Magnesium Oxychloride Cement with partial replacement of fly ash and Magnesium Sulphate

Vignesh R[1], Suresh Babu KP[2], Vengadesh P[3], Sriram S[4], Selvam B[5]

[1234]UG Student, [5]Assistant Professor, Department of Civil Engineering, Sree Sakthi Engineering College, Coimbatore, India

---

Abstract – *Magnesium Oxychloride Cement with addition of fly ash has been evaluated. MOC Fly ash mix material with various composition of fly ash having good workability and attains early strength. MOC Fly ash mix attains 20-68 MPa as compressive strength after the air curing. Concrete sets within 4hrs. Very good aggregate-cement bonding and excellent failure patterns are observed. Fly ash as 20% addition with the MgO gives high strength with comparing other combinations.*

Key Words: MOC Fly ash mix, fly ash, Chemical reaction, Magnesium Sulphate, Compressive strength.

1.INTRODUCTION

Magnesium Oxychloride Cement (MOC, Sorel's cement/ Magnesia cement), discovered by Sorel in 1867. The cement is a mixture of Magnesium Oxide with Standard Solution of Magnesium Chloride. Approximate chemical formula is $Mg_4Cl_2(OH)_6(H_2O)_8$. It can withstand (Jana Jurisova 2015) 69-83 MPa which is substantially more than standard Portland cement concrete. It does not require humid curing. It is a tough, stone like fire proof compound that can be used for light and heavy floorings. Having tremendous load bearing capacity, it can withstand vibrations from heavy cast iron wheel moment without least trace of cracks or fissures. It has low coefficient of thermal expansion and shows negligible volume change during setting. It is relatively light (AK Misra 2007) in weight. In use its generally combined with filler materials such as glass powder, dolomite powder and saw dust. It is used for industrial flooring, grindstones, tiles and artificial stones.

1.1 Chemical Composition

Sorel cement is therefore based of the reaction of components in the system MgO-$MgCl_2$-H_2O. These reaction proceeds at ambient temperature under formation of crystalline phases marked on the base of molar ratio:

$n(Mg(OH)_2) : n(MgCl_2)$ (Sorel 1980)

I.Phase 5 – $Mg_3(OH)_5Cl.4H_2O$
Resp., $5Mg(OH)_2.MgCl_2.8H_2O$ [5.1.8]
Molar ratio = 5:1

II.Phase 3 - $Mg_2(OH)_3Cl.4H_2O$
Resp., $3Mg(OH)_2.MgCl_2.8H_2O$ [3.1.8]
Molar ratio = 3:1

III. $Mg(OH)_2$; $Mg_{10}(OH)_{18}Cl.5H_2O$ are minor, and undesired phases. (Jana Jurisova 2015)

The well crystallized needle-like structure of phase 5 of chemically bonded MOC has been described as scroll-tubular whiskers. The mechanical interlocking and unique fibrous microstructure resulting from the intergrowth of the crystals is a major source for the strength development of MOC cement. Therefore, the physical properties of MOC cement depend largely on the phase's formation and subsequently on the appropriate proportions of the starting materials. (Karthikeyan N 2014)

1.2 Scope of research

MOC cement draws much research interests recently due to the energy saving consideration as it can be used as Portland cement replacement on many occasions. Recent research going on to build a structure by 3D printing using this MOC cement in Mars project. The production of light burnt MgO used in MOC requires a much lower calcinations temperature compared to that for Portland cement, thus reducing vast amount of energy production, fly ash is one of the major industrial by-products and being utilised in the construction industry for decades. By incorporation of fly ash into MOC cement, an energy saving and environmentally friendly construction material can be formed for industrial applications. In addition, water resistance of MOC system is a key issue in the research before MOC related products could be utilised in industry. To that end, the effects of the fly ash on MOC cement including flow property, setting time, strength development, exposure to moisture and workability have been investigated.

2. MATERIALS

2.1 Magnesium Oxide

Magnesium oxide is used in this study was obtained from TANMAG, Salem that was produced by calcination of Magnesium Carbonate. It is produced by clinkering raw magnesite in shaft kiln at a controlled temperature around 600-1000°C by using furnace. Without calcination process, the MgO is not suitable for MOC. Raw material can't be used for Sorel cement paste. Calcinated MgO produced in Class A, B, C, D and its based on the percentage of MgO. Remaining percentages are impurities. The main consideration is particle size of MgO. They produce 200 μm and 300 μm mesh passing. 200 μm mesh passing MgO with 85% purity (B grade) is used for this research.

Table -1: Chemical Composition of Magnesium Oxide

Ingredients	Percentage (%)
Magnesium Oxide (MgO)	84.05
Calcium Oxide (CaO)	2.98
Silica (SiO_2)	8.5
Alumina (Al_2O_3)	0.35
Ferric Oxide (Fe_2O_3)	0.23
Loss on Ignition	3.89

2.2 Magnesium Chloride

Magnesium Chloride is used in this experiment was obtained from Salem Magnesite dealers. $MgCl_2$ is the by product from the agriculture fertilizer (urea) industries. Magnesium Chloride also extracted from the brine or sea water. Magnesium Chloride Hexahydrate flakes ($MgCl_2.6H_2O$) are used in this research. These salts are typical ionic halides, being highly soluble in water. Mixed with Magnesium Oxide, Magnesium Chloride forms hard material called Sorel cement.

Table -2: Chemical Composition of Magnesium Chloride

Ingredients	Percentage (%)
Magnesium Chloride ($MgCl_2$)	97
Sulphate (SO_4)	0.04
Calcium (Ca)	0.01
Lead (Pb)	0.001
Iron (Fe)	0.002
Phosphate (PO_4)	0.004

2.3 Magnesium Sulphate

Magnesium Sulphate commonly known as Epsom salt, is a mineral. Magnesium Sulphate occurs as a colourless crystal. A method of producing magnesium sulphate comprises the steps of interacting ferrous sulphate with compounds including magnesium carbonates, oxides and hydroxides, with magnesium sulphate being produced. Magnesium Sulphate is also available in Salem at low cost. Magnesium Sulphate ($MgSO_4.7H_2O$) is used for this research and partially replaced with the Magnesium Chloride.

Table -3: Chemical composition of Magnesium Sulphate

Ingredients	Percentage (%)
Magnesium Sulphate ($MgSO_4$)	99
Chloride (Cl)	0.02
Sodium (Na)	0.1
Lead (Pb)	0.0005
Iron (Fe)	0.001
Calcium (Ca)	0.01
Arsenic (As)	0.00001

2.4 Fly ash

Fly ash, also known as flue-ash, is one of the residues generated from the combustion and comprises the fine particles that rise with the flue gases. In an industrial context, fly ash usually refers to ash produced during combustion of coal. Fly ash is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys of coal-fired power plants and together with bottom ash removed from the bottom of the furnace is in this jointly known as coal ash.

Two classes of fly ash are defined by ASTM C618: Class F fly ash and Class C fly ash. The chief difference between these classes is the amount of calcium, silica, alumina and iron content in the ash. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned.

The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash. This fly ash pozzolanic in nature, and contains less than 5% lime (CaO). Possessing pozzolanic properties, the glassy silica and alumina of Class F fly ash requires a cementing agent, such as Portland cement, quicklime or hydrated lime with the presence of water in order to react and produce cementitious components. In this research Class F fly ash is obtained from Indian Steel Industry, Coimbatore and is partially replaced of MgO.

Table -4: Chemical Composition of Class F fly ash

ASTM C618 Requirements	
Ingredients	Percentage (%)
$SiO_2+Al_2O_3+Fe_2O_3$	70
SO_3	5
Moisture content	3
Loss on Ignition	6

3. METHODOLOGY

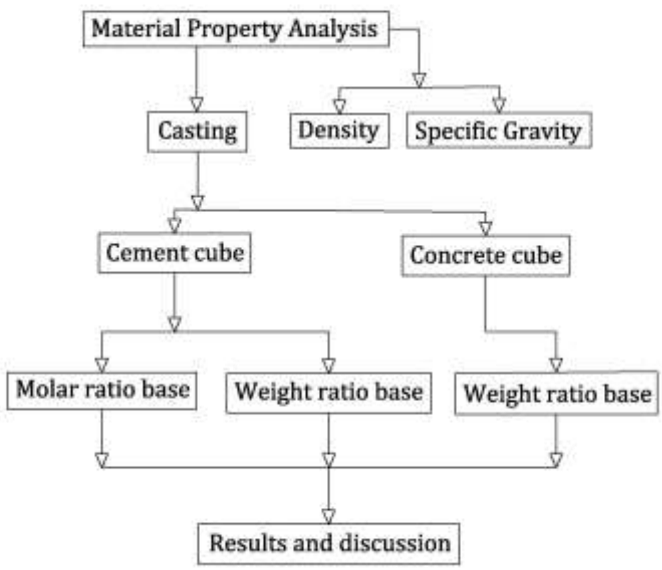

Chart -1: Methodology

4. EXPERIMENTAL

4.1 Tests on material

Various tests have been conducted for Magnesium Oxide, Magnesium Chloride, Magnesium Sulphate, fly ash, fine aggregate and coarse aggregate. The basic parameters were observed for the materials such as specific gravity, density, fineness modulus, sieve analysis (aggregate) and water absorption.

Table -5: Tests on material

Tests/ Materials	Fineness modulus %	Specific Gravity	Density (g/cm^3)	Water absorption%
MgO	80	3.58	3.58	2
$MgCl_2$	Nil	2.32	2.32	Nil
$MgSO_4$	Nil	2.66	2.66	Nil
Fly ash	98	2.33	2.33	0.2
F. Agg.	Nil	2.55	2.55	0.86
C. Agg.	Nil	3.67	3.67	0.5

4.2 Sorel cement preparation using molar ratio

Magnesium Oxychloride Cement is prepared by mixing the Magnesium Oxide with the 30% standard solution of the

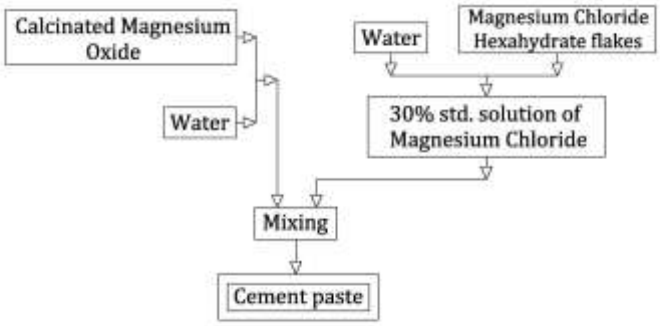

Chart -2: Sorel's cement paste preparation

Magnesium Chloride. Magnesium Chloride solution have to be prepared before mixing. Magnesium Chloride Hexahydrate flakes are mixed with the water by means of 30% of its mass. For example, 30g of $MgCl_2$ is mixed with 70g of water, which becomes 30% standard $MgCl_2$ Solution. The mixing may contain many impurities and undissolved

Sample	M1	M2	M3	M4	M5	M6
n(MgO)/n($MgCl_2$)	9/1	7/2	8/1	6/1	7/1	5.5/1
MgO (g)	400	400	400	400	400	400
$MgCl_2$(g)	96	122	112	144	122	172
30% std. solution(g)	320	410	376	480	410	572
H_2O (g)	110	64	54	74	66	88

Table -6: Samples for molar ratio

$MgCl_2$ flakes, which should be removed. Stir the solution until it become colourless. Pre weighted Magnesium Oxide mixed with some amount of pre measured water. In a pan, Magnesium Chloride solution poured with the Magnesium Oxide with the various combination of each time. Totally 9 no. of 70.6mm x 70.6mm x 70.6mm moulds were prepared for each combination.

4.3 Sorel cement partial replacement of fly ash (weight ratio)

Magnesium Oxychloride Cement is prepared by mixing the

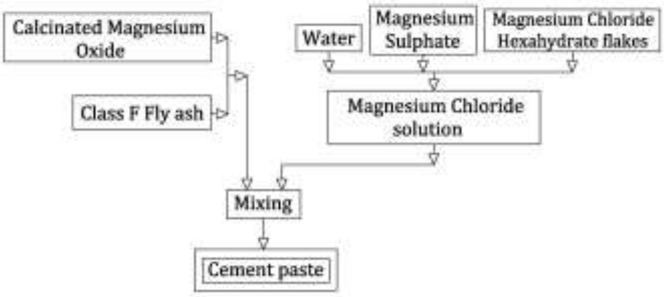

Chart -3: Fly ash mix cement paste preparation

Magnesium Oxide and Magnesium Chloride. In this research Magnesium Chloride solution remains constant for all the samples. High crystalline product of Phase 5 is taken as the origin for the entire sample calculations. Only Magnesium Oxide and fly ash content may vary by their mass. Different

Table -7: Samples for fly ash replacement 1

Samples	F1	F2	F3	F4	F5	F6
MgO(g)	400	360	320	280	240	200
F.A. (g)	0	40	80	120	160	200
$MgCl_2$(g)	180	180	180	180	180	180
$MgSO_4$(g)	20	20	20	20	20	20
H_2O (g)	150	150	150	150	150	150

solutions from original molecular ratio is prepared for better results. So, the water content to the Magnesium Chloride solution varies from the standard 30% standard solution. 10% of the Magnesium Chloride is replaced by the

Table -8 : Samples for fly ash replacement 2

Samples	F7	F8	F9	F10	F11
MgO(g)	160	120	80	40	0
F.A. (g)	240	280	320	360	400
$MgCl_2$(g)	180	180	180	180	180
$MgSO_4$(g)	20	20	20	20	20
H_2O (g)	150	150	150	150	150

Magnesium Sulphate to determine whether it increases durability, water resistance and corrosion resistance of the final product material. First of all, water is measured in measuring jar and Magnesium Sulphate is mixed until it dissolves, that the water become colourless. Hereafter Magnesium Chloride is added with the solution and mixed until all the flakes to be dissolved. After mixing the water, it becomes white colour like milk. Now the solution is directly mixed into the dry Magnesium Oxide with fly ash. The sample should be mixed well using trowel. All the materials should be combined in mixing like honey jell, which becomes paste. Then the paste is poured into the 70.6mm x 70.6mm x70.6mm mould for each combination.

4.4 Concrete cube casting

Magnesium Oxychloride Cement concrete cube casting is done by mixing the aggregated with the pre made cement paste. Fine aggregate passing through a 4.75 mm IS sieve and retaining on a 75μm IS sieve were taken. Coarse aggregates passing through a 20mm IS sieve and retaining on a 4.75 mm IS sieve were taken. Due to insufficient verified calculation data for MOC concreting, there is no any particular mix design for it. So, test results were adopted by replacing the standard OPC 53 grade cement by Fly ash mix cement paste. Mix design for M30 grade concrete is adopted. The weight of cement replaced by the weight of MgO and fly ash. Water is added as per w/c ratio. Due to moderate humid condition w/c ratio taken as 0.45 from IS456:2000. (All the IS standards can't be adopted for the MOC concreting. Its only for sample preparation as reference, not for commercial and private works, still it's been under research. New mix design has to be developed by combining BIS and ACI codes.) Or 75% weight of the $MgCl_2$ can be added as water to the cement paste. For example, 75ml water added to 100g of $MgCl_2$ (not replaced). Then the prepared cement paste is added to the aggregates. The concrete should be mixed well. Due to its quick setting property, the concrete should be moulded within 5-7min. The MOC concrete cubes were moulded in 150mm x 150mm x 150mm moulds with various combination (Fly ash mix) of cement paste. Each combination was moulded in 9 no. of cubes.

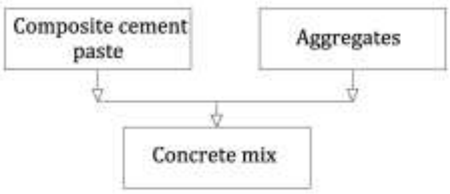

Chart -4: MOC concrete mixing

Table -9: M30 design for OPC 53 grade by MOC Fly ash mix

Samples	C1	C2
MgO (g)	1900	950
Fly ash (g)	0	950
$MgCl_2$ (g)	855	855
$MgSO_4$ (g)	95	95
H_2O (g)	710	710
Fine aggregate (g)	2700	2700
Coarse aggregate (g)	4630	4630

5. RESULTS AND DISCUSSION

5.1 Setting time of MOC cement

Wet mixes were prepared by gauging Magnesium Oxide powder with Magnesium Chloride solution of known concentrations. The standard consistency, initial setting and final setting times were determined as per IS10132-1982 using Vicat apparatus. MOC cube mixing was had high amount of water. It was in liquid form for long time. But MOC Fly ash mix paste has high viscosity. So, started to set in quick time. Without any compaction, Fly ash mix paste settles its place smoothly. The test conducted at the room temperature 27°C. Setting time increase as the water content increases, because MOC is the non-hydraulic cement.

Table -10: Setting time MOC and MOC Fly ash mix

Setting time	Initial setting time	Final setting time
MOC as molar ratio	60 min	160 min
MOC Fly ash mix	20 min	50 min

5.2 Workability of MOC paste and concrete

MOC paste has good workability, because it has no filler materials. But with the filler materials the workability reduces but its negligible. In concrete, 100% MgO has moderate workability, true slump occurred for that. Partially replacement of fly ash makes increase the workability of the concrete. For 50% replacement of fly ash makes 120mm slump value. Water can be added with 10ml rise to increase workability. Concrete will not set until all the water evaporates, unlike standard Portland concrete sets within few minutes including excess addition of water. So MOC Fly ash mix has good workability than the standard Portland cement concrete.

5.3 Compression strength of cubes

5.3.1 Compressive strength for MOC cubes

Magnesium Oxychloride cements as per the molecular ratio was tested by compression testing machine. The results were very poor. Most of the cubes did not carry any load. 9/1 molecular ratio cube attained maximum strength as 8 MPa in

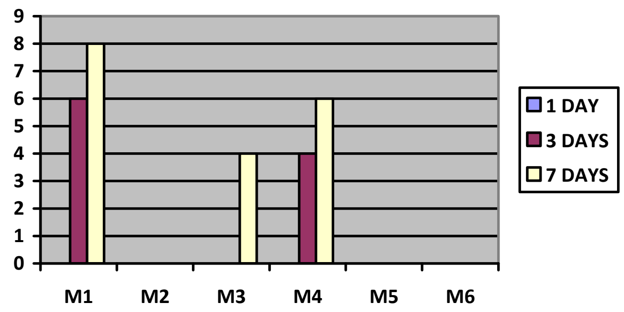

Chart -5: Compressive strength for MOC cubes

7 days air curing. Shrinkage cracks occurs almost every cube. Some of the cubes have huge cracks up to 10mm. The chemical reactions were not completed for entire cubes. Moisture content were remained after 7 days of air curing. Some of the cubes broken in hand pressure. Some of them broken while fitting them in the compression test machine. Failure pattern were very bad. There were many no. of voids into the cube. The voids diameter ranges up to 3mm which is clearly visible to open eyes. The surface of the cube can be scratched by the own finger nails. For water penetration test, the tested cubes were submerged into the water for 1 day. That all cubes were totally dissolved in water and feels like lime. Water absorption is 20%, which is not good. After 15 days, the surface area from 15mm depth, totally suspended like creep.

Table -11: Compressive strength of MOC cubes

Curing days	1st day (MPa)	3rd day (MPa)	7th day (MPa)
M1	0	6	8
M2	0	0	0
M3	0	0	4
M4	0	4	6
M5	0	0	0
M6	0	0	0

5.3.2 Compressive strength for MOC Fly ash mix cubes

Magnesium Oxychloride Cement Fly ash mix were tested using the compression testing machine. Magnesium Oxide partially replaced by the fly ash and Magnesium Chloride partially replaced by the Magnesium Sulphate. So various materials were used except the original Sorel's cement, so it was named Fly ash mix Sorel cement [1]. Very good

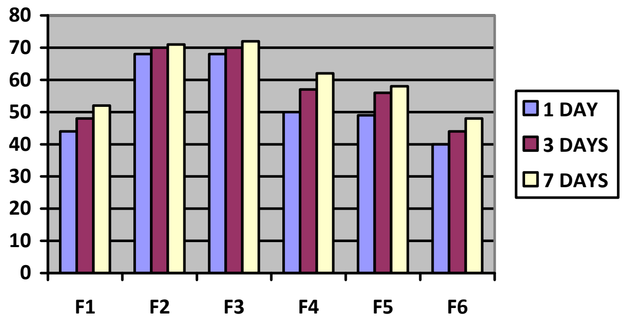

Chart -6: Compressive strength for MOC fly ash mix 1

compression test results were obtained. 20-40% replacement of MgO by fly ash gives best results. Fly ash can be replaced up to 70% of MgO, which is more than standard Portland cement 40%. From the observation the compressive strength gradually increases as the time period increase, as same as the Portland cement. 100% MgO gains low compressive strength that the partial replacement. Because the fineness modulus is not enough for the filling (Jana Jurisova 2015) in the micro structures. Fly ash is the very fine particles, which is up to 40% below 40μm. So, in the Fly ash mix material structure fly ash acts as a filler and bonding agent for the chemical reaction. The failure pattern of the cube is good. It gains very early strength. Very sharp edges were obtained. No cracks and shrinkage are visible. Very good finish like marble surface finish occurred in all the

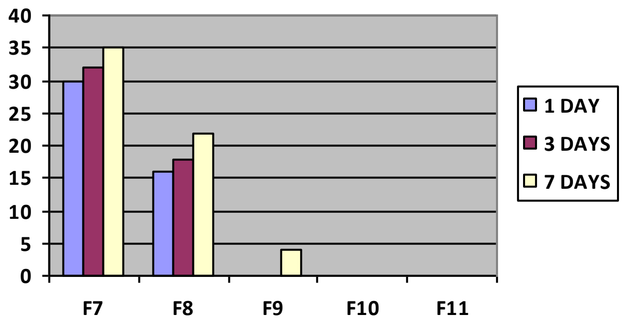

Chart -7: Compressive strength for MOC Fly ash mix 2

faces. Comparing with normal OPC 53 grade cube, MOC Fly ash mix was light in weight. Cube was very tough and very smooth finishes. Water absorption was 2%. Tested cube was submerged into the water for 1 day, it did not absorb any water. It remains same.

Table -12: Compressive strength of MOC Fly ash mix cubes

Curing days	1st day (MPa)	3rd day (MPa)	7th day (MPa)
F1	44	48	52
F2	68	70	71
F3	68	70	72
F4	50	57	62
F5	49	56	58

F6	40	44	48
F7	30	32	35
F8	16	18	22
F9	0	0	4
F10	0	0	0
F11	0	0	0

5.3.3 Compressive strength for MOC Fly ash mix concrete

MOC Fly ash mix cement were prepared and mixed with the aggregates. Mix design were designed for OPC 53 grade cement for M30 mix ratio. OPC 53 grade was replaced by MOC Fly ash mix by its mass. Compression test results gave best results than the OPC 53 grade cement. For M30 design MOC Fly ash mix reaches 35 MPa within 3 days, when OPC 53 grade takes same compressive strength in 28 days of water curing. And also, its strength increases as curing day increases. As same as the MOC Fly ash mix cement cube, MOC concrete also has good face finishing, toughness and marble like finish. Water absorption was 3% which is lower than the normal concrete.

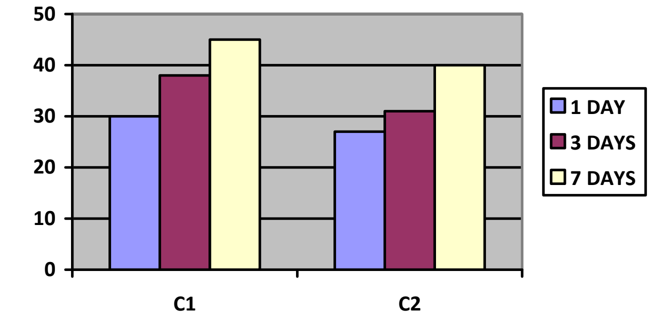

Chart -8: Compressive strength for MOC Concrete

Table -13: Compressive strength of MOC Fly ash mix concrete

Curing days	1st day (MPa)	3rd day (MPa)	7th day (MPa)
C1	30	38	45
C2	27	31	40

6. CONCLUSIONS

MOC, MOC Fly ash mix cement and concrete cube's compressive test results are compared. MOC Fly ash mix having very good workability. Fly ash act as a good replacement for filler material. Water absorption decreased and compressive strength increased. MOC Fly ash mix gives better results in concrete than the Portland cement. Setting time can be increased or decreased by presence water content. Purely air curing reduces water usage. Due to early strength achievement, demolding time can be decreased to 4hr. The corrosion resistance of the steel bar in MOC Fly ash mix concrete has to be investigated and developed in future.

REFERENCES

[1] Jana Jurisova, Pavel Fellner, Ladislav Pach, "Characteristics of Sorel cement prepared from impure material"., Acta Chimica Slovaca, pp. 87-90. 2015.

[2] AK Mishra and Renu Mathur, "Magnesium oxychloride cement concrete"., Indian Academy of Sciences, pp. 239-246. 2007.

[3] Karthikeyan N, Sathiskumar A and Dennis Joseph Raj W,"Effects on stting, strength and water resistence of Sorel cement on mixing fly ash as an additive"., 2014.

[4] Leslie W. Austin, San Jose and Danial Rhodes,"Stabilized Sorel cement and method of making"., 1949.

[5] Ashok Santra, Christopher, Danial, Keith, Dwain King,"Sorel cements and methods of making and using same"., 2010.

[6] Sam A. Walling and John L. Provis,"Magnesia based cements: A journey of 150 years, and cements for the future?"., American chemical society. 2016.

[7] Martin Liska, John Bensed," Magnesium Oxychloride"., Sciencedirect. 2019.

[8] George Swanson,"Magnesium Oxide, Magnesium Choride, and Phosphate-based cements"., 2016.

[9] Ronan M.Dorrepaal and Aoife A. Gowen,"Identification of Magnesium Oxychloride Cement Biomaterial Hetergeneity using Raman Chemical Mapping and NIR Hyperspectural Chemical Imaging"., 2018.

[10] Terry A. Ring and Eric Ping,"Sorel Cement and their Kinetics"., Salt Lake city. 2014.

BIOGRAPHIES

Vignesh R
UG Student,
Dept.of Civil Engineering,
Sree Sakthi Engineering College,
Coimbatore – 641104

Suresh Babu KP
UG Student,
Dept.of Civil Engineering,
Sree Sakthi Engineering College,
Coimbatore – 641104

Sriram S
UG Student,
Dept.of Civil Engineering,
Sree Sakthi Engineering College,
Coimbatore – 641104

Vengadesh P
UG Student,
Dept.of Civil Engineering,
Sree Sakthi Engineering College,
Coimbatore – 641104

Selvam B
Asst. Professor,
Dept.of Civil Engineering,
Sree Sakthi Engineering College,
Coimbatore – 641104