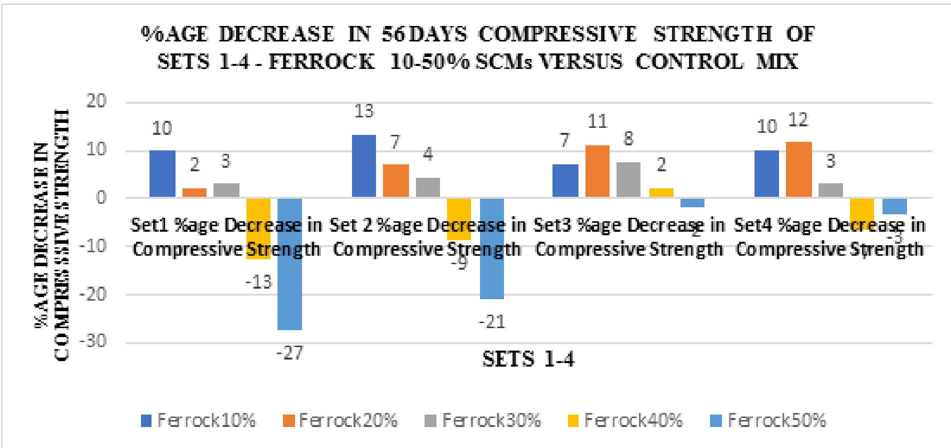

Figure 5: %age decrease in 56 days compressive strength of sets 1-4 - ferrock 10-50% SCMs versus the control mix.

Compressive Strength of Conventional Binary Ferrock-Based SCMs (Set 1)

Set 1 contains the conventional ferrock composed of 60% Fe, 20% PFA, 10% $CaCO_3$, 8% MK and 2% oxalic acid (table 2). On seven days of curing, the control mix with 46.5 MPa performed better than all 20-50% ferrock-based SCMs except the 10% mix exhibiting 51.8 MPa strength with an 11% increase. 10-30% ferrock replacement SCMs exhibited more compressive strength than the control mix on 28 and 56 days of curing. However, 40-50% of mixes exhibited a gradual decrease on the increased use of ferrock (figure 6). The findings are in line with the study of Vijayan et al. (2019) and Shivani et al. (2022), who found that up to 12% replacement of conventional ferrock with OPC performs better than the control mix on 7, 14 and 28 of curing. However, Karthika et al. (2021) elucidated in their study that SCMs with 15% and more ferrock replacement resulted in decreasing compressive strength, as suggested by this study also. However, on 56 days of curing, 10-30% mixes performed better than the control mix as the pozzolanic-ferrock-based SCMs tend to achieve compressive strength on more curing age with the increased formulation of C-S-H gel and $FeCO_3$. But the excessive presence of silica in pozzolans starts converting into $Si(OH)_4$ on hydration and results in swelling silica-hydrated compounds, which cause swelling/ cracking and reduction in strength (Nadir & Ahmed, 2022; Nadir & Ahmed, 2022). Therefore, 40% and 50% ferrock mixes have shown a 13% and 27% decrease in compressive strength on 56 days of curing. All the SCMs are achieving the target of C32/40 or M40 concrete strength at 56 days of curing, and 10 and 20% mixes can be used as high-strength concrete/ SCMs (≥60 MPa), and 30-50% can be used for C32/40 or M40 concrete (The Concrete Society, 1966; ACI Committee, 2007).

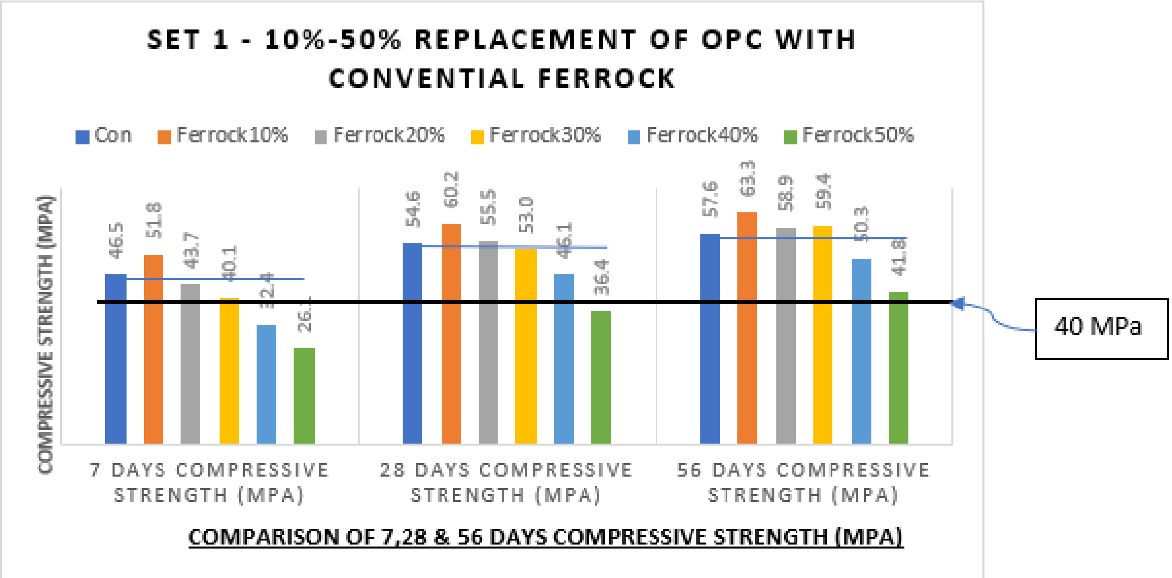

Figure 6: Compressive strength of conventional ferrock-based SCMs (Set 1)

Compressive Strength of Modified Binary 20%GGBS-Ferrock-Based SCMs (Set 2)

Set 2 contains the modified ferrock composed of 60% Fe, 20% GGBS, 10 % $CaCO_3$, 8% MK and 2% oxalic acid (table 2). On seven days of curing, the 10 and 20% modified binary ferrock mix performed better than/ at par with the control mix with 51.4 and 46.2 MPa strengths (figure 7). Generally, all 10-30% modified ferrock-based SCMs exhibited more compressive strength than the control mix and set 1 on 28 and 56 days of curing. However, 40 and 50% of mixes exhibited a gradual decrease on the increased use of ferrock at all ages of curing (figure 7). Moreover, the performance of the mixes of set 2 (20%GGBS) is found to be better than the mixes of set 1 (20% PFA) because the GGBS is considered as the direct cement replacement exhibiting the at-par performance of OPC and containing ingredients close to OPC composition (table 1) (Neville, 2011; Hewlett, 2017; Oner & Akyuz, 2007; Prasanna et al., 2019; Sakai et al., 2013; Samad et al., 2017; Cunliffe et al., 2021). The findings are in line with the contemporary studies where the researchers have suggested up to optimum 15% use of ferrock with OPC (Vijayan et al., 2019; Karthika et al., 2021; Shivani et al., 2022). However, the cement-like characteristics of GGBS suggest 20% GGBS-ferrock-based SCMs as better performing composites than the control/ set 1 mixes. The 10% composite of set 2 exhibited the maximum increase in compressive strength with 65.3 MPa on 56 days of curing (13% increase), elucidating it as the best mix ratio/ material. In contrast, the least compressive strength was exhibited by the 50% mix in set 2 with a 21% decrease, suggesting that 10 and 20% are optimum mix ratios and 40 and 50% are least performing ratios. However, all the SCMs are still achieving the target of C32/40 or M40 concrete strength within 28/56 days of curing and are suitable to use for high strength (10&20% mixes)/standard concrete requirements (10-50% mixes) (Samad et al., 2017; The Concrete Society, 1966; ACI Committee, 2007).

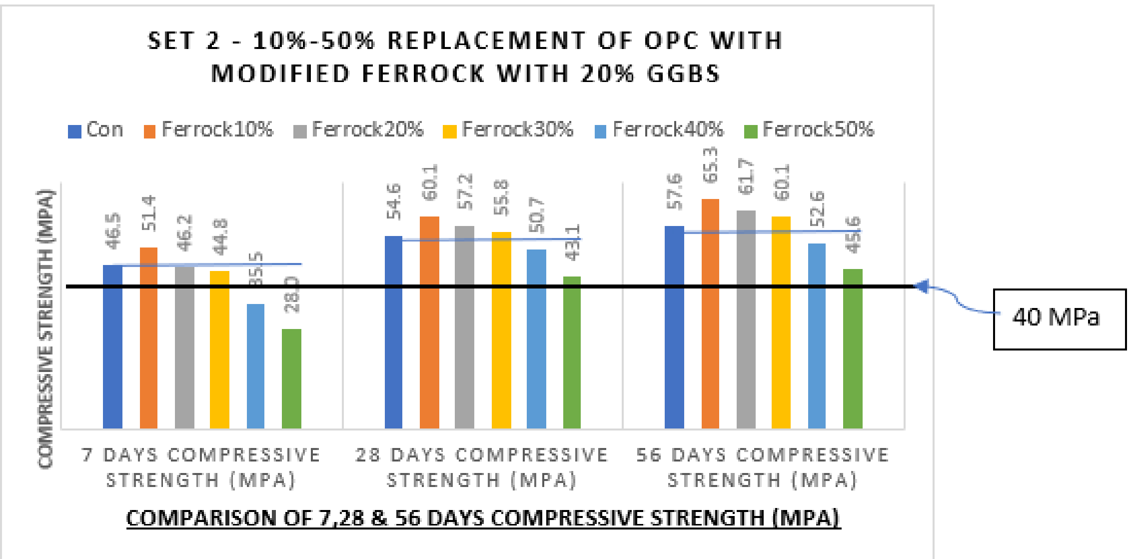

Figure 7: Compressive strength of modified binary 20% GGBS-ferrock-based SCMs (Set 2)

Compressive Strength of Modified Ternary 10%PFA+10%GGBS-Ferrock-Based SCMs (Set3)

Set 3 contains the modified ferrock composed of 60% Fe, 10%PFA+10%GGBS, 10% $CaCO_3$, 8% MK and 2% oxalic acid (table 2). On seven days of curing, the 10-30% modified ternary ferrock mix exhibited more compressive strength than the control mix with up to 51.7 MPa (figure 8). Generally, all 10-30% modified ferrock-based SCMs exhibited more compressive strength than the control mix and set 1 and 2 on 28 and 56 days of curing (figures 4,6-8). However, 40 and 50% of mixes exhibited a sharp decrease in strength at seven days, and 40% showed an increase in strength, but a gradual decline was observed with a 50% mix ratio at 28/56 days on increased replacement of modified ferrock (figure 8). The performance of all the mixes of set 3 (10%PFA+10%GGBS) is found to be better than the mixes of set 1 and set 2 (20% PFA and 20% GGBS replacement) because the use of 10% PFA incorporated better pozzolanic reaction due to increased silica contents and 10% GGBS incorporated the at-par performance of OPC (Samad et al., 2017; Cunliffe et al., 2021). The findings are in line with the contemporary studies where the researchers have suggested up to optimum 15% use of ferrock with OPC (Vijayan et al., 2019; Karthika et al., 2021; Shivani et al., 2022). However, the cement-like characteristics of GGBS and silica-rich PFA suggest 10%PFA+10%GGBS-ferrock-based SCMs as better performing composites than the control, set 1 and set 2 mixes. The 10 and 20% composite in set 3 exhibited the maximum increase in compressive strength with 64 MPa on 28 and 56 days of curing (11% increase in figure 5), suggesting it as the best mix ratio/ material. In contrast, a gradual decrease in compressive strength was observed by 40 and 50% mixes in set 3 with a nominal reduction of only 2% (figure 5,8), suggesting that 10-30% are optimum mix ratios and 40/ 50% are performing little lesser in strength but still better than the control/ set 1/set2. All the SCMs were observed achieving the target of C32/40 or M40 concrete strength within 28/56 days of curing, and 10-30% mixes can be used as high-strength concrete/ SCMs (≥60 MPa), and the mixes with even 40 and 50% ratios at 56 days also demonstrated performance very close to the of high strength concrete (Samad et al., 2017; The Concrete Society, 1966; ACI Committee, 2007).

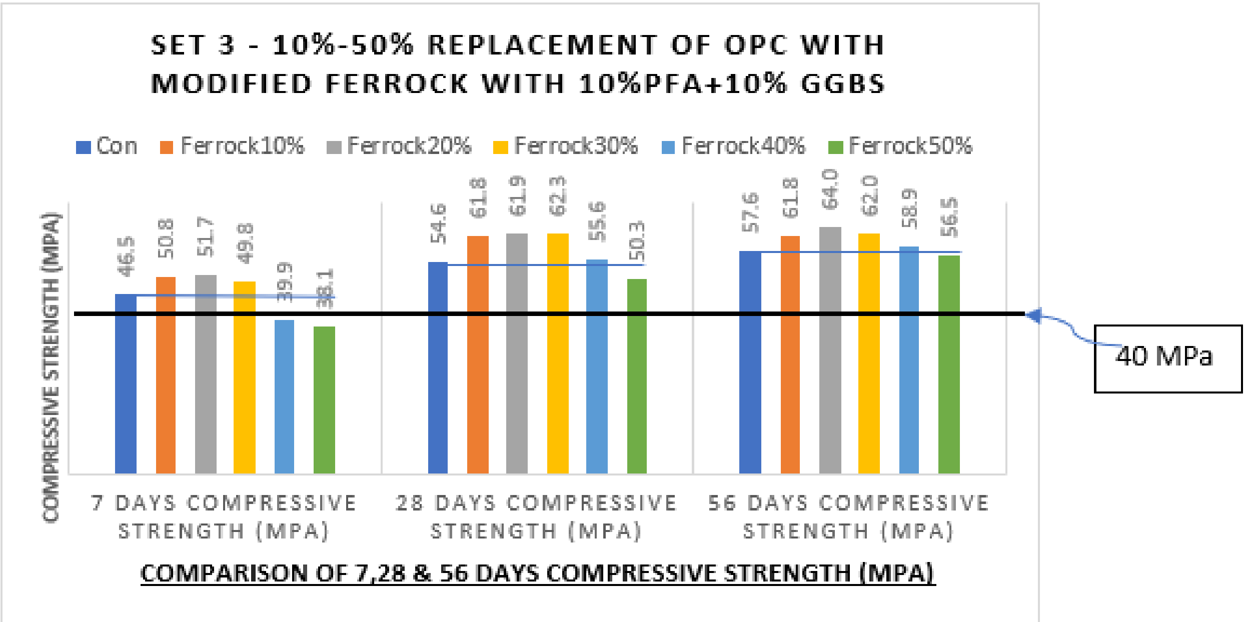

Figure 8: Compressive strength of modified ternary 10%PFA+10%GGBS-ferrock-based SCMs (Set 3)

Compressive Strength of Modified Ternary 10%PFA+10%SF-Ferrock-Based SCMs (Set4)

Set 4 contains the modified ferrock composed of 60% Fe, 10%PFA+10%SF, 10% $CaCO_3$, 8% MK and 2% oxalic acid (table 2). On seven days of curing, the 10-20% modified ternary ferrock mix exhibited more compressive strength than the control mix with up to 49.7 MPa (figure 9). Generally, all 10-30% modified ferrock-based SCMs exhibited more compressive strength than the control mix and sets 1&2 but little lesser than set 3 at 28 and 56 days of curing (figures 4, 6-9). However, 40-50% of mixes exhibited a sharp decrease in strength at 7 seven days of curing. The 50% mix exhibited more compressive strength at 56 days, although, a gradual decline was observed with a 40% mix at 28/56 days on increased replacement of modified ferrock (figure 9), indicating a slight variation within 10% of strength. The performance of all the mixes of set 4 (10%PFA+10%SF) is found to be better than the mixes of set 1 and set 2 (20% PFA and 20% GGBS replacement) because the use of 10% PFA and 10% SF incorporated better pozzolanic reaction due to increased silica contents but overall set 4 exhibited slightly less strength than set 3. The findings are in line with the contemporary studies where the researchers have suggested up to optimum 15% use of ferrock with OPC (Vijayan et al., 2019; Karthika et al., 2021; Shivani et al., 2022). The 10 and 20% composites in set 4 demonstrated the maximum increase in compressive strength with 64.4 MPa on 56 days of curing. However, no mix could cross the high strength threshold of 60 MPa at 28 days of curing (12% increase in figure 5), suggesting it as the best mix ratio/ material with increased curing time. 40% mixes observed a gradual decrease in compressive strength in set 4 with a reduction of 7%; on the contrary, the 50% mix showed only a 3% decrease (figure 5,9), suggesting that 10-30% mixes are optimum mix ratios and 40 and 50% are performing little lesser in strength but still better than the control/ set 1/ set 2. All the SCMs were observed achieving the target of C32/40 or M40 concrete strength within 28/56 days of curing, and 10-30% mixes can be used as high-strength concrete/ SCMs (≥60 MPa), whereas 40/50% mixes can be used with increased age of curing for all normal concrete uses of M40-M50. (Samad et al., 2017; The Concrete Society, 1966; ACI Committee, 2007).

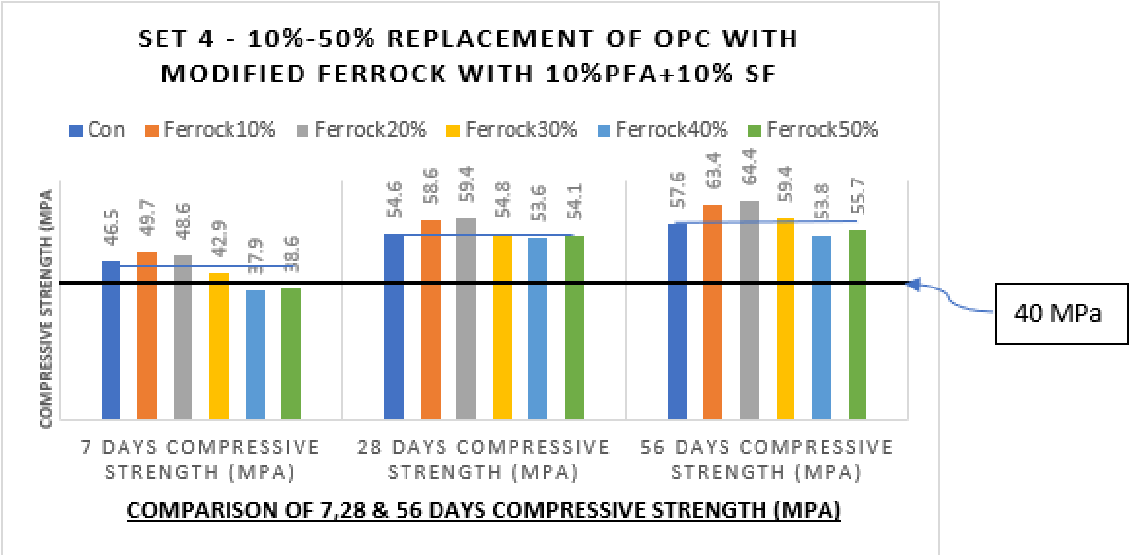

Figure 9: Compressive strength of modified ternary 10%PFA+10%SF-ferrock-based SCMs (Set 4)

Flexural Strength of Set 1-4 10-50% Binary/ Ternary Ferrock-Based SCMs

The prisms of 500x100x100 mm have been tested for flexural strength on 91 days of air curing, in conformance with BS EN 12350-1 and were tested on a flexural testing machine with gradual hydraulic three-point loading and taking readings in figure 2 (BS EN 12350-1:2019, 2019). Generally, SCMs with 10-30% ferrock replacement exhibited better flexural strength on 91 days of curing, as shown in figures 10&11. Karthika et al. (2021), Das and Stone et al. (2015) researched to elucidate the impact of ferrock on the flexural strength of beams. They elaborated that the increases in the flexural strength of beams is due to the inbuilt flexibility of iron particles which impart ductility to ferrock-based SCMs and result in a better performance against flexural stress on beams/ prisms (Widera & Stone, 2016; Das et al., 2015; Brander& Davis, 2012). The intra-aggregates bonding with iron powder and pozzolanic fillers increases the flexural strength of ferrock-based SCMs. However, increased pozzolans produce silica hydrates Si(OH)4 compounds during hydration, which can cause swelling/ cracking and reduce flexural strength after a certain mix ratio (Karthika et al., 2021; Nadir & Ahmed, 2022; Nadir & Ahmed, 2022). In this experimental study, all the mixes of conventional/ modified ferrock-based SCMs exhibited improvement in flexural strength except 40% and 50% mixes of set 1 (conventional ferrock) compared to the control mix. As observed earlier, set 3 containing 10%PFA+10%GGBS ternary pozzolanic SCMs exhibited the best flexural strength for all 10-50% mixes compared to the control mix and set 1-3. The 20% mix ratio of set 3 exhibited 32% more flexural strength with 5.8 MPa than the control mix. 10, 30 and 40% mixes exhibited more than 5 MPa, whereas the 40% mix achieved 4.9 MPa, slightly less than other mixes in set 3, showing an anomaly in results. Since it is within 10% variation, so has been included in the research data. Set 2, containing 20% GGBS as binary pozzolanic SCMs, exhibited the second-best performance in achieving around 5 MPa or more strength. 10% and 30% mixes of set 2 achieved 5.3 MPa, and 20% mix showed 5 MPa followed by a slight/ gradual decrease in strength with 40% and 50% mixes. GGBS being the direct replacement of cement, having similar ingredients as OPC, on mixing with iron powder, is expected to increase the flexural strength imparting more ductility and strength to SCMs due to increased pozzolanic reaction. Set 4 containing 10%PFA+10%SF ternary pozzolanic SCMs remained the third-best performer, with a 20% mix of set 4 gaining the maximum flexural strength of 5 MPa. However, all other mixes of set 4 exhibited 4.4-4.7 MPa strength, slightly more than the control mix. The 40% mix achieved 4.4 MPa, somewhat less than other mixes in set 4, even lesser than the 50% mix, showing an anomaly in results. Since it is within 10% variation, it has not been excluded from the research data. Set 1, containing conventional ferrock-based SCMs, demonstrated less strength than mixes of set 2-4, achieving a maximum of 5 MPa flexural strength by 30% mix, whereas 10% and 20% mixes reached 4.7 and 4.4 MPa and the minimum flexural strengths were exhibited by 40 and 50% of set 1 as 3.7 and 3.8 MPa (figure 10). Generally, 20-30% replacement of ferrock exhibited more flexural strength as optimum mixing ratios in all the sets, followed by 10% mixes and the least by 50% and 40% mixes, respectively, elucidating a specific range of beneficial use of iron powder, GGBS and pozzolans to act as filler/ silica imparting material and to impart ductility/ increased strength by producing additional C-S-H gel and $FeCO_3$ (figure 11).

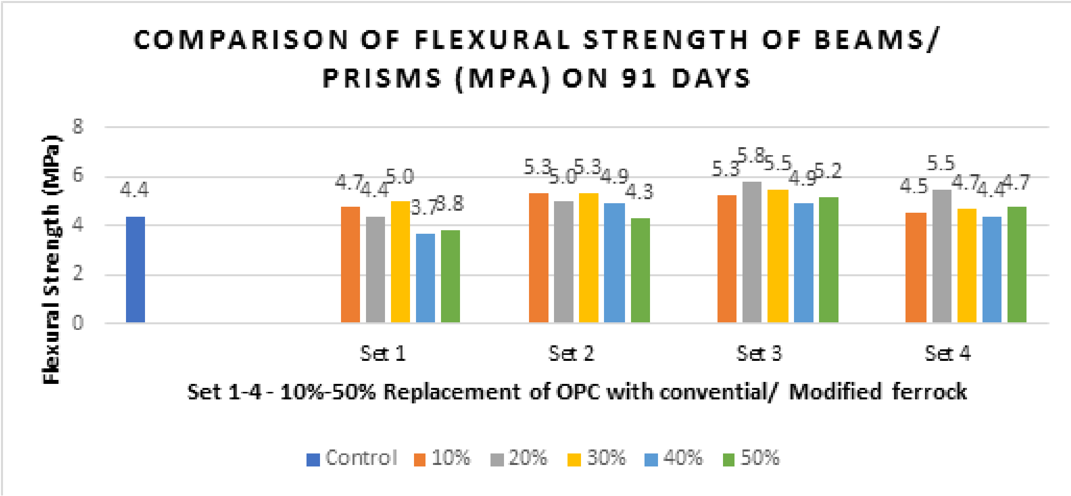

Figure 10: Comparison of set-wise flexural strength of beams/ prisms (MPa) on 91 days

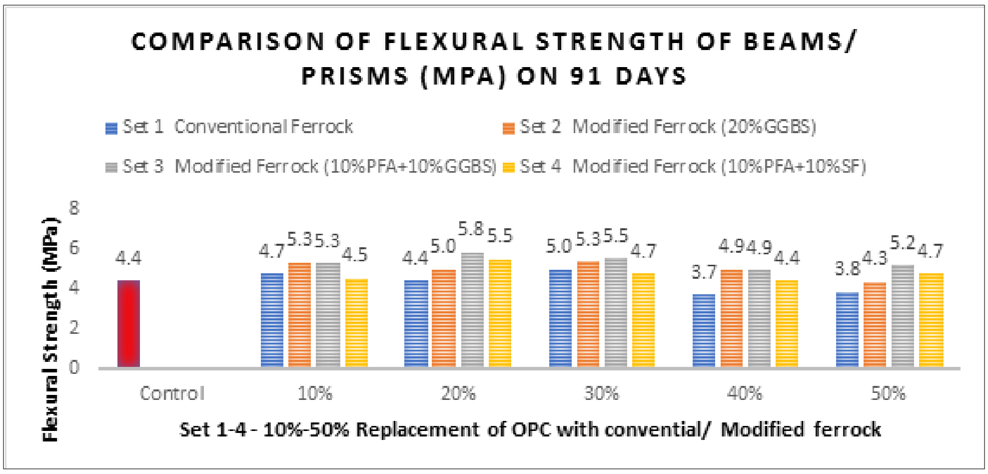

Figure 11: Flexural strength of 10%-50% mixes of binary/ ternary ferrock-based SCMs (set 1-4).

Comparison of Energy/ Water Use and Global Warming Potential of OPC Versus Ferrock

Stone and Widera (2016) introduced ferrock as a novel material as low energy embodied, CO_2 negative, environmentally friendly material which absorbs around 9-12% CO_2 of its weight of use from the environment (Vijayan et al., 2019; Widera & Stone, 2016; Das et al., 2015; Brander & Davis, 2012). The study by Garcia et al. (2017) elucidated that ferrock is CO_2 negative, either absorbing CO_2 from the environment or absorbing CO_2 produced during hydration of OPC if ferrock is used as SCM with cement concrete (García et al., 2017). They have estimated/ compared the energy use in MJ/FU (megajoules per fibrin unit), use of water in L/FU (litres per fibrin unit) and global warming potential/ emission of CO_2 in Kg CO_2 equivalent per fibrin unit for OPC and ferrock as illustrated in figure 12 (García et al., 2017). They assumed the production of ferrock as a by-product/ waste material obtained during shot blasting and cleaning/ milling of scrap iron in steel mills; therefore, CO_2 emission or energy and water used during this process are actually consumed by purification/ production of steel, not by the production of ferrock. It is suggested that the energy used by cement production is 5887 MJ/FU, which is ten times higher than the energy used by the production of ferrock with 557 MJ/FU. 10100 litres/ FU of water is used by cement which is 45 times higher than the use of water by ferrock production (220 litres/ FU). The cement is estimated to contribute 1040 Kg CO_2-eq/FU (emission of 1 ton of CO_2/ ton of OPC). In contrast, ferrock is estimated to consume/ absorb 50 Kg CO_2-eq/FU from the environment for carbonation of iron powder during the formation process of $FeCO_3$, creating a negative balance and resulting in almost 21 times lesser contribution to global warming potential (García et al., 2017). The ferrock's contribution to the absorption of CO_2 from the environment/ hydration process of OPC, if used as an SCM, suggests it as a greener, environmentally friendly material which exhibits at par engineering properties to OPC. However, its economic use is still a question mark on its large-scale use due to less production from steel mills and transportation costs from steel mills to the point of sales/ use. Therefore, using ferrock as an SCM is highly recommended near steel mills where easy supply with lesser transportation cost is feasible.

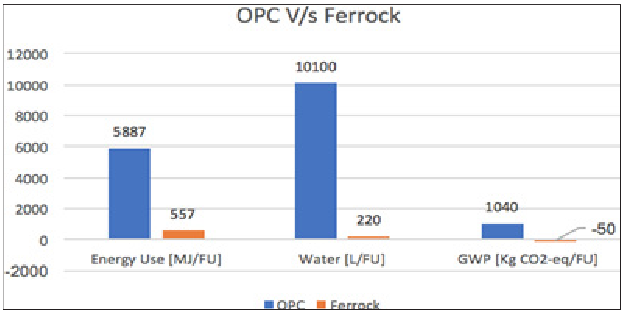

Figure 12: Comparison of energy use and global warming potential of OPC versus ferrock [19]

Conclusion

- The study exhibited very interesting/ promising results, supported well by contemporary research, which elucidated ferrock as a feasible/ sustainable SCM.
- The use of conventional ferrock, as introduced by David Stone has been explored by different researchers. However, this study has fruitfully endeavoured to fill in the gap, employing the modified use of binary and ternary ferrock-based SCMs, which all achieve the target strength of C32/40 or M40 concrete.
- Use of 10%PFA+10%GGBS (set 3) in place of 20% PFA in conventional ferrock exhibited the best-performing set of ternary mixes. The SCMs with 10-30% mix ratios of set 3 demonstrated the best compressive and flexural strength, achieving high strength threshold of more than 62 MPa. The mixes containing 10%PFA+10%SF (set 4) in place of 20% PFA in conventional ferrock exhibited the second best-performing set of ternary mixes. The SCMs with 10-20% mix ratios of set 4 demonstrated the second-best compressive and flexural strength, achieving high strength threshold of more than 60 MPa. The use of 20% GGBS (set 2) in place of 20% PFA in conventional ferrock exhibited the third best-performing set of ternary mixes. The SCMs with 10-30% mix ratios of set 2 showed the third-best compressive and flexural strength, achieving high strength threshold of more than 60 MPa. However, almost all mixes of the modified ferrock, including 10-50% SCMs achieved the target of M40 concrete ad can be used beneficially for M40-M50 concrete with reduced CO_2 footprints.
- The ferrock is assumed to absorb 9-12% of CO_2 from the environment/ hydration of OPC, making it a greener, environmentally friendly material. Therefore, using 10-50% modified ferrock-based SCMs for achieving high-strength/ M40-M50 concrete with around 10-50% lesser global warming potential is a beneficial/ sustainable use of novel materials.
- The economical use of ferrock as full cement replacement is not feasible due to the considerable cost of iron powder/ lesser commercial availability compared to OPC. However, 10-50% ferrock-based SCMs or ferrock with less than 60% iron powder (after further elaborations) can be suggested as a sustainable material considering economy versus environmental benefits, lesser CO_2 emission rather than the creation of negative CO_2 balance by its absorption during the carbonation of iron powder, reduced use of energy/ water, a better absorption option of waste from the steel industry and better engineering properties of ferrock-based SCMs than cement concrete.

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