INTERNATIONAL JOURNAL OF SUSTAINABLE CONSTRUCTION ENGINEERING AND TECHNOLOGY
Vol. 11 No. 4 (2021) 90-98

IJSCET

http://penerbit.uthm.edu.my/ojs/index.php/ijscet
ISSN : 2180-3242 e-ISSN : 2600-7959

International Journal of Sustainable Construction Engineering and Technology

Ferrock: A Carbon Negative Sustainable Concrete

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DOI: https://doi.org/10.30880/ijscet.2021.11.04.008
Received 26 July 2020; Accepted 29 December 2020; Available online 31 December 2020

Abstract: In this fast-growing world, people are focusing on the infrastructural development, where construction sector plays an important role. Cement is the most prominent material being used in construction that emits approximately 6-8% of the total carbon dioxide in the world during its production which is the major constituent of global warming. Thus, focusing on the carbon emission reduction and also utilization of the waste products for a better environment, a product named Ferrock was constituted. This paper is a review over a product that is stepping towards carbon negativity and waste management. It shows the best usage of iron ore waste powder obtained during the mining process that is just dumped away from the mines, causing air pollution, health hazards and also consuming larger area. The product indirectly reduces the carbon dioxide released by its unique strength gaining mechanism, which is in contrary with that of the cement and thus stands out among many other supplements of cement. Ferrock involves a curing process with carbonation and air curing in varied number of days for better strength in terms of compression, tensile strengths and achieving desirable properties. Ferrock is thus a more promising eco friendlier binding material in terms of its carbon negativity and in best usage of the waste.

Keywords: Carbon footprint, cement replacement, waste management, ferrock, carbon negative

1. Introduction

Now a days global warming is one of the major threats to our eco system. Amongst the greenhouse gases leading to global warming, carbon dioxide is of the maximum percentage that is 76% is as shown in Fig. 1. Aiming to reduce the total percentage of carbon dioxide being emitted, analysis over the sources of it were done and sorted. Working on towards a greener environment, civil engineers are contributing by analyzing the carbon emitters and finding ways to solve it.

In this fast-growing world, infrastructure development is given more importance leading to a linear increase in constructions of multi-stories or high-rise buildings, roads, bridges, towers, etc... The most important material used in this construction is the cement. Cement is the binding material used to gain strength in order to sustain the loads applied on it. It is an artificially manufactured product which releases carbon dioxide in the process of its manufacture which contributes to the total environment by approximately 6 to 8% (Andrew, 2018).

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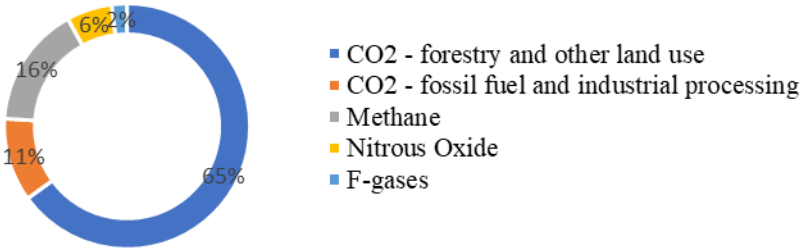

Fig. 1 - Total CO_2 percentage among the greenhouse gases.

The manufacturing of clinkers in cement production involves carbon dioxide emissions at every step of it. The Fig. 2 shows the carbon dioxide major emission in clinker production which is thermal, process emissions and minor emission during transport, grinding, mixing etc, Cement in concrete is a minor proportion compared to aggregates but has a major carbon footprint in it.

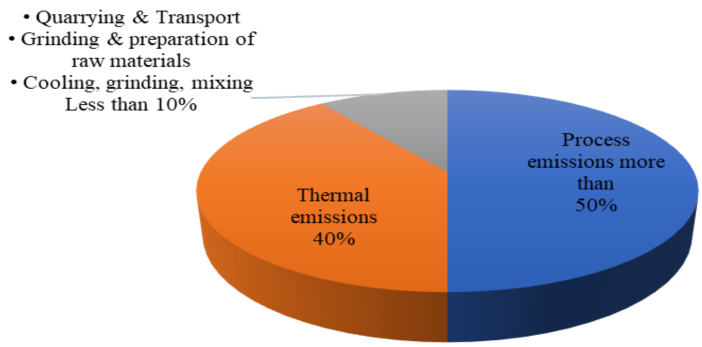

Fig. 2 - CO_2 emissions in clinker production.

The Fig. 3 shows the concrete composition and the concrete carbon footprint. In view of reduction of carbon dioxide, replacement to cement is one such attempt which has led to innovations and introduction of supplements to cement like fly ash, GGBS, rice husk ash, silica fumes, etc. Ferrock is one such product which is carbon negative by nature and also which can be used as a supplement to cement which was advocated by David stone, university of Arizona in the year 2017. Ferrock is made up of raw materials like the iron powder, metakaolin, fly ash, limestone and oxalic acid. This product is being used as a replacement to cement initially by Professor David stone (Das, Hendrix, Stone, & Neithalath, 2015; Das, Souliman, Stone, & Neithalath, 2014; Das, Stone, Convey, & Neithalath,2014; Widera, & Stone, 2016). This product consumes carbon dioxide gas for its strength gaining mechanism unlike the cement using the water.

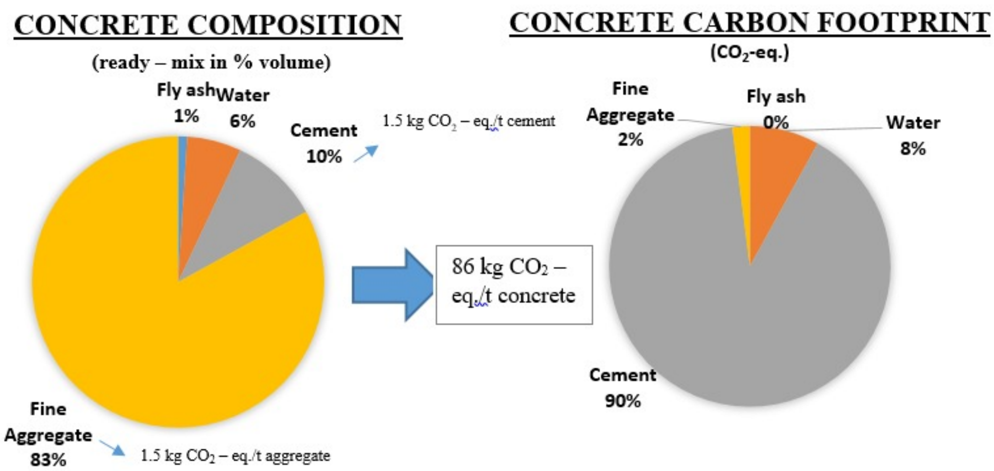

Fig. 3 - Proportion of cement in concrete and its carbon footprint.

2. Cement

Cement is the most widely used building material used all around the globe because of its low cost, ease of use and its versatility. Cement is a binding material, a substance used for construction that hardens and adheres to aggregates to bind them together to form concrete. Cements used in construction are usually inorganic, often with a lime or calcium silicate base and can be characterized as either hydraulic or nonhydraulic, based on its ability to set in the presence of water. Portland cement which is largely used in the construction industry is an example of hydraulic cement. They set and become adhesive due to an exothermic chemical reaction between the cement and the water. The chemical reaction also called as hydration of cement results in mineral hydrates. This reaction results in the hardening and strength gaining of cement (Turner, 2013).

2.1 Ingredients

The raw materials used in the manufacturing of cement mainly consists of lime, silica, alumina and iron oxide. The oxides interact with one another in the kiln at high temperature to form more complex compounds. The relative proportions of these oxide compositions are responsible for influencing the wide range of properties of cement. The table1 shows the approximate oxide composition limits of ordinary Portland cement.

Table 1 - Raw material proportioning of cement by percentage (Turner, 2013).

Oxide	Percentage content
CaO	60-67
SiO_2	17-25
Al_2O_3	3.0-8.0
Fe_2O_3	0.5-6.0
MgO	0.1-4.0
Alkalies (K_2O, Na_2O)	0.4-1.3
SO_3	1.3-3.0

2.2 Carbon Footprint

With the consumption rate of 1m3 per person per year concrete is the most used construction material in the world. Ordinary Portland Cement (OPC) has traditionally been used as the binder material in concrete. On the contrary OPC has carbon emissions in the range of 0.66-0.82kg of CO2 emitted for every kilogram of OPC manufactured. The contribution of OPC is approximately 5-7% of global CO2 emissions (Turner, 2013). The main reasons for high contribution to CO2 emissions from the manufacture of OPC have been attributed to:

1. Calcination of limestone, one of the key ingredients, which leads to formation and release of CO_2.
2. High energy consumption during manufacturing, including heating raw materials within a rotating kiln at high temperatures in the range of 1400°C.

The estimation of CO2 due to cement manufacturing is a more complicated problem due to the chemical liberation of CO2 due to decomposition of limestone during calcination, variation of the limestone source and also the use of calorific wastes in cement kilns which provide energy as a substitute fuel. The reported emission factor for cement production is 0.82 kg of CO2/kg. The estimate includes the emissions contributed from the mining of raw materials, cement manufacturing, and all transport associated, including the freight of cement to concrete batching plants. (Laurent Barcelo et al., 2013) stated that the cement industry is a major producer of CO2 accounting to 5-7% of man-made CO2 emissions. In cement manufacturing the CO2 emissions comes majorly from the decarbonation of limestone. (Ernst Worrell et al., 2001) discussed that, the emissions of CO2 can be reduced by the production of blended cements with fly ash and GGBS. By adopting this we can reduce both fuel and process related CO2 emissions. M Schneider et al., (2011) observed that the reduction in energy and raw material consumption and also complying with quality, performance and cost requirement is quite a challenge. The innovative use of industrial residue like fly-ash and GGBS in the production of cement solves both the problems of environmental crisis and the waste disposal. Nurdeen M Altwair et al., (2010) analysed that the solution to reduce the environmental impact is to use 'Green concrete' which eliminates the negative impact of the cement industry. To make a greener concrete we must replace as much as cement possible by supplementary cementitious material, especially those that are the byproducts of industrial processes such as fly-ash, rice husk ash, silica fumes etc. Chen Li et al., (2011) stated that the CO2 emission consists of emission by raw materials, fuel and electricity. The direct CO2 emissions are 0.8 ton per ton of cement clinker, and the total CO2 emissions are 0.66 tons CO2 per ton of cement. Particularization is the reverse process of generalization. Once a feasible specialized chain is obtained, it is particularized into its corresponding mechanical device in a skeleton drawing.

3. Other Substitutes of Cement

In various studies, many components such as fly ash, GGBS, rice husk ash, bagasse ash, etc. have been used as a substitute for cement in small proportions. In this study, few commonly used supplementary cementitious materials are studied.

3.1 Flyash

During thermal power generation, coal combustion results in a by-product called fly-ash. This product exhibit pozzolanic Properties and has high amounts of silica and this is incorporated as a mineral admixture for cement. Every year around 490 tons of fly-ash is produced all around the world. H Yazici et al., (2005) concluded that the early strength development of fly ash blended concrete is less compared to that of the conventional concrete but the strength over the longer durations are appreciable. The early strength can be improved by adopting steam curing and this can be an advantage to the precast industries. The setting time of high-volume fly-ash concrete is somewhat prolonged which can be countered using suitable admixtures. Karina E Seto et al., (2017) proved that the results of life cycle analysis on concrete with fly ash show that the increasing percentages of fly ash have lower environmental impacts. Increased replacement of cement by fly ash can help reduce emissions and waste in the manufacturing stage of cement production. Y L Wong et al., (1999) stated the Replacement of cement by fly-ash improves the mortar aggregate interfacial bond strength and fracture toughness over the long period but the early interfacial bond strength can be underperforming compared to the conventional mortar. Fly ash mainly contributes towards the interfacial properties mainly due to the pozzolanic effect. Strengthening of the interface leads to higher long-term strength and excellent durability than conventional concrete. Tarun R Naik et al., (1997) analysed that the inclusion of fly ash in concrete reduces the setting times of concrete. The amount of delay can vary with the source of fly ash. At about 60% a reverse trend was noted, like the rapid set of the mass. At high volume cement replacements above 70% use of gypsum or other retarding admixtures can keep the concrete workable up to the placing period.

3.2 GGBS-Ground Granulated Blast Furnace Slag

GGBS is present in the construction industry for quite a long time. It exhibits pozzolanic property and is used as a mineral admixture to concrete. The use of pozzolanic materials like GGBS is well accepted in the industry. Oner et al., (2007) stated that the inclusion of GGBS increases the workability of the concrete mix. The pozzolanic reaction is slow and the formation of calcium hydroxide requires time. Hence, the early strength of GGBS concrete is lower than that of the conventional concrete with the same binder content. The optimum replacement of cement by GGBS is about 55-59% by volume of the binder. J M Khatib et al., (2005) proved that the incorporation of up to 60% of GGBS to partially replace Portland cement in concrete causes an increase in the long-term compressive strength but the early strength decreases. Addition of metakaolin in low proportions can compensate for the loss of early strength. J M Gao et al., (2005) experimentally proved that the GGBS significantly decreases the content of calcium hydroxide crystals in the aggregate mortar interaction zone which can be determined by XRD and SEM analysis. It reduces the mean size of the calcium hydroxide crystals and then making the interaction zone denser and stronger. Due to the effect of the above-mentioned densification, it becomes possible for concrete with an optimum amount of GGBS to develop higher strengths. D Suresh et al., (2015) analyzed that GGBS blended concrete is more resistant to attack in aggressive environment because of its dense and strong microstructure of interfacial transition zone. The lower percentage of composition of aluminates and portlandite in GGBS than OPC probably contributes to the resistance. Rafar Siddique, (2014) observed that the GGBS blended concrete being resistant to attack in aggressive environments reduces the corrosion rate of rebar in the concrete. Also, the sulphate resistance of the concrete increases as the permeability of the concrete increases due to the densification of the interfacial transition zone.

4. Ferrock

Ferrock is a carbon negative and thus an eco-friendlier product. It acts as a waste management tool, where in the waste is being best utilized. The raw materials of ferrock are iron powder, fly ash, metakaolin, limestone, oxalic acid (Das, Hendrix, Stone, & Neithalath, 2015; Das, Souliman, Stone, & Neithalath ,2014; Das, Stone, Convey, & Neithalath,2014; Widera, & Stone, 2016). These raw materials are varying in proportions to get the best use of it in terms of strengths. The major proportion in the ferrock is of the iron powder. Other components of ferrock are considered based on the comparison with that of cement as this product is a replacement to cement, and also keeping in view the compatibility with other materials for construction. The strength gaining mechanism of ferrock is by consumption of carbon dioxide which react with the iron and forms the iron carbonate that adheres strongly to the substrate. With reference to the paper of Sumanta Das et al., (2015) and Vijayan D S et al., (2019) the net reaction can be given as:

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2\uparrow \qquad (1)$$

Here water is used just for transferring and mixing of the raw materials unlike cement that uses it during its strength gaining process, the curing process.

4.1 Raw Materials

Ferrock is a binding material which was mainly introduced as the cement replacement. Thus, in order to obtain the binding property for the product, materials similar to cement were used and trails were done in order to obtain the same. Thus, considering the minor ingredients such as metakaolin, fly ash, limestone, oxalic acid was used along with the major ingredient iron powder, ferrock was manufactured.

4.1.1. Iron powder

Major constituent of ferrock is the iron powder which is obtained from the wastes of steel industries and mines which in-turn does a waste management and it doesn't sum up on to the carbon dioxide content in the atmosphere during its manufacturing process. The iron powder being used is ferrock is taken from the heaps of bag house dust waste of the shot blasting operations of steel and also electric arc furnace manufacturing process of steel. This component is not economically viable to recycle and get the iron content from it thus it has been a landfill at great costs in the world. Sumanta Das et al., (2014) have used the metallic iron powder of median size 19 microns which is a waste from structural steel fabrication that has been a burden in dumping it and in turn consuming lot of space. It consists of 88% Fe, 10% O and traces of Cu, Mn, Ca, etc… Iron powder is examined and stated that they are elongated and angular in shape. However, the large surface area helping it to provide greater reactivity. Sumanta Das et al., (2014) mentions about the class F fly ash being used in ferrock as the silica source for reactions, while the fine limestone powder provides nucleation sites and metakaolin imparting cohesiveness to the paste because of its clayey origins. Sumanta Das et al., (2014) have provided the specifications of the iron powder he used in his research work. They stated that the iron powder is elongated and plate like particle of median size 19 microns helping in better reactivity because of its larger surface area. It is obtained from shot blasting, consisting of 88% Fe and 10% O along with small amounts of Cu, Mn and Ca. Sumanta Das et al., (2014) used the iron powder from industrial shot blasting operation that are elongated and angular in shape of 19.03 microns, influencing in the rheological properties of fresh mixture and higher reactiveness in turn owing to high surface to volume ratio. Alejandro Lanuza Garcia et al., (2017) have stated that the iron powder used in ferrock is a by-product of shot blasting where the micro particles has become a threat to health while working on it and has ineffectual applicability. It is also obtained in the finishing techniques in the steel manufacturing industry.

4.1.2. Other Raw Materials of Ferrock

Sumanta Das et al., (2014) states that the other ingredients of ferrock include fly ash as a source of silica for formation of iron silicate, limestone powder providing nucleation sites and metakaolin for the cohesiveness in the paste. Sumanta Das et al., (2014) mentions about the class F fly ash being used in ferrock as the silica source for reactions, while the fine limestone powder provides nucleation sites and metakaolin imparting cohesiveness to the paste because of its clayey origins. Barbara Widera et al., (2016) specified that the other material used in ferrock in addition to that of iron powder is the fly ash of class F as silica source in iron silicate formation where its spherical shape enhances the workability, fine limestone powder of 0.7 microns size confirming to ASTM C 568 that is added for creating the nucleation sites and metakaolin confirming to ASTM C 618 is to provide cohesiveness in its mixture's fresh paste.

4.2 Proportioning of Raw Materials

The raw materials are mixed together in proportions to get the maximum usage of it, and to gain considerable strength and desired properties. Thus, tests were conducted with varied proportions of the raw materials. Sumanta Das et al., (2014) carried out work on varied proportions of iron powder, fly ash, metakaolin and limestone. Focusing on the important raw material used for binding, the iron powder is varied from 58 – 69 % along with variations of the other raw materials, weak oxalic acid being kept constant of 2%. The best results among these varied material proportions were seen with 60% iron powder, 20% fly ash, 10% metakaolin, 8% limestone, 2% oxalic acid. Sumanta Das et al., (2014) conducted an experiment on the mix proportioning of ferrock and concluded that the best proportioning of raw materials is the 60% iron powder, 20% fly ash, 10% metakaolin, 8% limestone, and 2% oxalic acid.

Table 2 - Variations in proportioning of raw materials of ferrock [4].

Component materials	% by mass of total powder							
	mixture number							
	1	2	3	4	5	6	7	8
Iron powder	64	60	62	58	69	65	67	63
Fly ash	20	20	20	20	15	15	15	15
Limestone	8	8	10	10	8	8	10	10
Metakaolin	6	10	6	10	6	10	6	10

Sumanta Das et al., (2014) stated about the experimental study on various mix proportions of the raw materials. The results were observed that the mix proportion of 60% iron powder, 20% fly ash, 10% metakaolin, 8% limestone, 2% oxalic acid gave better results than other trials in terms of the desired properties of a binding agent. Alejandro Lanuza Garcia et al., (2015) have tabulated the ferrock mix proportioning of the various raw materials is as shown in Table 3. It shows the percentage by weight of the raw materials to be used to make the component Ferrock. It also shows the specifications of the basic properties for the raw materials of Ferrock.

Table 3 - Summary of raw materials required for ferrock manufacturing (Suresh, 2015).

Material	Percentage (by weight)	Specifications
Iron powder	60%	Waste metallic iron powder with a median particle size of 19.03μm
Fly Ash or Glass	20%	Class F fly ash conforming to ASTM C 618 or ground glass particles
Limestone	10%	Limestone powder (medium particle size of 0.7 μm) conforming to ASTM C 568
Metakaolin	8%	Conforming to ASTM C 618
Weak Oxalic Acid	2%	Oxalic acid has been used as catalyst in previous research

(Mouli Prashanth et al., 2019) have conducted experiments on the mix proportions with 60% iron powder, 20% fly ash, 10% metakaolin, 8% limestone, 2% oxalic acid. But with varied molarity of the oxalic acid from variations of 4 to 12% with increments of 2%. It was experimentally proven that the 10 moles of oxalic acid gave the best results out of all other variations.

Table 4 - Different molarities of oxalic acid considered (Prashanth et al., 2019).

Mix	Ferrock (kg/m^3)	Fine aggregate(kg/m^3)	Oxalic acid (catalyst)	
			Moles	(Kg/m^3)
M1	390	1170	4	42.12
M2	390	1170	6	63.18
M3	390	1170	8	84.24
M4	390	1170	10	105.3
M5	390	1170	12	126.3

4.3 Curing Process

Sumanta Das et al., (2014) conducted the curing process by demoulding immediately after the compaction, later when the samples were kept for carbon dioxide curing in plastic bags with 100% carbon dioxide at room temperature was refilled every 12hrs to maintain saturation for 1 to 4 days. Then the samples were placed in air at room temperature letting the moisture to evaporate from about 1 to 30 days. Sumanta Das et al., (014) carried out a similar experiment as above and to determine the optimal combination of carbon curing duration and air curing durations. They observed that there was no appreciable increase in compressive strength after 4 days of carbon curing and 3 days of air curing. The upper limit of carbonation duration was determined by a thermogravimetric analysis. Variation in carbonation durations were made and experimentally tested starting from one day carbon curing which showed very low mechanical strength. They also conducted experiment with less carbon curing duration and higher air curing duration, however it was observed that air curing was effective only with the increase in carbon curing duration, as the average pore size decreased with increased carbonation duration. And, a significant increase in strength is observed for specimens carbonated for a longer duration and when the air curing time was increased. This is due to the fact that larger pores in initial days of carbonation exert less internal moisture pressure under compression test and thus loss of moisture in air curing after lesser carbonation duration doesn't have a larger effect on internal pressure and in turn on the compressive strength. In increased carbonation duration, pore size is reduced and thus more sensitive to compressive strength and loss of moisture during the air curing. Sumanta Das et al., (2014) conducted the curing process of beams by initially keeping the polythene moulds in the carbon curing and then after the mould is removed the samples ae kept in 100% carbon curing for 5 days with refilling carbon dioxide for every 12 hours and then allowed to air cure for days to let the moisture evaporate. They considered this curing duration to be appropriate beyond which significant changes were not observed.

4.4 Strengths

The basic important characteristic of a concrete block is the compressive strength of it to sustain all the load implied on it. Thus, while supplementing the binding material cement in the normal ordinary Portland cement concrete with the ferrock as a binding material in ferrock blended concrete should be checked with at least its compressive strengths. Sumanta Das et al., (2014) during the experimental studies on ferrock compressive strength and its characteristics has discovered that the samples with mixture 1 and 2 of table 2 gave the highest strengths at curing durations of 3 days carbon curing and 2 days air curing. Vrajesh M Patel et al., (2018) in the year 2018 conducted a combination of cement and ferrock in concrete as a binding material, with supplementing cement by about 20 to 30%. Greater compressive strengths were observed at supplementation of cement by ferrock of 27%. Vijayan D S et al., (2019) conducted experiments on ferrock blended cement concrete at varied replacement by percentages with increment of 4% from 4-12%. It is concluded that 8% substitution gives better results in terms of compression, flexural and split tensile strength.

5. Discussions

The works conducted on ferrock composition gave a clear picture on the complete replacement of cement with ferrock as the binding material. It has been also concluded that the composition of ferrock as 60% iron powder, 20% fly ash, 10% metakaolin, 8% limestone, 2% oxalic acid. Carbon curing duration and air curing duration was finalized to 4 days and 3 days respectively for ferrock blended concrete for better compressive strengths. The experimental works conducted on ferrock are majorly focusing on complete replacement of cement by ferrock with carbon and air curing. Not many Experimental Studies are carried out on the combination of ferrock and cement in concrete. Further studies can be made on the ferrock blended cement concrete with a suitable curing method to both the binding materials which have a different strength gaining mechanism. Experiments can be conducted to determine the optimum percentage of supplementing cement using ferrock with the optimum strengths and desirable properties.

6. Summary

A product named ferrock is a binder material used as a replacement to cement. Ferrock was constituted based on testing with different proportions of the raw materials. The composition of ferrock thus finalized as 60% iron powder, 20% fly ash, 10% metakaolin, 8% limestone, 2% oxalic acid in terms of rheological characteristics. The pore and micro structural properties of the best performing system was considered as the ferrock. The experimental studies on the curing process were conducted and determined by trial-and-error methods based on number of days of curing by carbon dioxide and number of days of air curing. It was suggested that carbon curing of 4 days and air curing of 3 days gives the best result.

Acknowledgement

The authors would like to thanks the NIE and those respective parties who have made this paper possible.

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