MULTICOMPONENT SULPHUR COMPOSITE USING INORGANIC WASTE FROM PETROCHEMICAL INDUSTRY: SYNTHESIS & CHARACTERIZATION

By
ISHITA RAVAL
(16MCHE08)

DEPARTMENT OF CHEMICAL ENGINEERING
INSTITUTE OF TECHNOLOGY
NIRMA UNIVERSITY
AHMEDABAD-382481
MAY-2018

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ISHITA RAVAL

MAY 2018

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Major Project

Submitted in partial fulfillment of the requirements
For the Degree of

Master of Technology
In
Chemical Engineering
(Environmental Process Design)

By

ISHITA RAVAL

(16MCHE08)

Guided By

Dr. Femina Patel

Dr. Chintansinh D. Chudasama

NIRMA UNIVERSITY
INSTITUTE OF TECHNOLOGY
NAAC ACCREDITED 'A' GRADE

DEPARTMENT OF CHEMICAL ENGINEERING
INSTITUTE OF TECHNOLOGY
NIRMA UNIVERSITY
AHMEDABAD-382481

MAY-2018

1.1.

2.1. Declaration

This is to certify that the thesis comprises my original work towards the degree of Master of technology in Environmental Process Design at Chemical Engineering Department, Institute of Technology, Nirma University and not been submitted elsewhere for a degree. Due acknowledgement has been made in the text to all other material used.

ISHITA RAVAL
(16MCHE08)

3.1.

4.1. Undertaking for the Originality of the Work

ISHITA RAVAL (16MCHE08), gives undertaking that the major project entitled **“MULTICOMPONENT SULPHUR COMPOSITE USING INORGANIC WASTE FROM PETROCHEMICAL INDUSTRY: SYNTHESIS & CHARACTERIZATION”** submitted by me, towards the partial fulfillment of the requirements for the degree of Master of Technology in Chemical Engineering (Environmental Process Design) at Chemical Engineering Department, Institute of Technology, Nirma University, Ahmedabad is the original work Carried out by me and I give assurance that no attempts of plagiarism has been made. I understand, that in the event of my similarity found subsequently with any published work or any dissertation work elsewhere, it will result in severe disciplinary action.

ISHITA RAVAL

Date:

Place: Ahmedabad

Endorsed by

Dr. Chintansinh D, Chudasama
General Manager
Speciality Inorganic Chemicals
R&D Centre, Vadodara Manufacturing Division
Reliance Industries Limited,
Vadodara – 391346 Gujarat

Certificate

This is to certify that the Project Report entitled "MULTICOMPONENT SULPHUR COMPOSITE USING INORGANIC WASTE FROM PETROCHEMICAL INDUSTRY: SYNTHESIS & CHARACTERIZATION**" submitted by** Ms. ISHITA RAVAL (16MCHE08)**, towards the partial fulfillment of the requirements for the award of Degree of Master of Technology in Chemical Engineering (Environmental Process Design) of Nirma University is the record of work carried out by her under my/our supervision and guidance. The work submitted has in my/our opinion reached a level required for being accepted for examination. The results embodied in this major project work to the best of my/our knowledge have not been submitted to any other University or Institution for award of any degree or diploma.**

Project Guide/Guides:

Dr. Chintansinh D. Chudasama
Research Guide
General Manager
Speciality Inorganic Chemicals
R&D Centre, Vadodara Manufacturing Division
Reliance Industries Limited,
Vadodara – 391346 Gujarat

Dr. Femina J. Patel
Research Guide
Associate Professor,
Department of Chemical Engineering
Institute of Technology
Nirma University

Dr. Jayesh Ruparelia
Professor, Head of Department
Chemical Engineering Department
Institute of Technology
Nirma University

Dr. Alka Mahajan
Director,
Institute of Technology
Nirma University

Examiners: **i.** ____________________

ii.____________________

iii. ____________________

iv. ____________________

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Abstract

Chemical industry called as most diversified industrial sectors that performs key steps in converting raw materials into utilizable products like paints, types of plastics for wide range of applications, fertilizers, synthetic rubber etc. Chemical industries provides building blocks for mainly downstream industry like Textiles, Pharmaceutical, Paints, detergents etc., from all these industries, petrochemical industry is major concern because it produces varieties of products that builds huge impact for survival of human life and it is the main source of energy in the world today. As varieties of products produce through petrochemical industry and simultaneously it is also generating waste as well as side products which required additional management for handling. Major petrochemical waste and side products are oil spillage, VOC, refused catalyst and elemental sulfur from desulfurization unit.

Huge quantity of elemental sulfur is generated from desulfurization unit of petrochemical industries and due to strict environmental regulation by government agency, it is necessary to take mandatory action for oil-industry to compulsory reduce the amount of sulfur in their fuel products. Due to this action elemental sulfur generated incrementally in all over the world form petrochemical plants. Numbers of applications have been found for effective use of elemental sulfur like, in fertilizers, sulfuric acid, making of Li-s battery etc. Though presence of all these applications, the consumption rate of sulfur is very lower compared to its generation rate.

Another inorganic waste that is generated in petrochemicals industry from fluidized catalytic cracking unit, where deactivated catalyst consider as a spent, and disposed of because of minor applications have been found for it. Elemental sulfur and spent FCC catalyst both have important characteristics that can be useful in construction material, as construction industry facing different problems related to their potentiality of construction material in accordance to their strength, durability in extreme weather or environmental conditions, other environmental problems related to production of cement, fly ash etc. because it generate greenhouse gases during production of cement, also thermal effects during production of cement concrete like chemicals present in cement can burn the skin of workers etc.

In this study sulfur composites prepared from the sulfur & spent FCC for making usefulness in construction material, property of elemental sulfur can be enhance through modifying elemental sulfur with the help of different organic modifier. Unmodified sulfur fails by repeating cycles of freezing and thawing, humid conditions therefore to get desire property for construction application modified sulfur is used Characterization of modified sulfur prepared form 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene modifier confirmed through XRD and IR. In this study prepared sulfur polymer concrete (SPC) using modified sulfur and spent FCC for further experimental work. Prepared SPC tested against critical environmental conditions like immersing in different concentration of sulfuric acid for acidic environment, sodium hydroxide for alkaline atmosphere and in sodium chloride for saline conditions, the results compared with standard Portland cement concrete by providing same environmental conditions. Durability tested with reference to physical and chemical effects occurred after immersion. From the results through all conditions it can be said that sulfur polymer concrete is more durable, cost-effective and eco-friendly compared to Portland cement concrete.

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CHAPTER -1
INTRODUCTION

Chemical and petrochemical industry plays an important role for economic development of nation. India's Chemical industry is the 6th largest in the world and 3rd largest in Asia (In terms of volume) with size of $108.4 billion [1]. Chemical industry called as most diversified industrial sector, that covering around 70,000 of commercial products Chemical industry provides building blocks for mainly downstream industry like Textiles, Pharmaceutical, Paints, detergents etc. Petrochemical industry plays a significance role in our day to day life [1]. It covers the entire spectrum of daily use items like clothing, construction, automobile, agriculture, electrical & Electronics etc.[1], Petroleum product processing generate enormous amount of waste that can cause environmental threats. Petrochemical plant generate solid waste and sludge from different processes, the waste consider as a hazardous in nature because generated waste consist toxic organics and heavy metals. Sulfur is a byproduct that generate from petroleum, natural gas and other related fossil resources. Sulfur obtained as hydrogen sulfide and as organosulfur compounds. 60 million tons of elemental sulfur produced annually [2].

In the initial stage of purification, petroleum contain undesirable impurities, that is purified through hydrosulfurization process [3],

$$R - S - R + 2H_2 \rightarrow 2RH + H_2S \qquad \ldots (1)$$

Hydrogen sulphide resulting through this process (it can also occurred in natural gas). Resulted hydrogen sulfide is converted into elemental sulfur by the Claus process. It is an oxidation of hydrogen sulfide to sulfur dioxide, and with the equal proportion of hydrogen sulfide and sulfur dioxide will generate elemental sulfur [3]. This recovered elemental sulfur use in a different industrial products like; as a fertilizer, pharmaceuticals, and food preservation etc. because of useful properties of sulfur.

$$3O_2 + 2H_2S \rightarrow 2SO_2 + 2H_2O \qquad \ldots (2)$$

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O \qquad \ldots (3)$$

5.1. Sulfur Chemistry

Sulfur is called as a Le roi du sol (The king of ground). It is 16^{th} most abundant element in nature. Sulfur is vibrant in color, the bright yellow color is little bit mystery to science. None of the theories can explain why crystals of elemental sulfur (atomic crown) radiate with characteristics vibrant glow [4]. One unusual property of sulfur is that its melts a temperature slightly above the boiling point of water. Native of sulfur is commonly found within anhydrite-gypsum deposits. Anhydrite and gypsum are form calcium sulfate. Anhydrite convert to gypsum when it's come in contact with water. Sulfur deposits are not created by geophysical process that is also one unexpected feature of sulfur [4]. German chemist Eilhard Mitscherlich discovered sulfur's allotropy in 1823 [5]. Sulfur derived from molten sulfur is called monoclinic sulfur, when it derived from crystalizing a solution is called rhombic sulfur, both from consist S_8 rings [5].

Sulfate (SO_4^{-2}) and sulfides (S^{-2}) are the minerals form of sulfur (S_8). Sulfides are most important mineral form. It is found in pyrites as iron sulfide, FeS_2 and it can also term as copper sulfide. Spain was a dominant supplier of pyrites in the world. Sulfur dioxide is releases from smelting unit by smelting metal sulfides, like copper nickel and zinc that produce sulfur dioxide which is a source of "Acid Rain". Capturing of sulfur dioxide for production of "metallurgical" sulfuric acid [4].

Sulfur is generate from volcanoes. Popularized form of sulfur is known as "fire and Brimstone". Elemental sulfur is formed from the reaction of sulfur dioxide and hydrogen sulfide in the volcano gases, like "sulfataric". Sulfur is stumble out from hot spring and steam vents. U.S. is the largest producer of sulfur, but sulfur mines was never operated in this country. Canada stands second in the rank, Canadian sulfur largely originates from the purification of gas. Industrial sources of sulfur generation are petroleum, oil sands and coal, where sulfur stands as a component with including complex mixture of other organic compounds [4].

Sulfur is an essential element for all life and always found in the form of organosulfur compounds or metal sulfides [3]. Three amino acids and two vitamins are organosulfur compounds [3]. It is one of the core chemical elements needs for the biochemical functioning and is an elemental macronutrients for all organisms [3]. Life on Earth may have been possible because of sulfur. Conditions in the early seas were such that simple chemical reactions could have generated the range of amino acids that are the building blocks of life [3]. The crystallography of sulfur is complex. Depending on the specific conditions, sulfur allotropes form several distinct crystal structures [3].

Natural source of sulfur is oil sand, oil sands are a geological formation of a mixture of sand, water, clay and bitumen (it is a tar like thick heavy oil, with sulfur content of around 4.8%) [4].

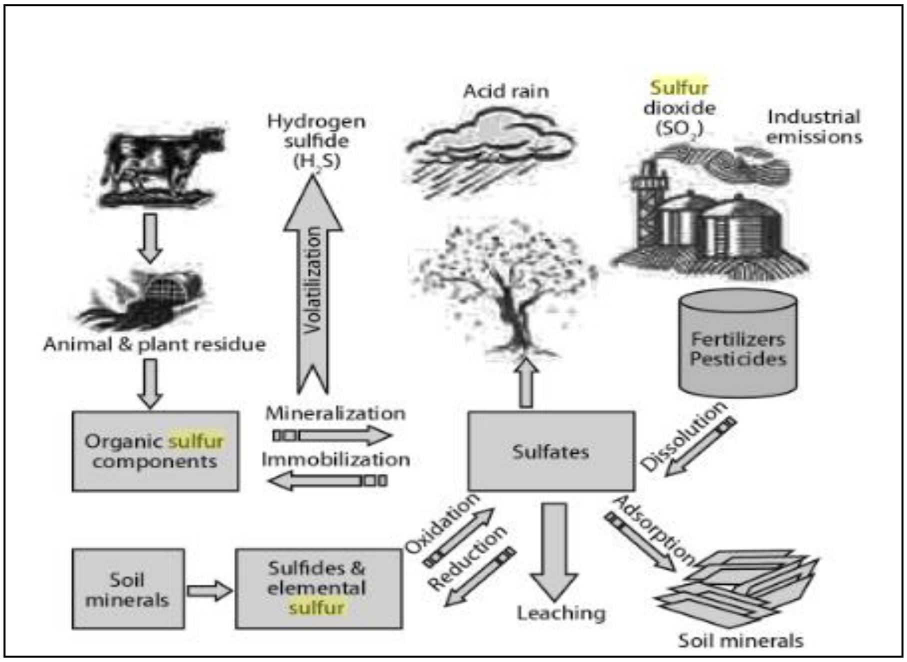


Figure 1 The global sulfur cycle

1.1.1. **Allotropes of sulfur**

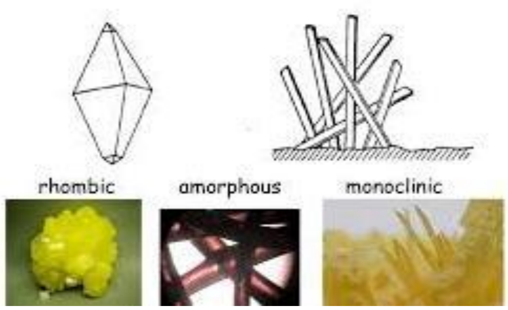


Figure 2 Allotropes of sulfur

(1) Rhombic sulfur, S_8 (room to 96^{o}C)

(2) Monoclinic sulfur, S_8 (stable between 96-119^{o}C)

(3) Plastic sulfur, long polymeric chains.

Rhombic sulfur (S_α) is a stable solid comprised of cyclic S_8 molecules. At 95.5 °C, rhombic sulfur becomes monoclinic sulfur (S_β) [8]. The crystal structure found in monoclinic sulfur differs from that of rhombic sulfur. Amorphous sulfur an elastic variety of sulfur of a resinous appearance, obtained by pouring melted sulfur into water [7].

1.1.2 **Chemical property of sulfur**

Table 1 Chemical property of Elemental sulfur

Boiling Point	444.667 °C		
Melting Point	112.8 °C		
Formula	S_8		
Atomic Number	16		
Periodic Table Classification	Non-metal		
Physical State	Yellow Crystalline solid (at room temperature)		
Auto Ignition Temperature	Dust Clouds	Dust Layers	Liquid Sulfur
	190 °C	221 °C	248°-261 °C
Flash Point	168°-188°C		
Vapor Pressure	< 0.0001 mm, Hg at 20°C		
LEL of Dust in air	35 g/m^3		
UEL	1400 g/m^3		
Solubility	Insoluble in water		
Specific Gravity	1.92-2.07 (depending on its crystalline form)		
Corrosivity	Dry		
Reactivity	Burns to form sulfur dioxide. May form explosive mixture with powerful oxidizing chemical such as chlorates nitrates		

Toxicity	Non-Toxic (can form very toxic compounds such as H_2S, ethyl mercaptant)
Odor	Odorless, but makes very odorous compounds

1.1.3. **Applications of Sulfur**

- Sulfur is also used in batteries, detergents, fungicides, manufacture of fertilizers, gun power, matches and fireworks. Other applications are making corrosion-resistant concrete which has great strength and is forts resistant, for solvents and in a host of other products of the chemical and pharmaceutical industries [3].

- The major derivative of sulfur is sulfuric acid (H_2SO_4), one of the most important elements used as an industrial raw material [3].

- Sulfur is used in the vulcanization of black rubber, as a fungicide and in black gunpowder. Sulfites are used to bleach paper and as preservatives for many foodstuffs. Many surfactants and detergents are sulfate derivatives. Calcium sulfate (gypsum) is mined on the scale of 100 million tons each year for use in cement and plaster [3].

1.1.4. **Sulfur Waste- crucial problem for Refineries**

Sulfur found in abundant quantity in petroleum refineries [8], because of environmental harm of sulfur to human health and ecological system [10].

	2009	2010	2015
U.S.A	7,630	7,875	9,400
Europe	3,359	3,230	4,230
West Asia	1,955	1,975	2,905
Asia	7,903	7,600	9,020
-China	1,300	1,540	2,300
-India	1,450	1,600	2,000
Others	2,837	3,110	4,070
Total	22,674	23,790	29,625

Figure 3 Oil-Recovered Sulfur Production (1000 tons)

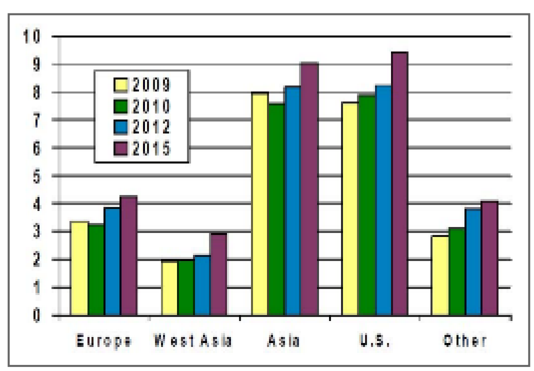


Figure 4 Oil-Refinery Recovered Sulfur (Million tons)

Sulfur release from gasoline and diesel as SO_2 gas. Stringent environmental regulation adopted for petroleum refinery to reduce sulfur amount in their petroleum products. Sulfur from fuel can be reducing through desulfurization process, and this process adopted all over world so abundant amount of sulfur can be obtained from the petroleum refinery [10]. Around 57 million tons of sulfur obtained from petroleum refinery that is 10-20% larger than the worldwide demand [10]. Because of that oversupply of sulfur dramatically reduce demand, and also critical problem arise due to shortage of storage spaces for sulfur waste in petroleum refinery.

1.2. **Spent Fluidized Catalytic Cracking Catalyst**

In petroleum refinery operations, for improvement of process efficiency solid catalysts are largely used [12]. The catalyst material contain metals, metal oxides, metal sulfides etc., that helpful in refinery to produce full range of clean transportation fuels with specification by hydrocarbons transformation [12]. Catalyst are highly used in the conversion of heavy oils and residues to more valuable light and middle distillate and feedstock in petrochemicals [12].

The catalyst used in these refining processes deactivate after some repetitive cycles [13]. When activity of the catalyst declines below the acceptable level, it is targeted to regenerate and reuse. But this regeneration task is not always possible, after few cycle of regeneration, the activity decreases at very low level, so regeneration could not be acceptable to economic point of view and spent catalysts are discarded as solid waste [13].

In most refinery, major portion of spent catalyst wastes come from the hydroprocessing unit, because large portion of catalysts use for hydrotreating processes for purification and upgrading of various petroleum streams and residues [13].

Reason for higher volume of spent catalyst through hydroprocessing unit are: (1) a rapid growth in distillates hydrotreating capacity to meet the increasing demand for ultra-low sulfur transportation fuels. (2) Reduced cycle times due to higher severity operation in diesel hydrotreating units. (3) A steady increase in the processing of heavier feedstock containing higher sulfur and metal contents to distillates by hydrogen addition technology. [13]

In Fluidized catalytic cracking (FCC) process Zeolite use as a catalyst, which has superior activity, gasoline selectivity and stability characteristics compared to original amorphous silica alumina catalyst [14]

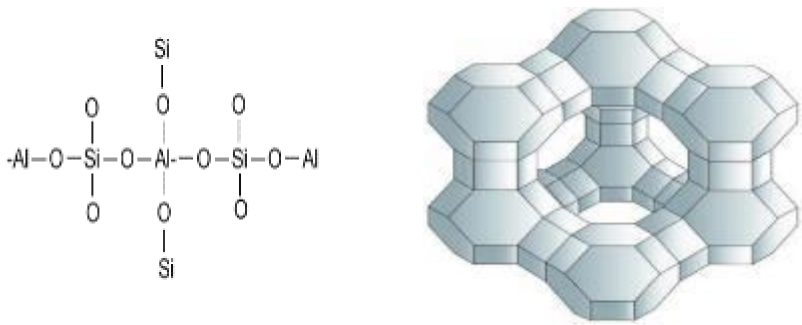


Figure 4 structure of Catalyst

FCC catalyst is porous spray dried micro-spherical powder with particle size distribution of 20-200 micron & particle density~144 kg/m3 [14]

1.2.1. **Uses of Spent FCC**

- Use in an ion-exchange beds in domestic and commercial water purification, softening, and other applications [5].
- Zeolites are also widely used as catalysts and sorbents. Their well-defined pore structure and adjustable acidity make them highly active in a large variety of reactions [5].
- Zeolites have the potential of providing precise and specific separation of gases, including the removal of H_2O, CO_2 and SO_2 from low-grade natural gas streams. Other separations include noble gases, N_2, O_2, Freon and formaldehyde [5].
- Synthetic zeolite used as catalysts in the petrochemical industry, for instance in fluid catalytic cracking and hydro cracking [5].
- Spent FCC is one type of solid waste that is generated due to deactivation of catalytical activity of the catalyst [5].

1.3 **History of Construction materials/industries**

Construction is the process of constructing building or infrastructure. Construction industry comprises six to nine percent of the gross domestic product of developed countries [16]. Construction industry mainly divided into three parts, (i) construction of buildings (ii) Road, highway and other "infrastructure" construction (iii) specialty trades [**Error! Reference source not found.**]. Construction work cannot fulfill without use of concrete that gives the strength of any construction material. Use of concrete for construction documented to be thousands year old. Concrete like material used to be since 6500 B.C. by Nabataea traders or Bedouins, they discovered the importance of hydraulic lime which have self-cementing property. Ancient Egyptian re-discovered by adding volcanic ash in mix so concrete can stay stable in underwater work. Roman architectural revolution called as a key event in history [18]. Roman concrete made from quicklime, pozzolana and pumice (aggregate). It was a revolutionary design in terms of both structural complexity and dimensions [18].

In that era, concrete showed good performance in compressive strength but poor resistance toward tensile strength, due to absence of reinforcement. In 1759, British engineer John Smeaton developed a concrete made with hydraulic lime (with pebbles and powder brick as an aggregate)[18]. As in 1824, Joseph Aspdin invent Portland cement [18]. The cement concrete develop with use of Portland cement. Reinforcement in concrete was pioneered by Joseph Monier in 1849. [18] In 1889, first Reinforcement Bridge was built and in 1936, first large concrete dams were built (Hoover dam and Grand Coulee dam) [18]. Concrete became more sophisticated with numerous application in each and every construction work.

1.3.1. Modern Concrete

Concrete consist of a cement (mainly Portland cement) as a binder, and aggregate. Two types of aggregates basically use coarse aggregate (gravel, lime stone or granite) and fine aggregate such as sand. These all contribute most for higher compressive strength. Reinforcement with steel bar will important for gaining higher tensile strength. There are chemical admixtures use for gaining varied properties, like accelerate or slow down the hardness rate of concrete, to increase tensile strength or for entrainment of air and water resistance.

There are certain mineral admixtures (inorganic material like fly ash, blast furnace slags etc.) became popular nowadays. Research is going on to improve the property of concrete or to improve the efficiency and durability of concrete. Different types of concrete developed by researchers, like

1. <u>Pervious concrete</u>: it is a special type of concrete contains continuous interconnected voids. It is made up of specially graded coarse aggregate with no-fine aggregate [29]. It use as a concrete material in 1852, for the first time and patented in 1980 [27,28]. Important properties of pervious concrete are high porosity, noise absorption capability and resistance towards heat sock [28].

2. <u>NanoConcrete</u>: this type of material created by high energy mixing (HEM) of cement, sand and water. This process provides dissipation of energy and increase shear stresses on the surface of cement particles. Example of NanoConcrete is nano-SiO_2 (NS) that is most interesting topic of research nowadays. NS has been introduced recently in an advanced pozzolana for improving the microstructure and stability of cement-based systems [30].

3. <u>Microbial concrete</u>: Researchers invent concrete made with some bacterial colony, to improve compressive strength and for improve resistance towards corrosion. Bacteria such as Bacillus pasteurii, Bacillus pseudofirmus, Bacillus cohnii, Sporosarcina pasteuri, and Arthrobacter crystallopoietes increase the compression strength of concrete through their biomass. And Bacillus sp. CT-5 can reduce corrosion of reinforcement in reinforced concrete by up to four times [23]. It is a novel strategy to restore or remediate concrete structure by bio mineralization of calcium carbonate using microbes such as Bacillus species [31].

4. <u>Polymer concrete:</u> it have been used as a quick repairing of structural materials [32]. This type of concrete prepared by mixing a polymeric resin with aggregate mixtures [33]. Types of resin used are polyester resin, epoxy resin, furan resin, polyurethane resin, and urea formaldehyde resin [34]. Advantages of use of polymer concrete is that, it has significant compressive, flexural and tensile strengths without reinforcement, fast curing, low permeability, and improved protection against corrosion and it is impervious to water [32].

1.3.2. Types of concrete degradations:

Degradation of concrete occurs through aggregate expansion, fire, sea water effects, bacterial corrosion, physical damage and chemical damages due to carbonation chlorides, sulfates and distilled water.

1.3.2.1. Acid Attack on concrete

Cement concrete made up from cement and aggregates. Cement content lime $Ca(OH)_2$ in a higher concentration [19]. During sulfur attack sulfate ions attack on concrete directly [19]. They react with the calcium present in the cement to form gypsum and react with calcium aluminium hydrate to form ettringite [19]. That produce product cause major increase in the volume of the cement and thereby leads to cracking and damaging the structure. (Volume increase rate is 124% by gypsum and 227% by ettringite) [19].

$$2H_2O + Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4.2H_2O \quad \ldots (3)$$

$$Ca(OH)_2 + 2H_2S \rightarrow Ca(HS)_2 + 2H_2O \quad \ldots (4)$$

Acid attack also cause through bacterial action, Cement concrete construction use in a sewer pipeline, where an H_2S is present in a humid conditions [19]. Aerobic bacteria through atmosphere will oxidize H_2S in H_2SO_4, which form Biogenic Sulfuric acid (BSA). [19] It create a thick layer consist of gypsum ($CaSO_4$ of various hydration state) & moisture [19]. Acid formation will increase with increase in a thickness of layer. Formation of "ETTRINGITE" occurs that is expensive and causes internal cracking pitting in concrete [19]. It provides a larger surface area for a chemical reaction, and also provide further site to penetration of the acid in to the concrete [19]. These conversion of the concrete to gypsum & Ettringite weakens the structural integrity of the concrete [19].

1.3.2.2. Biodeterioration

Concrete structure also face Biodeterioration that caused by organisms which are grows in environments that offers favorable conditions like proper accessibility of water, low pH [20].

Relative humidity between 60% and 98%, , long cycles of humidification and drying, freezing and defrosting, high CO_2 concentrations, high chloride ions or salts or high amount of sulfates and small amounts of acids these all are the major factors for biodeterioration. [20].

It has been found that biodeterioration-associated structural problems squeeze billions of dollars in a year for infrastructure aliment and repair [20].

Figure 5 Acid attack on concrete

Figure 6 Bacterial attack on concrete

1.3.3. Environmental and health effect by construction activity

Each year three tons of concrete are consumed by per person so it's become most widely used man made material. India stands second in the cement production in world after china [3]. Total installed capacity of cement production in 2010 was 200.7 Million metric ton. 7% of total emission of CO_2 through cement production [22]. Limestone's uses during Portland cement production require heating about 1400^0 C for hours that need large amounts of fossil fuels consumed to provide energy to kiln for heating [21]. These all processes generates about 1 ton of CO_2 per each ton of cement and contribute to 5% of global anthropogenic generation of CO_2 [21].

1.3.4. Application of industrial by-product for construction work

Industrial by product can become a source for construction material, studied from last decade numerous by-products of industries become useful for construction work. Here summarized some specific industrial by-products that have been applicable for construction work [23].

1.3.4.1. Fly Ash

Fly ash is an industrial waste generated from the thermal power plants [23]. Over the years the fly ash produced were lying in the yard without any usage. Early strength developed through use of fly ash, and it also affect to durability of concrete because the high specific surface of nanomaterial usually poses higher water retention capacities and affects workability [35, 36].

1.3.4.2. Red mud

Red mud generated out of Bayer's process for alumina production from Bauxite is a high volume solid waste [23], coarse fraction (>75 mm) of red mud used as an alternate construction material [37]. Also recently red mud used in light weight concrete [38] and as a pozzolanic material for replacement of fly as in self compacting concrete [39].

1.3.4.3. Copper slag

Copper slag is a byproduct obtained during the smelting and refining of copper. It is brought from the sterlite industries. Utilization of copper slag in application such as Portland cement substitution and as aggregates has advantages of eliminating the costs of dumping and minimizing the air pollution [23]. Some important properties of copper slag suggested by researchers are that high presence of iron oxides in copper slag can be beneficial to remove heat of hydration, shrinkage, absorption and permeability and improve sulfate resistivity in concrete [40]

1.3.4.4. Silica fumes

Silica fumes are the waste generated from the production of silicon and ferrosilicon alloys. It has wider application in the construction industries due to its pozzolanic properties [9]. Silica fumes used as a supplementary cementitious materials that help to upgrade strength, durability, economic aspect (waste utilization) of ordinary cement [41]. The durability of concrete with SCM was improved due to the pozzolanic reaction which occurs during the process of hydration in cement [41].

The industrial wastes (fly ash, red mud, and copper slag and silica fumes) have already been tried in the application of cement production and partial replacement of construction materials in civil engineering field. But it doesn`t have the large scale use of wastes anywhere in the industries except fly ash because of durability, strength gaining time and hazardous or less economical [23].

1.4. Sulfur in construction industry

Application of sulfur in construction industries have been found from early 20th century [24]. At that time sulfur treated materials were utilized for manufacturing of tanks or vents in handling leach or pickling solutions, in pipes or tiles where to deal with acidic solutions specifically in industrial plant, and sewage supply pipes, in a flooring material and patch material for concrete floors and walls in industrial area. [24].

Stringent environmental regulations have been adopted for petroleum refinery, because sulfur release from gasoline and diesel as SO_2 gas that affect to the human health and ecological system [1]. As per regulation, refinery starts to adopt the desulfurization process through which sulfur can be recovered and it is solidified as elemental sulfur and stored. This recovered sulfur use in a different industrial products like; as a fertilizer, pharmaceuticals, food preservation etc., [10] but recovery of sulfur is higher than the demand. Around 57 million tons of sulfur have been recovered through desulfurization process in petrochemicals industries that is 10-20% larger than demand for different applications [1].

Sulfur carries number of interesting properties like high electrochemical capacities, high relative indices [24] corrosion resistance, thermoplastic characteristics, high compressive strength and antifungal properties [24]. These all excellent properties made it candidate for possible use as a construction material in the chemical industry.

1.4.1. Thermoplastic characteristics

A thermoplastic; is a plastic material (Polymer) that became polymer above specific temperature and solidifies upon cooling [10]. Due to this characteristics, molten thermoplastic sulfur binds aggregates and fillers together and forms hardened concrete within a very short time period [10]. Sulfur mortar have high flexural and tensile strength because of their thermoplastic properties. Sulfur can be mixed easily with aggregates or fillers at high temperature, and they can be bound in hardened sulfur concrete at room temperature [25].

1.4.2. Corrosion Resistance

Sulfur composites have very low total porosity, sulfur concrete contains no water in mixing process [21]. The pores of the sulfur concrete are not connected so that this concrete became impermeable for gases and aggressive species which cannot be enter in concrete to cause steel corrosion [21].

1.4.3. Compressive strength

Compressive strength is the capacity of a material or structure to withstand loads tending to reduce size [24]. Sulfur Concrete can achieve very high compressive strength by addition of modifier. For strength development, Portland cement concrete take 28 day, while sulfur concrete with some amount of modifier the strength can be developed within a short period of time(give time). The fast curing of modified cement concrete can contribute to shortening the construction period [24].

1.4.4. Antifungal Properties

Elemental sulfur is one of the oldest fungicides and pesticides. Elemental sulfur powder is used as an "organic" (i.e. "green") insecticide against ticks and mites [3]. Small amounts of sulfur dioxide gas addition (or equivalent potassium metabisulfite addition) for fermentation of wine to produce traces of sulfurous acid (produced when SO_2 reacts with water) and its sulphite salts in the mixture, has been called "the most powerful tool in winemaking." [21]

1.5 Outline and scope of Study

- ✓ In this study sulfur composite prepared with a sulfur as a binder and spent FCC use as an aggregate. Study was conducted for finalizing spent FCC as an aggregate by comparing compressive strength of prepared sulfur composites with different materials like normal clay, spent adsorbent 4Azeolite and Fly ash. From these experiments spent FCC gain higher strength compare to others aggregates used. Composition of sulfur and spent FCC optimize with reference to same experiments.
- ✓ Sulfur composited prepared with unmodified (elemental) sulfur, the issue regarding durability of products had occurs because sulfur binder became highly stressed and fails during thermal and freezing thawing cycles because of at room temperature elemental sulfur stay as a orthorhombic form which is more denser than monoclinic form that affects its gaining of strength. So through modification, prepared modified sulfur became highly durable and stay as monoclinic phase at ambient temperature.

- ✓ Further study was carried out through preparing sulfur polymer concrete with elemental sulfur and spent FCC with optimized amount of modified sulfur.
- ✓ Characterization of prepared modifier conducted through x-ray diffraction for identified effect of crystallinity and FT-IR to identify the functional group of modifier combine with elemental sulfur.
- ✓ Resistivity experiments was carried out by making cubical specimens of size 30×30×30 mm compared with cubical specimens of Portland cement concrete specimens of equal size. Comparison of both the specimens through testing their physical and chemical resistivity in critical environmental situations.
- ✓ Resistivity in acidic medium identify through specimens immersed in sulfuric acid solution of different concentration like, 98%, 50% and 10% concentration.
- ✓ Alkaline resistance experiments carried out by taking sodium hydroxide solution of 40%, 20% and 5% Concentration.
- ✓ Saline water resistivity experiments carried out by taking solution of sodium chloride of 1, 3, 3.2 and 5 % solutions.
- ✓ Resistivity in normal conditions by providing De-ionized water medium. Specimens immersed with 7 days of period at ambient temperature.
- ✓ Physical resistivity effect was identified by mass changes and compressive strength changes of specimens before & after experiment. Chemical resistivity checked through elemental analysis by Inductive coupled plasma optical emission spectroscopy (ICP-OES).
- ✓ Comparison of all experiments was carried out with Portland cement specimen with same experimental conditions and concluded in this report.

CHAPTER-2 LITERATURE SURVEY

Sr. no.	Title	Author Name	Publication	Facts	conclusion
1.	Sulfur based hazardous waste solidification	Abdel-Mohsen O. Mohamed Maisa El Gamal	Environ Geol (2007) (Springer)	Unmodified sulfur concrete failed when passes through repeated cycle of freezing and thawing, humid conditions or immersion in water. When concrete is made from unmodified sulfur. During cooling cycle at 114°c, sulfur start to crystalizes as monoclinic sulfur (S_β) with volume decrease of 7%. On further cooling approx. at 96°c, the S_β begins to transfer to orthorhombic sulfur. The main advantages of sulfur polymer concrete is its use as a highly durable replacement for construction materials. Fast setting time and rapid gain of high strength and it can achieve most of its mechanical strength in less than one day. The presence of modified sulfur has two main effects different from the unmodified one: the homogeneity higher, which prevents the growth of big crystals and porosity is lower. Method for preparation of modified sulfur:- 2.5% of modifier and 97.5% of elemental sulfur mixed and mechanically stirred at 140°c. The temperature was maintained at about 135-140°c for 45-60 min. After the reaction the cooling rate is applied of 8-10°c/min. Method for preparation of sulfur polymer concrete:- The aggregates (Sand and Silica) were heated at 170°c for 2 h. The specified amount of sulfur was melted in a heated mixing bowl with temperature controlled at 132-141°c. The aggregates then transferred to the heated mixing bowl and properly mixed with the molten sulfur until a	In this paper the researcher evaluate a number of sulfur polymer modifiers and physical stabilizing agents, design a set of experiments and evaluate the hydro-mechanical properties.

2.	The use of elemental sulfur as an alternative feedstock for polymeric materials	Woo jin Chung, Jared j. Griebel Eui Tae Kim	Nature chemistry	homogeneous mixture can be obtained. More than 60 million tons of elemental sulfur are produced annually. In that major fraction contribute through the byproducts of the hydrodesulphurization process used to reduce sulfur dioxide emission from the combustion of fossil fuels in petroleum refining. Elemental sulfur exists primarily in the form of an eight-membered ring (S_8) that melts in to clear yellow liquid phase at 120-124° C. Rings with 8-35 sulfur atoms are formed and further heating of the liquid sulfur phases above 159° C (floor temperature) results in equilibrium ring opening polymerization (ROP) of the S_8 monomer into a linear polysulfane with diradical chain ends, which subsequently polymerize into polymeric sulfur of high molecular weight. This diradical form of polymeric sulfur a deep red color and depolymerize back to the monomeric ring forms. Stabilization of the diradical polymeric sulfur form of this material can be achieved by quenching of the radical chain ends via copolymerization with dienes, such as dicyclopentadiene, that chemically stabilize the polymer (still afford a brittle crystalline material).	In this article, the researcher use inverse vulcanization process to prepare modified sulfur polymer concrete from elemental sulfur and vinyl monomer. They prepared novel sulfur polymeric material for the application in the electrochemical active materials for battery applications.
3	Hydro-mechanical behavior of a newly developed sulfur polymer concrete	Abdel-Mohsen O.Mohamed Maisa El Gamal	Elsevier Cement & Concrete Composites	Concrete materials are corrode and disintegrate, due to the reaction of the transporting fluid with the hydraulic cement binder material and because of that service life means durability of the concrete material decrease. Use of sulfur concrete since from early 20^{th} century, where sulfur cement use for forming tanks or vents for holding leach or pickling solutions, for pipes or tiles for handling acidic sewer waters, flooring material for industrial plants and as such material for concrete floor or walls. SPC does not Support Combustion, sulfur present in the surface will slowly burn when exposed to direct flame but it self-extinguishes when	In this paper Sulfur polymer concrete made from the recycle materials like sulfur, fly ash and desert sand. The sulfur is modified through polymerization of the elemental sulfur

				<u>the flame is removed. The low thermal conductivity of sulfur results in slow penetration of heat.</u>	with the olefin hydrocarbon polymeric material. The durability of the specimens were analyze in terms of absorb water in different media means acid resistance, Salt penetration and leachability test as a function of medium and time.
4.	Performance of modified sulfur concrete exposed to actual sewerage environment with variable temperature, humidity and gases	Maisa M. El Gamal Amr S. El-Dieb Abdel-Mohsen O.Mohamed Khaled M. El Sawy	Elsevier Journal of Building Engineering	In biggest developed countries, annual losses due to corrosion in concrete construction is thousand dollars per capita. Porosity of concrete and damages in it causes diffusion of gases and other aggressive species can enter in it. Permeability of concrete is dependent on the pore sizes, degree of connectivity between pores, degree of packing and binder type. Concrete with low permeability resists the penetration of corrosive agents like, chloride and sulfate ions, oxygen and water and reducing the corrosive effects can be occurs due to these agents. In PCC, Thaumasite is formed during interaction between PCC and Sewage environment (Acidic Conditions). Sources for thaumastic production during sulfate attacks are calcium silicate, sulfate, carbonate ions and excess of humidity. Factors responsible for the concrete deterioration are soft water attack, alkali carbonate reaction, alkali silica reaction and chloride salt reaction. These all are arise due to moisture, oxygen, carbon dioxide, sulfates and	The paper study evaluates the physical and chemical effects of the sewerage environment on the Portland cement concrete (PCC), Sulfur-Resistance cement (SRC) and Modified sulfur cement (MSC) through the carbonation depth measurements and the corrosion of reinforced steel.

				chlorides through the pores of concrete. MSC solidifies and achieves high strength compare to PCC and SRC (Sulfate reinforced concrete) because power of the Modified sulfurs as an enfolding binder. There is a less chances of the interaction between the matrix components and the surrounding corrosive medium in MSC, because absence of capillary and porous structure. PCC and SRC takes around 28 days to reach its maximum strength, while MSC takes only several hours to cool and hardened for its full strength development. H^+ ions from an acidic ions attack to PCC and SRC, the pH values of Concrete will drop from 13 to less than 8 and because of that electrochemical corrosion of the steel starts to occur in the presence of moisture and oxygen.	
5.	Characterization of a sustainable sulfur polymer concrete using activated fillers	Juhyuk Moon Paul D. Kalb Laurence Milian Paul A. Northrup	Elsevier Cement and Concrete composites	During manufacturing of Portland cement limestone heated more than 1400°C in kiln to form clinker materials. For this process fossil fuels burned to power the kilns and carbon dioxide emission occur from the conversion of limestone to calcium oxide. This process generates about one ton of carbon dioxide per ton of cement. That contribute 5% of the global anthropogenic generation of CO_2	

6	Preparation of Sulfur Mortar from modified sulfur	Bahrami Adeh Narmin Mohtadi Haghighi Mohammad Hosseini Nahid	Iranian Journal of Chemistry and Chemical Engineering (IJCCE) Research Note	Addition of the fillers in the sulfur mortar increases the viscosity because it provide sufficient matrix relative to the amount of sulfur to obtain workable mixture and decreases the void spaces in a mortar. The main function of fillers is to stabilize the sulfur mortar and the amount of modified sulfur needed. Sulfur mortar have high flexural and tensile strength because of their thermoplastic properties. Compressive strength of sulfur mortar can be increase by changing mixture proportion and apply favorable grain distribution with little void space.	In this article, sulfur concrete made from mixtures of mineral aggregate and modified sulfur. Ratio: 10% filler, 58% aggregates and 32% molten sulfur. Olefinic additives use as a modifier to prepare modified sulfur. Mechanical properties of the sulfur concrete measure in terms of effects on reaction time and heating time.

7.	Sustainable sulfur composites with enhanced strength and lightweightness using waste rubber and fly ash	Seongwoo Gwon Yeonung Jeong Jae Eun Oh Myoungsu shin	Elsevier Construction and building materials	The global generation of sulfur is approximately 10-20% larger than the worldwide demand The worldwide sulfur generation is 57 million tons per year Cement production in the world yields about 7% of the total CO_2 emission. A DCDP modified sulfur polymer can expand and contract due allotropic transition of sulfur because of temperature changes, the higher the concentration of the modifier the less the volumetric changes.	

8	Spent FCC catalyst as a pozzolanic material for high-performance mortars	Hsiu-Liang Chen Yun-Sheng Tseng Kung-Chung Hsu	Cement & Concrete Composites Elsevier	Spent FCC catalyst is the byproduct use during oil cracking in refineries. Many industrial wastes are used in the construction material like silica fumes (SF), fly ash, and blast furnace slag. These are the most successful examples that use for construction activity as an admixtures because these material have cementitious or pozzolanic properties. These material behave as a micro fillers for enhancing the packing the cement paste-aggregate particle interface and forming a denser and more homogeneous microstructure in the transition zone. Spent FCC catalysts are classified as non-hazardous. 400,000 tons were produced annually. But most of the spent FCC solidifies and disposed as landfills. Use of spent FCC in the construction materials such as the filler for the asphalt and the production of brick and cement. Average particle size (D_{50}) of Spent FCC catalyst (E_{cat}) is 67.2 µm (measured by particle size analyzer) BET specific area 114 m^2/g. For E_{pcat} D_{50} is 1.7µm and BET surface area is 47.3 m^2/g. For additives such as SF and blast furnace slag, the surface area per unit mass derive from their external surface. But for spent FCC, high proportion of the surface area is from their internal surface. That will lead to difference in adsorption/absorption characteristics of the catalyst particles That are likely to be highly absorbent. Therefore they require to more water to achieve similar workability.	In this article the cement mortar is made from the replacement of the cement with spent FCC with different W/B (water/Binder) ratio. Researcher had check the compressive strength of that replaced mortar with applying different curing time.

9.	Spent FCC catalyst: Potential anti-corrosive and anti-biofouling	Palak A. Trivedi Preeti R. Paramar Parimal a. Parikh	Journal of Industrial and Engineering chemistry Elsevier	Acidophilic sulfur Oxidizing bacteria (SOB) like Thiobacillus Sp. Responsible for the corrosion deterioration of concrete. This bacteria oxidize sulfur compounds to produce sulfuric acid which react with free lime a corroding layer on concrete. Microbial etching of concrete: it occurs in bridge and especially sewer systems, where H_2S present. Bacteria on the concrete exposed to both air and H_2S oxidize and dissolve the concrete Concrete deterioration also occurs through Fungi. Weight loss and release of calcium occur when concrete exposed to Fusarium Fungal species are not so faster than thiobacillus Sp. But it can easily grow on humid environment. Anti-corrosive activity of spent FCC catalyst can be measured through two tests: (1) Weight loss (2) Electrochemical analyses	

CHAPTER 3 EXPERIMENTAL WORK

3.1. Flowchart of Experimental work

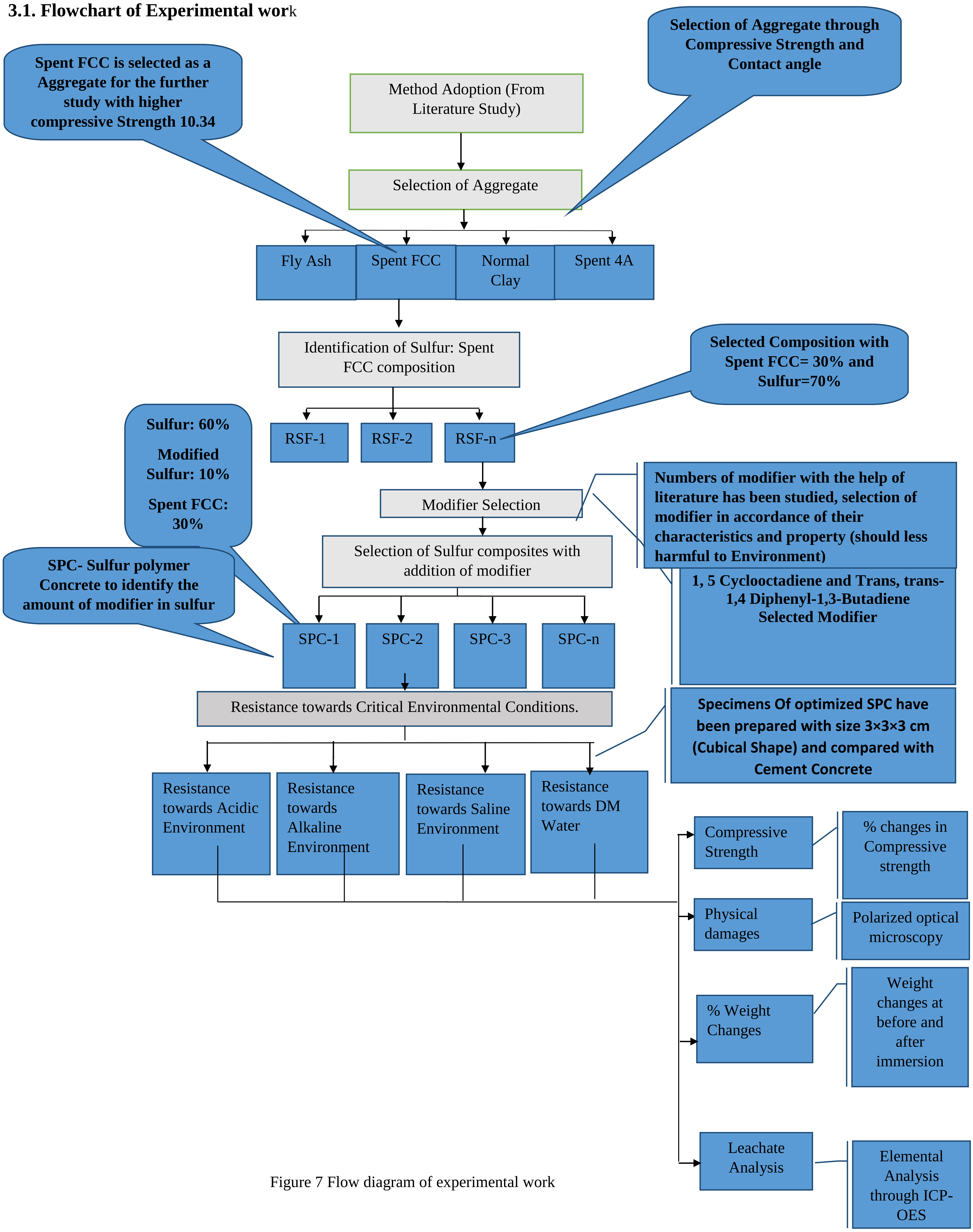


Figure 7 Flow diagram of experimental work

As mentioned in the flow chart, the work started with getting aware of the procedure of Sulfur concrete by referring literature. After finalizing the procedure, the first experiment was carried out for the identification of Aggregate. For that Sulfur composites were made with different aggregate like Fly Ash, Spent FCC, Normal Clay, and 4AES. Selection was based on their Compressive strength and Hydrophobicity. Sulfur composite with Spent FCC gain better result for said test compere to other counterparts, so Spent FCC was selected as aggregate for the rest of the study. Second stage was for the optimization of suitable composition with Elemental Sulfur and Spent FCC. Experiment done by taking the different ratio of Sulfur: Spent FCC (R1, R2…Rn). In the third stage of experiment different chemicals have been analyze for the modification of Sulfur property. Prepared modified sulfur was identified through its characterization and Property of modifier. 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene were selected as modifier for further experiment.

3.2. Instrumentation

3.2.1. X-ray diffraction spectrophotometer

XRD patterns were recorded on Bruker advance D8 to obtain crystallographic structure and chemical composition of solids. The patterns were recorded in order to verify the formation and nature of structure. The XRD patterns of modified sulfur were obtained using a Cu (Ka) radiation source (1.54060 Å) and operated at 40 kV and 30 mA. Samples were crushed to fine powder prior to measurement. XRD is a technique to identify the crystallinity of prepared modified sulfur. The crystallinity can be determined by comparing the intensity of a number of particular peaks to the intensity of the same peaks obtained by standard samples.

Figure 8 X-ray diffraction Instrument

The diffraction pattern is plotted based on the intensity of the diffracted beams. These beams represent ampere of reciprocal lattice parameter, known as Miller index (hkl) as a function of 2ɵ, which satisfy Bragg equation: $n\lambda = 2d \sin\theta$ where n is an integer number; λ is the wavelength of the beam, d is interplanar spacing and ɵ is a diffraction angle. Powder XRD pattern were recorded for all the samples in order to verify the formation and structure of various micro porous materials. The diffraction patterns were recorded in the 2ɵ range of 5-80°. The scan speed and step size were 2.5° min-1 and 0.02°, respectively.

3.2.2. FT-IR

FT-IR spectroscopy is used to identify the structure of modifier (1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene) and for characterization of prepared sulfur with modification. For analysis of structural changes in sulfur after modifying its property by using FT-IR (Nicolet 6700) using KBr pellets. Structural information can be obtained from the vibrational frequencies of the modified sulfur observed in the range 500-3000 cm^{-1}.

Figure 9 Fourier-transform infrared spectroscopy

3.2.3. Universal Testing Machine

Universal Testing Machine is used to test the compressive strength or tensile strength of materials. In this study, UTM of model no. EZ-20 by of company LLOYD instruments has been used. It consist of the following components (1) Load frame (consisting of two strong supports for the machine) (2) Load cell (can measure the load is required) (3) Cross head (4) Holding jaws and (5) environmental chamber (to control temperature, humidity and pressure). The specimens is placed between the grips, as machine is started the load will apply in increasing order. Throughout the tests control system and other associated software record the load and extension or compression of specimens.

Figure 10Universal Testing machine

3.2.4. Drop Shape Analyzer- DSA 25 (Kruss)

Instrument specifically used to measure hydrophobicity of a solid surface through contact angle, which measure the liquid droplet where liquid vapor interface meets a solid surface.

It qualify the wettability of a solid surface by a liquid via Young- Laplace equation:

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos \theta_c = 0$$

Where, γ_{SG} = Solid-vapor interfacial energy

γ_{SL} = Solid-liquid interfacial energy

γ_{LG} = liquid-vapor interfacial energy

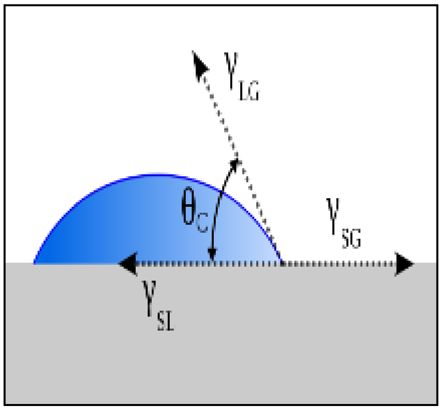


Figure 11 graphical representation of contact angle measurement

3.2.5. Inductively coupled plasma optical emission spectroscopy

ICP-OES (Perkin-Elmer, 4300 DV) analysis aims to identify trace elements presence in the aqueous samples. The technique is based upon the spontaneous emission of photons from atoms and ions that have been excited in radiofrequency (RF) - induced argon plasma using one of from variety of nebulizers. The sample mist reaching the plasma is quickly dried, vaporized, and energize through collisional excitation at high temperature. This atomic emission form plasma is viewed either a radial or axial configuration, collected with a lens or mirror, and imaged onto the entrance slit of a wavelength selection device.

Figure 12 inductively coupled plasma optical emission spectroscopy (ICP-OES)

Single element measurements can be performed cost effectively with a simple monochromator/photomultiplier tube (PMT) combination, and simultaneous multi element determinations are performed for up to 70 elements with combination of a polychromator and an array detector. The analytical performance of such system is competitive with most other inorganic analysis techniques.

3.2.6. Polarized optical microscopy

This technique is useful in identification of crystallographic properties of the crystals and to identify the damages on the surface of material. In this study, POM was use to analyze the effects on surface of Portland cement concrete, and sulfur polymer concrete after immersed in a different acidic, alkaline and saline medium. Measurement range set for analysis was 10X.

Figure 13 Polarized Optical Microscope- Leica (DM1000)

3.3. Materials & Method

For the preparation of sulfur composites various materials have been used, raw materials use for the sulfur concrete are elemental sulfur, aggregates (spent FCC, fly ash, normal clay and adsorbent 4AES), modifier (1,5 cyclooctadiene, Trans, trans-1,4 Diphenyl-1,3-Butadiene). Following section gives details of each material with their source and composition and give the information regarding material preparation of sulfur concrete (without modifier), modified sulfur and sulfur polymer concrete (with modifier).

3.3.1. Materials

3.3.1.1. Elemental Sulfur

In this study, Granular shape sulfur with 99 % purity has been used. Sulfur obtained from sulfur recovery unit (SRU) at Reliance Jamnagar Plant. Sulfur is obtained from Gas Plant in 1.10 million metric ton.

3.3.1.2. Spent FCC

Spent Catalyst received from Reliance industries Limited, Jamnagar. It mainly contains Zeolite Y, ZSM-5, additives and clay binders. Metal analysis of spent catalyst was performed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Table 2) using microwave digester and data are represented in Table 2.

Spent FCC is a mixture of different catalyst, which is obtained from regeneration plant of catalyst. As the activity of catalyst decrease, it requires regeneration. But at certain point regeneration of catalytic activity can’t be possible and is termed as a deactivated catalyst that are discarded as a solid waste and termed as Spent FCC

Table 2 elemental analysis of Spent FCC

Sr. no.	Elements	Unit	Spent FCC Content
1.	Ti	%	0.18
2.	V	mg/L	197
3.	Cr	mg/L	45
4.	Mn	mg/L	16
5.	Fe	%	0.30
7.	Co	mg/L	37
8.	Ni	%	0.18
9.	Cu	mg/L	6
10.	Zn	mg/L	41
13.	Na	%	0.15
14.	K	mg/L	311
15.	Ca	mg/L	215
16.	Mg	mg/L	251

3.3.1.3. Fly Ash

Fly ash used in experiment was collected from the thermal power plant site.

3.3.1.4. Normal Clay

Clay was obtained from the general sources nearby site.

3.3.1.5. Spent adsorbent 4A

Source of spent adsorbent from CA plant at Reliance industrial Ltd. of Dahej Cracker plant. 4 A represent the size of molecular sieve which are the crystalline aluminosilicate or synthetic zeolites having unique structure with regular pore size

3.3.1.6. 1,5 cyclooctadiene

It is use as a modifier, modification of the property of elemental sulfur through adding specific dosage of modifier in melted elemental sulfur at desired temperature. To resist orthorhombic transformation of sulfur at ambient temperature, and sulfur stay as a monoclinic phase. Modified sulfur contributes to increase concrete's compressive strength as compared to concrete made from unmodified sulfur.

3.3.1.7. Trans, trans-1,4 Diphenyl-1,3-Butadiene

It is use as a modifier, modification of the property of elemental sulfur through adding specific dosage of modifier in melted elemental sulfur at desired temperature. To resist orthorhombic transformation of sulfur at ambient temperature, and sulfur stay as a monoclinic phase. Modified sulfur contributes to increase concrete's compressive strength as compared to concrete made from unmodified sulfur.

3.3.2. Methods

Method for preparation of sulfur concrete, modified sulfur and sulfur polymer concrete was adopted with reference to different method adopted by researchers ([10], [21], [24], and [25]) and based on heat and trial, set of experiments were carried out to find the most convent methods.

3.3.2.1. Preparation of sulfur composite

Elemental sulfur heated up to 140°C, selected aggregates like Spent FCC, fly ash, normal clay and adsorbent 4AES were preheated at 120°C for 2 hrs. before mix it with elemental sulfur. Do proper mixing of composites until binder sulfur properly coated over aggregates. For each composite, ratio of sulfur and aggregates is 80% elemental sulfur and 20% aggregate. On basis of compressive strength of each composite made from different aggregate, one aggregate selected for further study.

3.3.2.2. Preparation of Modified Sulfur

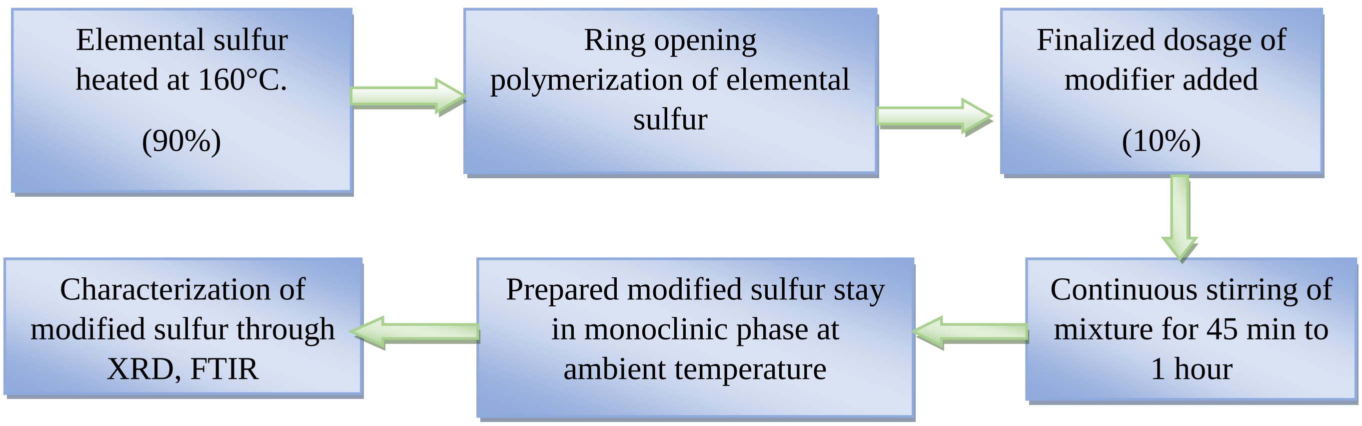


Figure 14 Flow diagram for preparation of modified sulfur

Figure 15 depicts the flow diagram about preparation of modified sulfur. Elemental Sulfur heated up to 160°C. Reason behind this temperature selection is that Ring opening polymerization (ROP) support near to this temperature range. Selected modifier was added in this temperature range. Both Polymerize sulfur and modifier were mixed continuously in the temperature range of 135-140°C for 45 min. Mixture was allowed to cool down at controlling rate of 8-10°C/min. The formed product is sulfur with modified properties. Distribution of Modifier was evaluated to Characterization of prepared modified sulfur by XRD, IR.

3.3.2.3. Preparation of sulfur polymer concrete

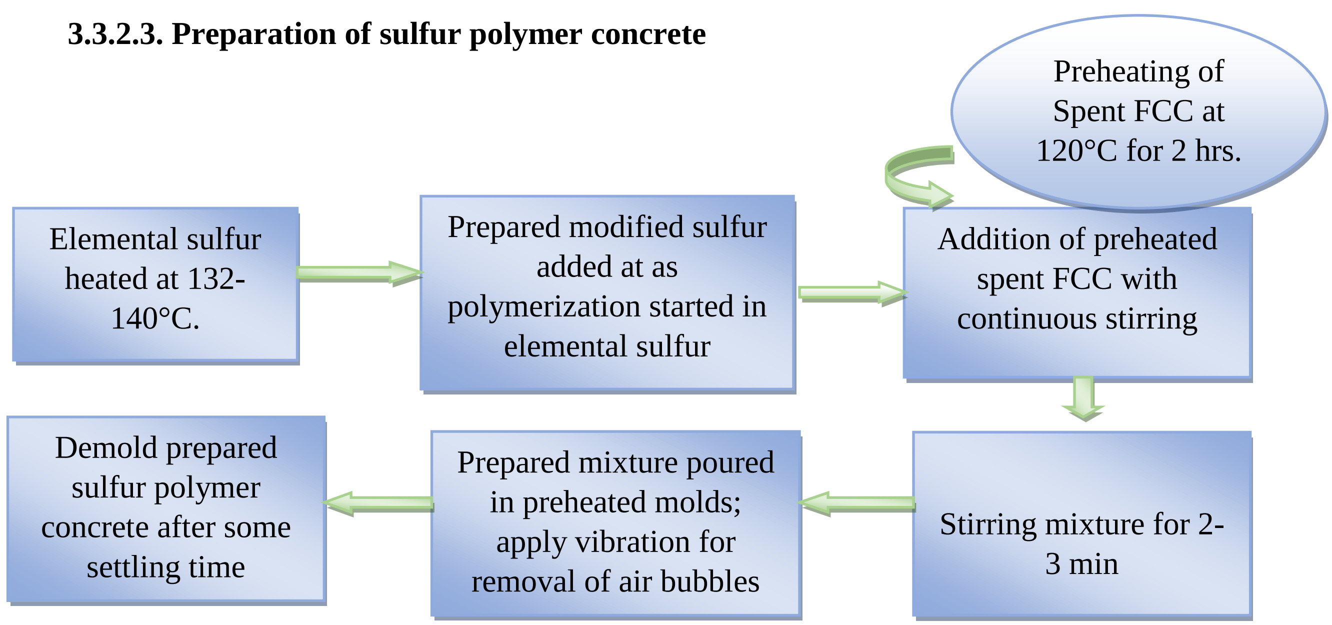


Figure 15 Flow diagram for sulfur polymer concrete

Sulfur concrete consists of a mixture of three basic ingredients, Elemental sulfur, modified sulfur and Spent FCC act as an aggregate. Selection of composition of each component was carried out based on their previous result of compressive strength. The optimize composition of the prepared sample is, elemental sulfur (60%), Modified Sulfur (10%) and Spent FCC (30%). Selected aggregate were preheated at 170°C for 2 hrs. Specified amount of Elemental sulfur was heated first at 132-140°C, as its start to polymerize, modified sulfur of pre-defined quantity was then transferred to the mixing bowl and allowed to reaction took place. After sometime as the reaction has been completed preheated aggregate mixed with the sulfur mixture and allowed to mix for 2-3 min. Then the prepared composite were fill in a pre-heated molds. Size of the cubic shape molds is 30mm×30mm×30mm and 12mm×18mm cylindrical shape molds. Air bubbles were removed through vibration. Demold the composites immediately. And rest the demolded mold for 1 day, so measurable strength can be build up.

Portland cement concrete (PCC) samples were also prepared to check the compatibility of the sulfur concrete. PCC samples were prepared through standard procedure. Resistance towards alkaline, acidic and saline condition, SPC and PCC samples were immersed in a different solutions. For acidic condition, 98% Conc., 50% and 10% H_2SO_4 solutions were prepared. To check resistance towards alkaline medium, 40%, 20% and 5% NaOH solutions were prepared, and for Saline condition 1 %, 3%, 5% and 3.2% (Salinity of the Sea water) NaCl solutions were prepared. And one sample was immersed in Demineralized water. Samples were characterized through %Weight loss, Moisture absorption, and Compressive strength, identification of Physical damages through polarized optical microscopy (POM), Leachate Analysis through Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and hydrophobicity measurement.

3.4. Experimental work

3.4.1. Selection of Aggregates

Study conducted on identification of suitable aggregate based on result of compressive strength of each sulfur composites. Aggregates used for this study are spent FCC, fly ash, normal clay and adsorbent 4AES. Composition of sulfur composite is 80% of elemental sulfur and 20% aggregate. Prepared sulfur composite tested for compressive strength analysis and contact angle measurement. Based on the result of previous mention test suitable aggregate was selected.

3.4.2. Selection of sulfur aggregate composition selection

Sulfur composite with elemental sulfur and spent FCC was prepared. Study was conducted for finalizing the composition of elemental sulfur and spent FCC. For that sulfur composites prepared with varying composition of 20, 30, and 40 % of Spent FCC. Prepared composites were tested for compressive strength analysis. Selection of composition was done according to their compressive strength results.

3.4.3. Selection of Modifier for sulfur polymer concrete

Modification of elemental sulfur is required for resist orthorhombic transformation from monoclinic phase to orthorhombic phase. Study was conducted through testing different organic modifier like mono ethylene glycol, vinyl isobutyl ether, ethylene glycol, 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene etc. identification of suitable modifier based on physical and chemical property of each organic modifier. Modifier 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene were selected according their property. And rest of the modifier failed in making sulfur that can be stay in monoclinic phase at ambient temperature. Composition of selected modifier in sulfur composites were tested by characterizing through XRD and FTIR spectroscopy.

3.4.4. Characterization of modified sulfur

Modified sulfur prepared with organic modifier, 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene. Study was carried out for characterization of prepared modified sulfur through XRD and FTIR.

3.4.5. Optimization of amount of modified sulfur in sulfur composite

Sulfur polymer concrete were prepared with varying blends of modified sulfur like, 1, 3, 5, 7 and 10% of modified sulfur was added in sulfur polymer concrete. Identification of concentration of modified sulfur was finalized from the result of compressive strength of prepared sulfur polymer concrete.

3.4.6. Effect of critical environmental conditions on sulfur polymer concrete

Study was conducted to check the resistance of sulfur concrete in critical environmental condition through conducting various physical and chemical resistivity tests. Comparison was done between sulfur concrete and standard cement concrete blocks. Cubical specimens of size 3×3×3 cm were prepared. Critical environmental conditions like Acidic, Alkaline, Saline and hydrating conditions. Specimens of Sulfur polymer concrete (SPC) and Portland cement concrete (PCC) were immersed in mentioned medium for 7 days, after that effect on their identified by classifying series of tests. For checking physical effect, compressive strength and effect on weight and Physical damages through POM was identified. And for chemical effect, elemental analysis of immersed solution was conducted through ICP-OES.

3.4.6.1. Durability in acidic condition

Acid resistance study was carried out for samples of SPC-1 and SPC-2 of 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene as a modifier respectively and PCC samples. Cubical samples with 30mm×30mm×30mm dimension were immersed in an Acidic solution with changing in composition of Acid, 98% Conc. H_2SO_4, 50% H_2SO_4 and 10% H_2SO_4 at 24°C for 7 days. Durability identified in a two way. (1) Physical durability which include the effect on weight and compressive strength of specimens and Surface damages due to effects of acidic conditions, and (2) Chemical durability that identify through leachate analysis by collection of solution in which specimens were immersed and elemental analysis has been carry forwarded through ICP-OES.

In physical technique initial weight and compressive strength of specimens have been taken before use those blocks for experiment. And as the period was over the final weight and compressive strength have been calculated. For elemental analysis 1 ml of solution from each immersed medium have been taken and diluted to 100 ml for ICP-OES.

3.4.6.2. Durability in alkaline condition

Samples of SPC-1 and SPC-2 of 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene as a modifier respectively and PCC samples were tested to check the resistivity against alkalinity through immersion in a different alkaline solution which were prepared through varying the concentration of NaOH (40%, 20% and 5% NaOH) at 24°C for 7 days of immersion period. Same tests mentioned for acidic resistance have been conducted for alkaline resistance.

3.4.6.3. Durability in saline condition

Samples of SPC-1 and SPC-2 of 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene as a modifier respectively and PCC samples were immersed in a saline solution prepared from varying Salinity. Samples were immersed in a 1%, 3%, 3.2% and 5% NaCl solution at 24°C for 7 days of immersion period.

3.4.6.4. Durability in hydrated condition

Samples of SPC-1 and SPC-2 of 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene as a modifier respectively and PCC specimens were immersed in de-ionized water for same immersion period for 24°C.

CHAPTER 4 -RESULTS & DISCUSSION

Sulfur composites based bricks are advantageous over cement concrete based counterparts in terms of strength and other important properties. This will also give additional benefit of hydrophobicity and antifungal activity which will make the surface waterproof and algae free. In this chapter development of sulfur composites bricks and comparison of its properties with cement concrete based bricks has been discussed. It covers aggregate selection, optimization of its composition, development of modified sulfur, final composition of modified sulfur in sulfur composites. This chapter also includes physical and chemical effects of critical environmental conditions on prepared sulfur polymer concrete.

4.1. Selection of aggregate

Study was conducted for selection of suitable aggregate for sulfur composite. Material tested are Fly ash, Normal clay, spent FCC and adsorbent 4AES. Composition for sulfur composites was set as 80% of elemental sulfur with 20% aggregate. Selection based on the compressive strength which was measured through universal testing machine. Table 3 gives the data on compressive strength of prepared sulfur composite.

Table 3 Compressive strength of sulfur composites with different aggregate

Binder (80%)	Aggregates (20%)	Compressive strength (MPa)
Sulfur	Spent FCC	14
Sulfur	Fly Ash	6
Sulfur	Normal Clay	11
Sulfur	4AES	10.00

From table 3, it can be identify that maximum strength of 14 MPa was gain through sulfur composites made up by using spent FCC as an aggregate, while minimal strength of 6 MPa gain from composite made up of clay and elemental sulfur. This is because spent FCC has a high pozzolanic property. It is mentioned by J.Monzo et al. [15]that Spent FCC use as raw material for high performance concrete (HPC). Spent FCC consist of SiO2-Al_2O_3 based zeolite structure, which react with hydrated lime for yielding strength. For this reason spent FCC gain better strength compared to normal aggregate system. Further study conducted to decide the optimum composition of sulfur composite with spent FCC.

4.2. Optimization of composition of spent FCC in sulfur concrete

As in previous section, spent FCC was selected as an ideal aggregate. Optimum amount of spent FCC for sulfur concrete discuss in the following section. Sulfur composite prepared with differing amount of spent FCC like with 20, 30, and 40 % of Spent FCC content sulfur concrete have been made and tested for compressive strength. Finalization of ideal composition was based on their compressive strength result.

Table 4 Compressive strength and contact angle of sulfur composite with various concentration of spent FCC

Sample Name	Sulfur (%)	Spent FCC (%)	Compressive strength (MPa)	Contact Angle (ɵ)	Density (Kg/m3)
RS	100	-	5	127	1473.20
RSF-1	80	20	10	119	1890.21
RSF-2	70	30	13	111	1725.92
RSF-3	60	40	12	116	1589.00

Table 4 give the details on compressive strength of sulfur composite with varying amount of spent FCC. It can be noticeable that sulfur composite made up with 30% of spent FCC content gain maximum strength of 13.044 Mpa and hence carry forwarded for further study Table 4 also give idea about the hydrophobic nature of spent FCC based sulfur composite. Measured contact angle (ɵ) is greater than 100°confirms it’s hydrophobic in nature of material

4.3. Modified Sulfur

When sulfur concrete made by hot-mixing of unmodified sulfur and aggregate, problems started to rise regarding durability of prepared product. Previous study has been investigate that unmodified sulfur failed when exposed to repeated cycle of freezing and thawing, humid conditions or immersion in water. Studies were carried out for finding reasons behind failure, sulfur exists as an orthorhombic sulfur (S_α) below 96°c, on further heating sulfur exists as a monoclinic sulfur (S_β), and ring opening polymerization has started at temperature ≥ 158°C.

In cooling process, sulfur first crystalize as monoclinic form at 114°C with volume decreases of 7%, by further cooling below 96°C, sulfur starts to transfer to orthorhombic sulfur that consider as stable form of sulfur at ambient condition.(Lin et al. 1995). Transformation is rapid which occurs in less than 24 h. S_α form is denser than S_β, that will lead to solid surface shrinkage through high stress, for this reason sulfur binder become highly stressed and fail prematurely. By modifying sulfur property resulted sulfur concrete would have good durability, reducing expansion/contraction of sulfur concrete during thermal cycling.

In this study elemental sulfur modified by testing different inorganic chemicals like mono ethylene glycol, vinyl isobutyl ether, ethylene glycol, 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene etc. identification of suitable modifier based on physical and chemical property of each organic modifier. Modifier 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene were selected according their property. And rest of the modifier failed in making sulfur that can be stay in monoclinic phase at ambient temperature. Composition of selected modifier in sulfur composites were tested by characterizing through XRD and FTIR spectroscopy.

(a) (b) (c)

Figure 16 (a) Elemental sulfur (b) 1,5 Cyclooctadiene modified sulfur (c) Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur

4.3.1 Mechanism of sulfur modification

Modification of sulfur by stabilization of polymeric sulfur against depolymerization by co-polymerization a large excess of sulfur with a modest amount of small molecule dienes, modification of sulfur will cause tunable thermo-mechanical property.

Elemental sulfur heated upto 158°C, that called as ring opening temperature of sulfur, so high concentration of sulfur diradical will generated from hemolytic cleavage of S_8 to promote efficient homo-propagation to sulfur diradicals and cross-propagation with selected modifier like 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene. Modifier supposed to add into molten sulfur at temperature ≥ 158°C, which after some mixing period resulted in homogeneous yellow solution. Mixing process continue for 45-60 min, after that verification of complete reaction can be notice through allowing mixture to cool down and it can be notice that the modified sulfur stay as a red color that prove that modified sulfur stay as a monoclinic phase at ambient condition. Cooling rate applied is 8-10°C/min.

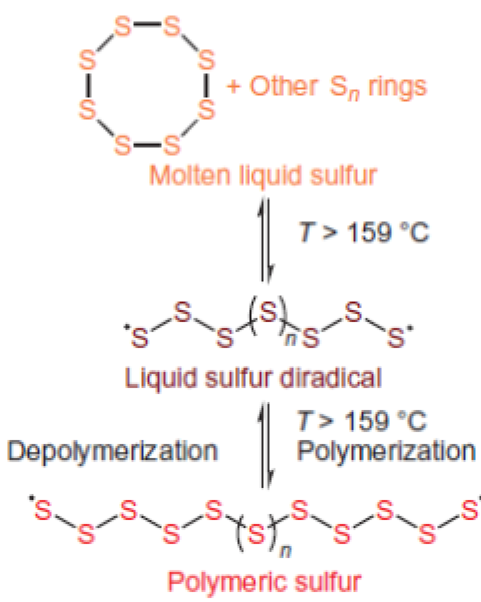


Figure 17 Polymerization of Elemental Sulfur

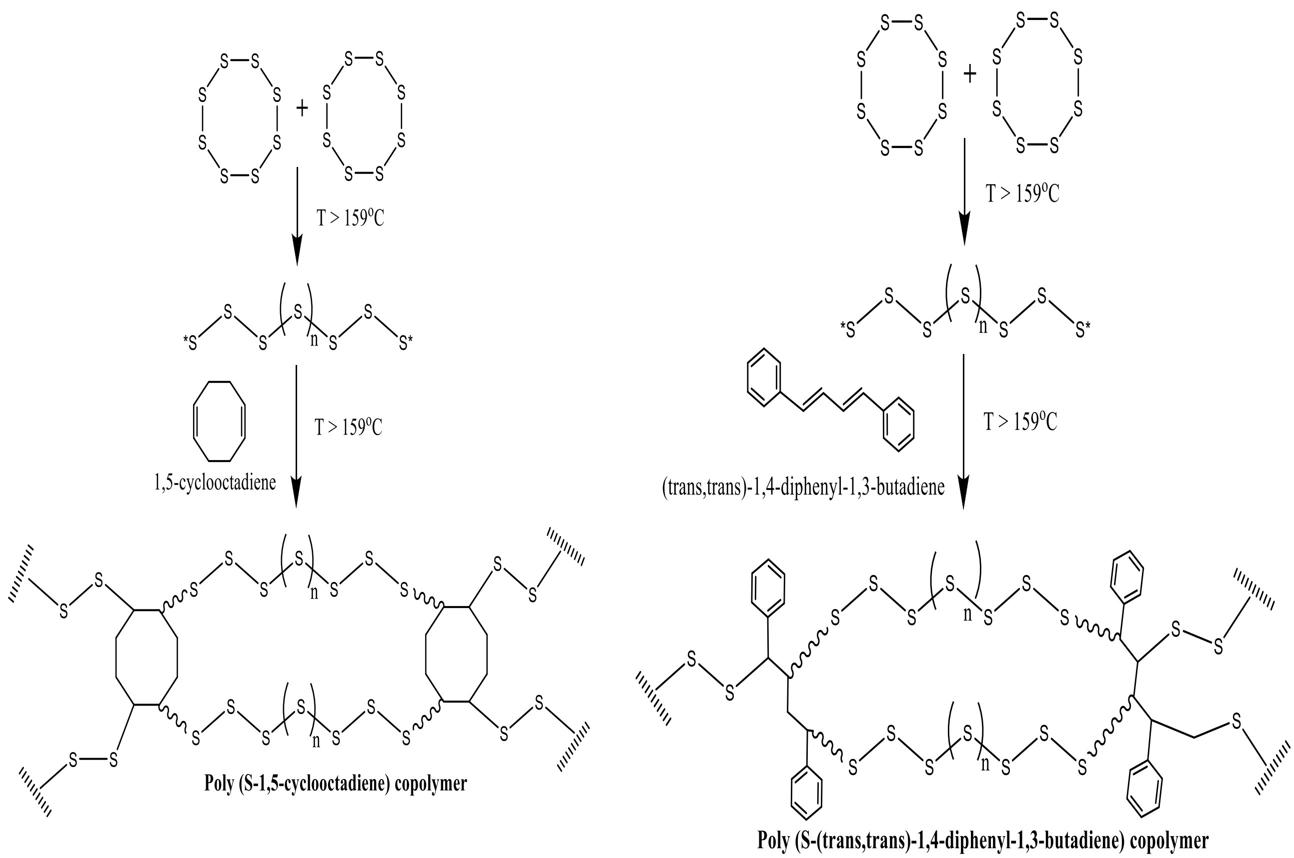


Figure 18 Reaction mechanism of Modified sulfur

4.3.2 Characterization of modified sulfur

Characterization of a material is to study measure material's structure and property with different analytical tools. Prepared modified sulfur is characterize with X-ray diffraction and Fourier transform infrared spectroscopy, to check the reaction between selected modifier 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene and elemental sulfur. XRD will investigate the crystalline nature of prepared modified sulfur against unmodified sulfur. And FT-IR study will reveal the structural changes and presence of 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene in modified sulfur after modification.

Fourier transform infrared spectroscopy (FT-IR)

The reaction between elemental sulfur and modifiers 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene was studied using FT-IR spectroscopy. The IR spectra of 1,5 cyclooctadiene and Trans, trans-1,4 Diphenyl-1,3-Butadiene were recorded. The IR spectra of 1,5 cyclooctadiene modified sulfur and Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur were taken through powder mixed with a small amount of kBr powder to make IR pellet. Fig. 19

gives overlay spectra between 1,5 cyclooctadiene, 1,5 cyclooctadiene modified sulfur and elemental sulfur respectively. Fig. 20 gives overlay spectra between Trans, trans-1,4 Diphenyl-1,3-Butadiene, Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur and elemental sulfur respectively.

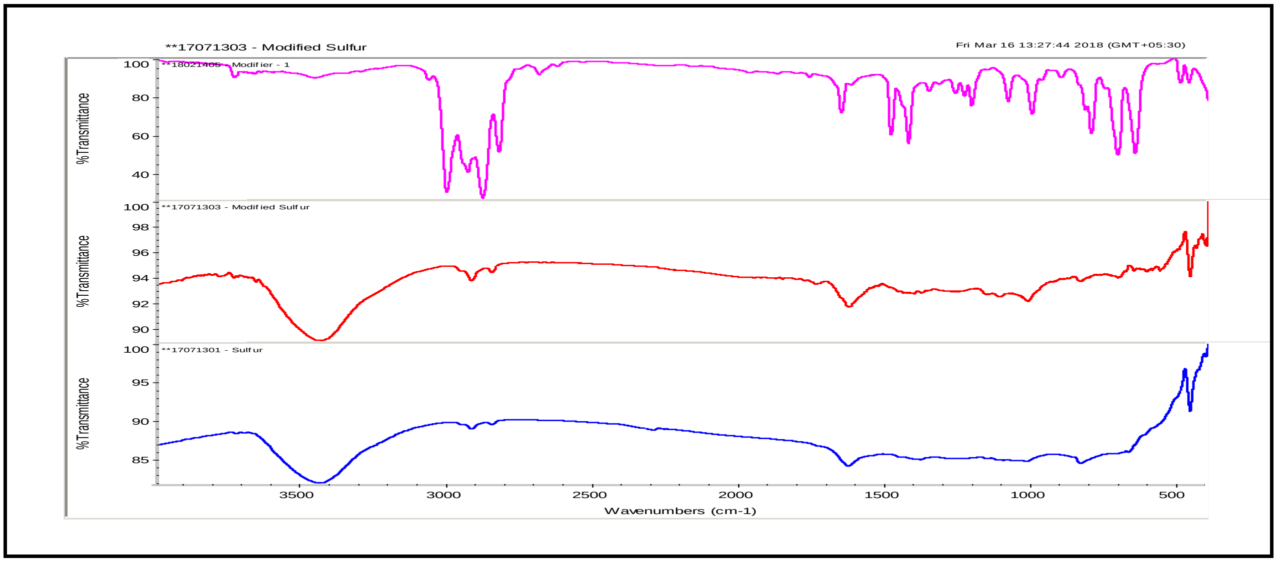


Figure 19 FT-IR overlays Spectra of 1,5 cyclooctadiene 1,5 cyclooctadiene modified sulfur and elemental sulfur

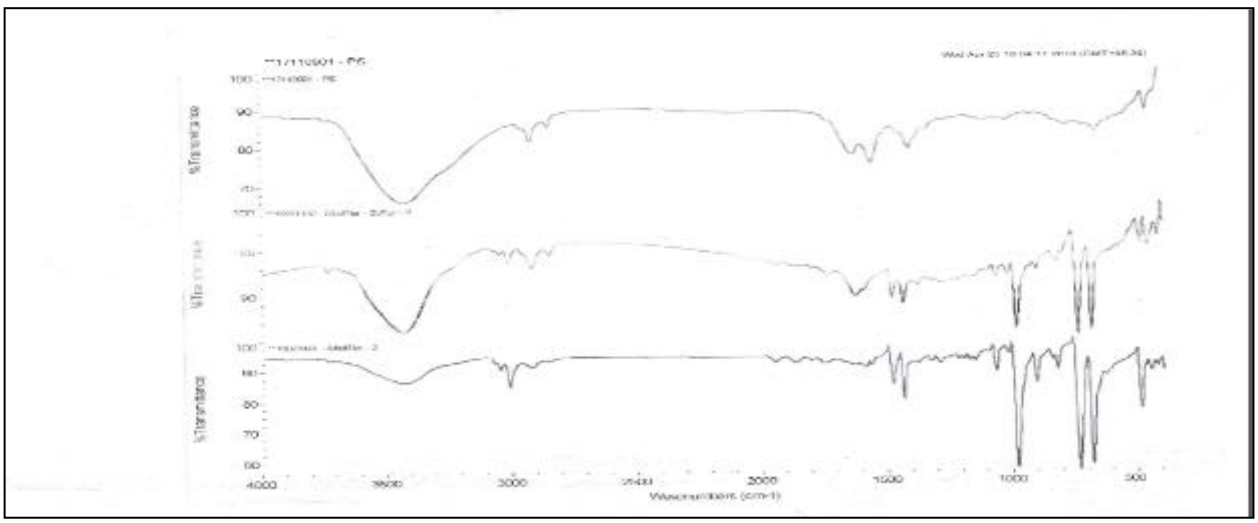


Figure 20 FTIR overlay spectra of Elemental sulfur, Trans-1,4 Diphenyl-1,3-Butadiene modified sulfur and Trans-1,4 Diphenyl-1,3-Butadiene modifier

Fig.19 represent the IR spectra of overlay between Elemental sulfur, 1,5 cyclooctadiene modified sulfur and modifier 1,5 Cyclooctadiene. FTIR spectra revel that in organic modifier alkene group (1656 Cm^{-1}) peak is disappeared in polymeric modified sulfur. This also supporting to organic modifier alkene group is attached to di-radical of sulfur at temperature 159^{o}C. After reaction completion the existence of organic modifier is merge with polysulfide.

Fig. 20 represent the IR spectra of overlay between Elemental sulfur, Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur and Trans, trans-1,4 Diphenyl-1,3-Butadiene modifier. In spectra of Modifier, peak at 1591.3 cm^{-1} was observed in IR spectra of modifier Trans, trans-1,4 Diphenyl-1,3-Butadiene that was of –C=C- presence that also disappeared in modified sulfur. So the FTIR spectra proves that both organic modifiers are present in respective polymerized sulfur.

X-ray diffraction (XRD)

XRD study is important tool to identify the crystallinity and phase of the material. XRD pattern of elemental sulfur was compared with modified sulfur as shown in Fig. 21 and 22 XRD pattern shows that no structural changes in modified sulfur compare to elemental sulfur without effective crystallinity of material.

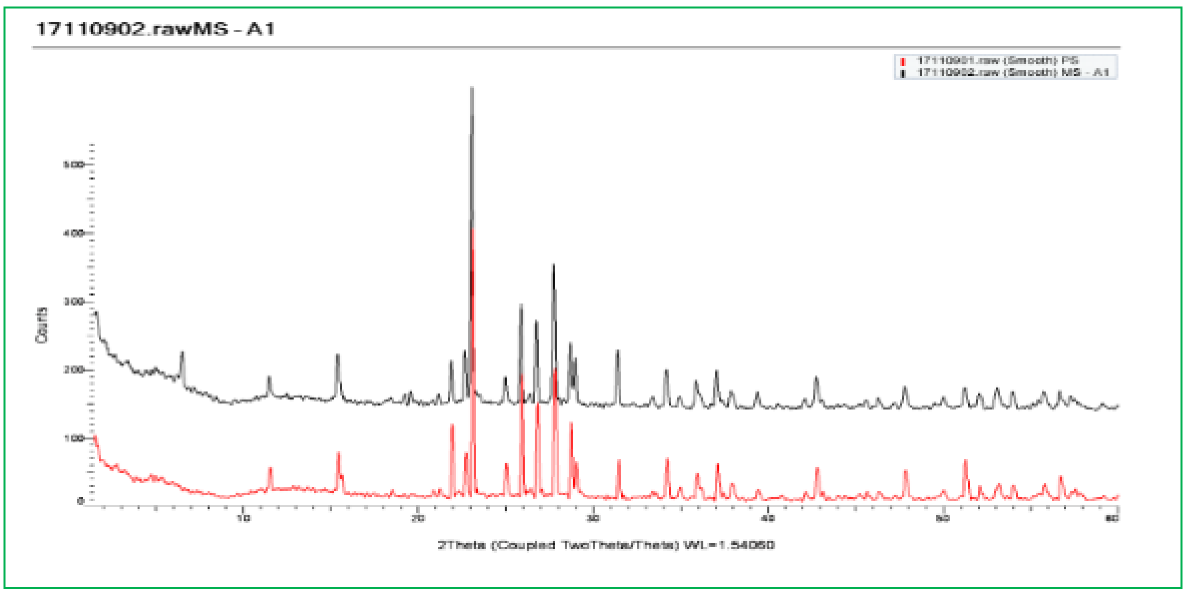


Figure 21 XRD spectrum of elemental sulfur and 1,5 cyclooctadiene modified sulfur

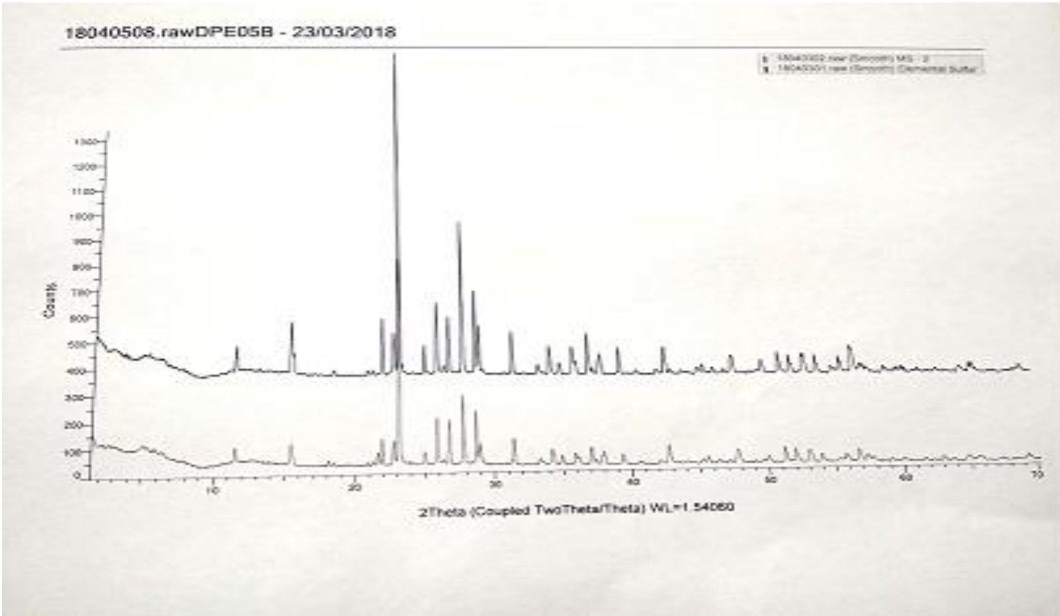


Figure 22 XRD spectrum of elemental sulfur and Trans-1,4 Diphenyl-1,3-Butadiene modified sulfur

4.4. Optimization of modified sulfur in sulfur polymer concrete (SPC)

1,5 cyclooctadiene and Trans-1,4 Diphenyl-1,3-Butadiene selected & characterize through XRD and FT-IR. Characterization result revels that preferred modifier have best outcome for modifying property of sulfur. For that sulfur polymer concrete made with varying dosages of modified sulfur in each. Selection of suitable amount on the basis of their compressive strength result. Table 5 gives the details of result of compressive strength of sulfur polymer concrete with different doses of modified sulfur -1 (modified with 1,5 cyclooctadiene) and table 6gives result of sulfur polymer concrete with different doses of modified sulfur-2 (modified with Trans, trans-1,4 Diphenyl-1,3-Butadiene)

Table 5 Optimization of modified sulfur concentration of 1,5 cyclooctadiene modified sulfur

Sr. No.	Sulfur	Modified Sulfur-1	Spent FCC	Compressive Strength (Mpa)
1	69	1	30	8
2	67	3	30	10
3	65	5	30	19
4	63	7	30	29
5	60	10	30	35

It can be observed that compressive strength of the sulfur composite is increasing with increased amount of modified sulfur. Maximum compressive strength can be achieve through use of 10% modified sulfur in prepared composites. Further study was carry-forwarded by taking 10% of modified sulfur concentration to make cubical specimens for further study.

Table 6 Optimization of modified sulfur concentration Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur

Sr. No.	Sulfur	Modified Sulfur-2	Spent FCC	Compressive Strength (Mpa)
1	69	1	30	8
2	67	3	30	9
3	65	5	30	10
4	63	7	30	12
5	60	10	30	14

Sulfur polymer concrete made with 10% modified sulfur gain compressive strength of 14 Mpa, that is higher compare to rest of the specimens with different concentration of modified sulfur. Here all the samples achieve minimum strength compare to sulfur polymer concrete by using 1,5 cyclooctadiene. Reason of loss of strength is that the Trans, trans-1,4 Diphenyl-1,3-Butadiene cannot work effectively for resist the orthorhombic transition of elemental sulfur. The characterization result also revel the same. So for both the case of modifier, ideal recommended amount of modified sulfur is 10% and further study was carry-forwarded by taking these dosages.

4.5. Physical & chemical resistance of sulfur polymer concrete in critical environmental conditions

Study was conducted to check resistivity of sulfur polymer concrete against critical environmental conditions. Sulfur polymer concrete made by both the modifier 1,5 cyclooctadiene and trans-1,4 Diphenyl-1,3-Butadiene has been taken for experiments. Resistivity of specimens of sulfur concrete compared with standard cement concrete. Cubical specimens of size 3×3×3 cm were prepared for this study. These samples are tested under critical environmental conditions like Acidic, Alkaline, Saline and hydrating conditions. Specimens of Sulfur polymer concrete (SPC) and Portland cement concrete (PCC) were immersed in mentioned medium for 7 days. Effect of these environments on those samples were by various tests.

For checking physical effect, compressive strength, effect on weight and surface damages were identified. And for chemical effect, elemental analysis of immersed solution was conducted through ICP-OES. For acidic environment, specimens were immersed in different concentration of Sulfuric acid solutions with 98% conc., 50% and 10% H_2SO_4 solution. In alkaline condition, 40%, 20% and 5% NaOH solutions were prepared. Saline resistivity was identified through preparing solution of 1, 3.2, 5 wt% NaCl solutions.

4.5.1 Durability in acidic condition

Specimens were immersed in Acidic environment for 7 days of immersion period, completion of the period samples were tested for Elemental Analysis. Fig. 23 represent the conditions of specimens of SPC blocks made with 1,5 cyclooctadiene modifier, Trans, trans-1,4 Diphenyl-1,3-Butadiene modifier and Cement Concrete prior to immersion.

SPC-1 (1,5 Cyclooctadiene)

SPC-2 (Trans, trans-1,4 Diphenyl-1,3-Butadiene)

Portland cement Concrete

Figure 23 SPC and Cement Concrete specimens prior to immersion

Fig. 24, 25 and 26 represent the post treatment condition of SPC 1, 2 and PCC blocks. It can be seen that a there is drastically changes over the structure of the Cement Concrete specimens (Fig. 23), while no changes found in a SPC specimens.

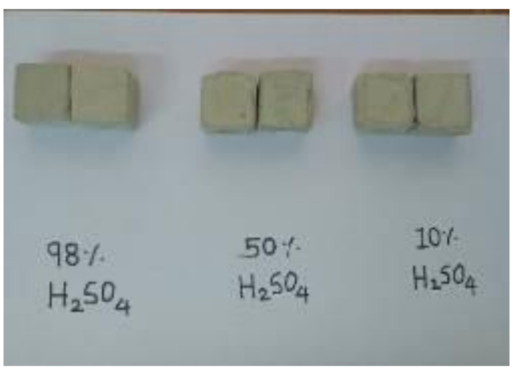


Figure 25 SPC-1 after immersion

Figure 24 SPC-2 after immersion

Figure 26 Portland cement Concrete after immersion

4.5.1.1 Chemical effects for acidic condition

[A] Leaching analysis for SPC-1 and PCC specimens

Specimens of SPC-1 that made with 1,5 cyclooctadiene modified sulfur and PCC were immersed in a solution of 98, 50 and 10% sulfuric acid. Leaching form these specimens have been tested through elemental analysis of acidic solution after completion of immersion period. Elemental analysis done through ICP-OES. Fig.27, 28 and 29 represent graphical interpretation of elements leached through SPC-1 series and PCC specimens. The results only indicate the elements which were leach in maximum amount. It can be see that a there is drastically changes over the structure of the Cement Concrete specimens (Fig 23), while no changes found in a SPC specimens. The leaching analysis give the more ideal result about their resistivity. Aluminium and Iron leached in higher concentration from cement concrete blocks (Fig. 27) compared to Sulfur polymer concrete (Fig. 28, 29). It can be say that Sulfur polymerize concrete stands better resistivity towards Acidic Environment.

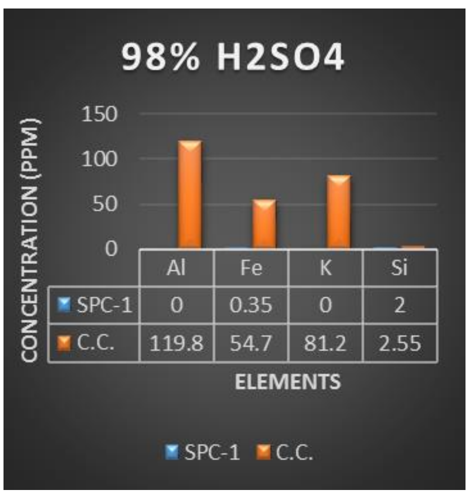


Figure 27 Comparison of elemental analysis of SPC-1 and C.C. immersed in 98 % H_2SO_4

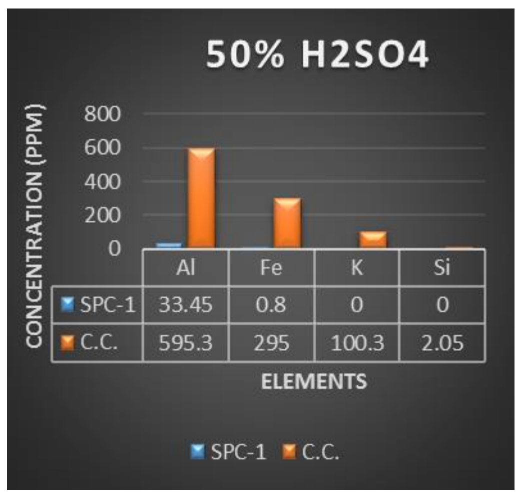


Figure 28 Comparison of elemental analysis of SPC-1 and C.C. immersed in 50% H_2SO_4

Figure 29 comparison of elemental analysis of SPC-1 and C.C. immersed in 10% H_2SO_4

[B] Leachate analysis for SPC-2 and PCC specimens

Leaching through SPC-2 specimens made from Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur calculated on the basis of same experiment conducted for specimens of 1,5 cyclooctadiene modified sulfur. Fig. 30, 31 and 32 represent graphical interpretation of elemental leaching from SPC-1, SPC-2 and Cement Concrete specimens respectively. Nearer same result obtain from the leachate test of SPC-2 and SPC-1, maximum concentration of elements leached through cement concrete specimens. Aluminium and iron leached in higher concentration for both the cases. Also Silica leaching more in 10% H_2SO_4 solution for cement concrete.

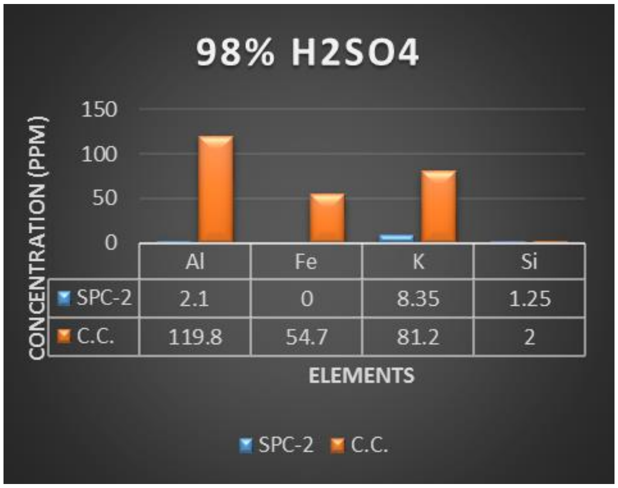


Figure 31 comparison of elemental analysis of SPC-2 and C.C. immersed in 98% H_2SO_4

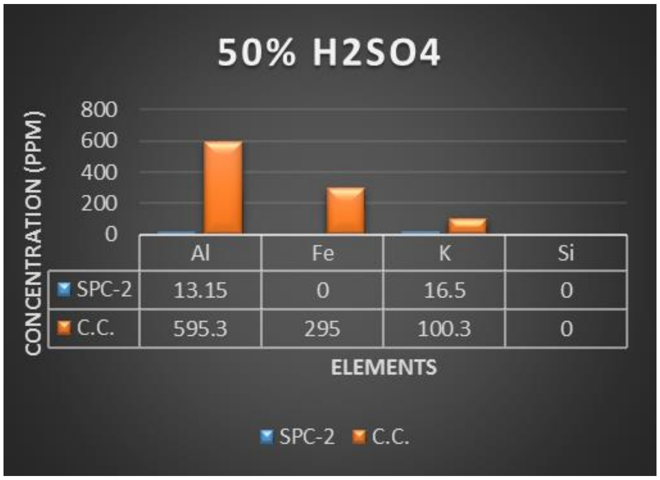


Figure 30 comparison of elemental analysis of SPC-2 and C.C. immersed in 50% H_2SO_4

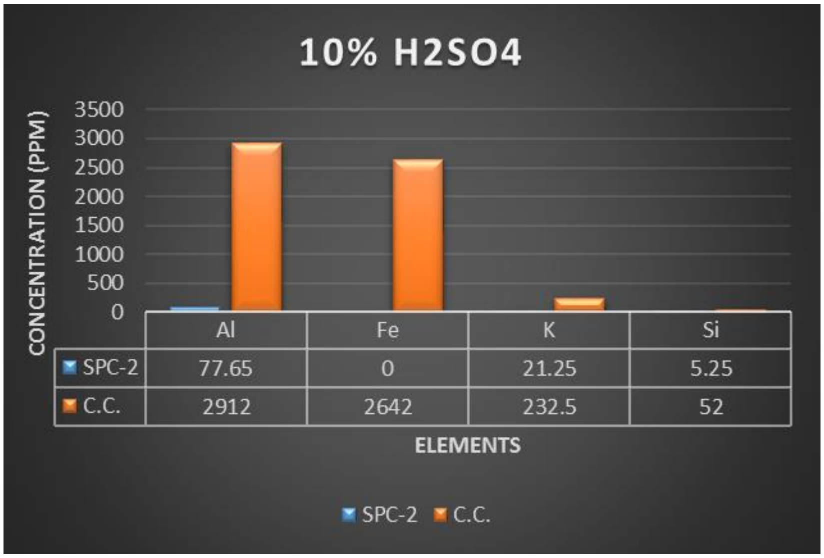


Figure 32 comparison of elemental analysis of SPC-2 and C.C. immersed in 10% H_2SO_4

4.5.1.2. Physical effects for acidic condition

Effects on Compressive strength

[A] Effects on Compressive strength of SPC-1 and PCC

Physical durability tested according to loss or gain of compressive strength of specimens due to effect on extreme environmental condition. Compressive strength of each specimens like SPC-1 and PCC have been taken prior to immersion. Effect can be tested through % loss or gain of strength after immersion.

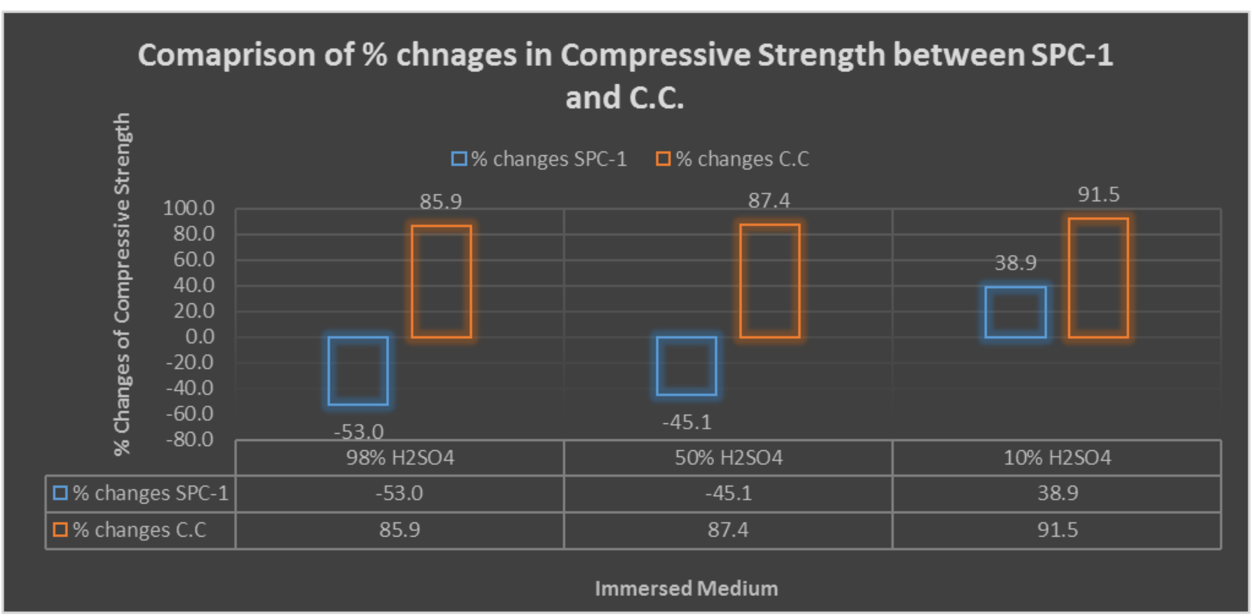


Figure 33 Effect on compressive strength of SPC-1 and C.C. in acidic medium

Fig.33 represent the plot of %changes of compressive strength for SPC-1 and Cement concrete blocks.

It can be identify that strength reduction is increases in case of PCC blocks, as more dilution increase the % of strength is increase, reverse scenario observed with Sulfur polymer concrete, where strength is increases after immersion, that is because concrete is made out of sulfur and it is acidic in nature and immersed medium is acidic, so strength of block is increase with 7 days of immersion. That is helpful application of sulfur composite in industrial purpose where material have to deal with acidic medium. Negative result indicate % strength increase.

[B] Effects on Compressive strength of SPC-2and PCC

Similar study conducted for sulfur composites made with Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur. Fig. 34 represent the plot of %changes of compressive strength for SPC-1 and Cement concrete blocks. Loss of compressive strength is higher fin cement concrete specimen compare to sulfur concrete. Around 86% of strength reduction observed in specimens that immersed in a concentrated sulfuric acid, while for SPC it is only 35.6%. In more diluted conditions, 90% of strength have been reduce for cement concrete specimen but for SPC with same medium only 30% reduction observed.

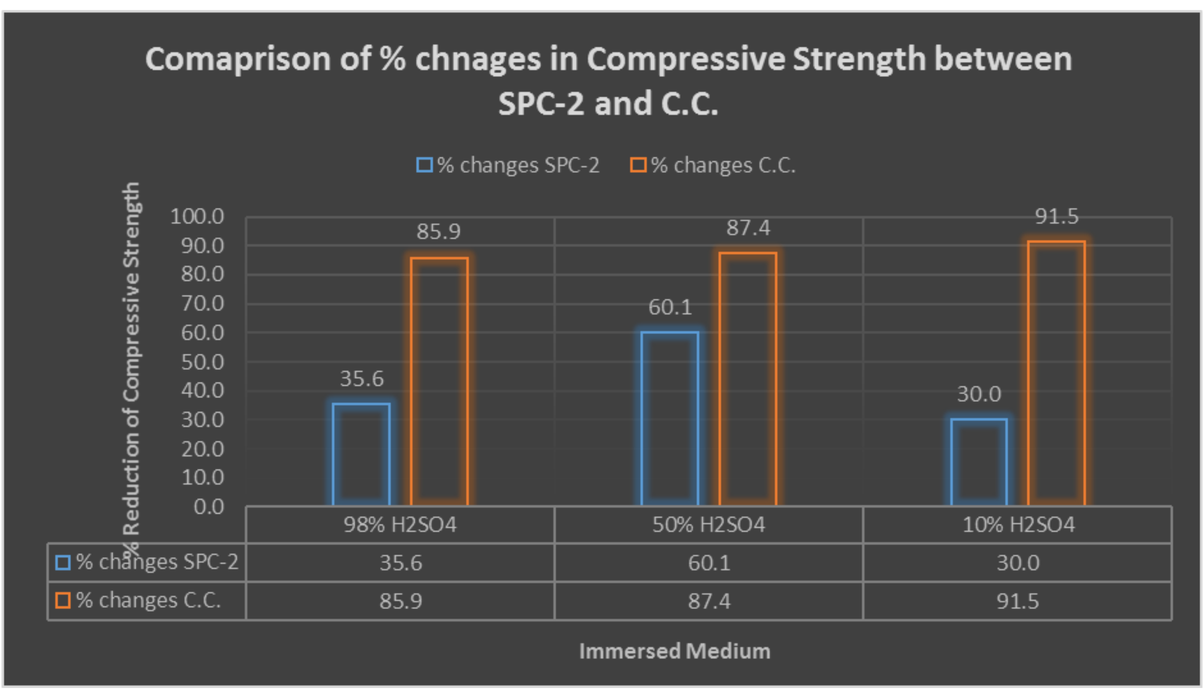


Figure 34 Effect on compressive strength of SPC-2 and C.C. in acidic medium

Effects on weight

Physical resistivity also checked by acidic effects on specimen's weight. Each of the specimens of SPC-1, SPC-2 and PCC series have been pre-weighted before immersion in a selected media. Effect of acidic condition on specimens observed through their weight gain or loss. Weight of immersed specimens calculates, and % of loss or gain calculated through following formula,

Initial weight of the samples taken before immersion and after completion of the period the final weight has been taken. % of Weight changes calculated by

$$\frac{(W_0 - W_f)}{W_f} * 100$$

Where, W_0 = Weight before immersion

W_f = Weight after immersion

Table 7 shows result of weight changes observed between PCC vs. SPC-1 and PCC vs. SPC-2 respectively. Weight of SPC samples after immersion is increases, SPC blocks contain Spent FCC which has tendency to absorb water. There is a higher amount of weight reduction in Cement Concrete samples which were immersed in an Acidic medium, while for SCP minor changes have been identify.

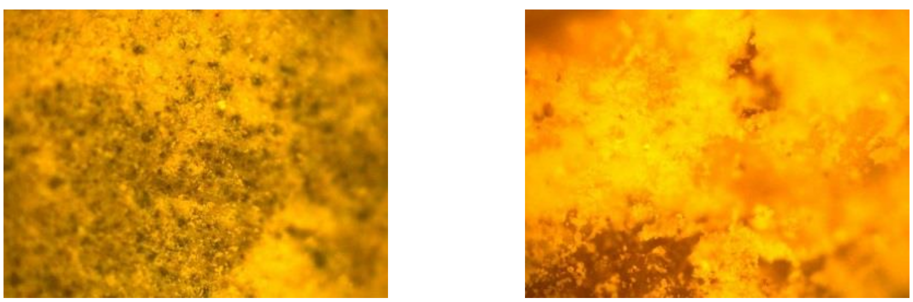
It is noticeable that weight of cement concrete blocks are decreases and in 10% sulfuric acid medium more weight reduction was observed. But for Sulfur polymer concrete blocks, weight of specimens increases after immersion.

Table 7 effects on weight of SPC-1, SPC-2 and Cement concrete after immersion in acidic medium

Acidic medium	% Weight changes in SPC-1	% Weight changes in PCC	% Weight changes in SPC-2
98% H_2SO_4	-0.61	1.98	-0.09
50% H_2SO_4	-0.05	9.30	-1.54
10% H_2SO_4	-0.10	31.30	-0.14

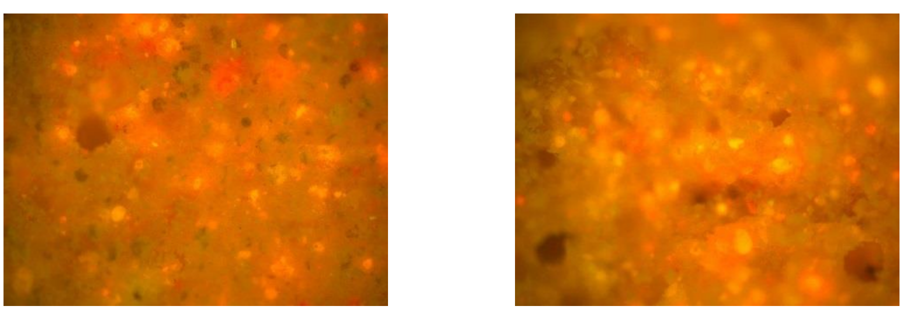
Effects on surface

Effects of acidic conditions was also identified through physical damages occurred on specimens during immersion, H_2SO_4 dispersed in a surface of specimens and it effect on it, that analyzed through Polarized optical microscopy (POM). Representative POM images are shown to observed changes on surface. Fig35, 36 and 37 give the images of affected surface of PCC, SPC-1 and SPC-2 respectively



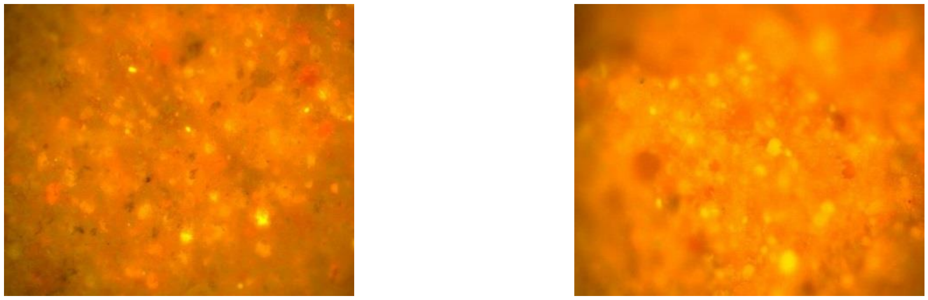
(a) (b)

Figure 35 Details of PCC specimens immersed in 50% H_2SO_4 (a)- Before and (b) after immersion



(a) (b)

Figure 36 details of SPC-1 specimens immersed in 50% H_2SO_4 (a)- Before and (b) after immersion



(a) (b)

Figure 37 details of SPC-2 specimens immersed in 50% H_2SO_4 (a)-Before and (b) after immersion

In case of PCC block, before treated surface is porous. Post acidic treatment, less pores are observed. This may be due to metal sulphate formation on surface after reaction with sulphuric acid which leads to block the pore. Whitening of the surface is also observed which proves the metal surface formation. However no significant changes are seen in both SPC-1 and SPC-2 specimens post acid treatment. This shows, there is no significant effect of acid environment of sulfur composite samples compare to PCC.

4.5.2. Durability in alkaline condition

Second extreme environmental condition is an area where highly alkaline material stored, specifically in industrial purpose. Specimens of SPC-1, SPC-2 and PCC specimens were immersed in 40, 20 and 5% of NaOH solutions for 7 days. Fig. 38, 39and 40 represent the after condition of immersed samples of SPC-1, SPC-2 and PCC respectively. It can be observed that sulfur polymer concrete samples get effected by alkaline condition, but these could not effect on their compressive strength and weight degradation.

Figure 39 SPC Trans, trans-1,4 Diphenyl-1,3-Butadiene sulfur blocks after immersion in alkaline medium

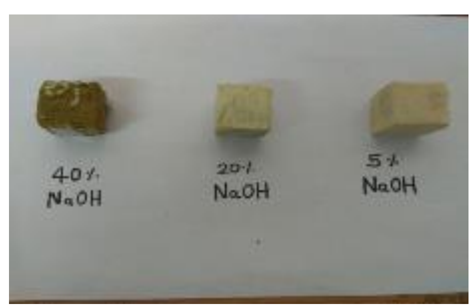


Figure 38 SPC- 1,5 Cyclooctadiene modified sulfur blocks after immersion in alkaline medium

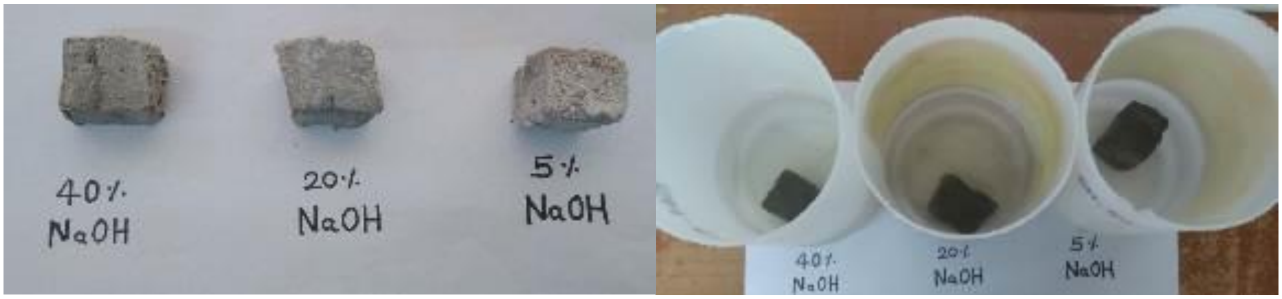


Figure 40 Portland cement concrete blocks after immersion in alkaline medium

4.5.2.1. Chemical effects after alkaline condition

[A] Leachate analysis for SPC-1 and PCC specimens

Leachate test for alkaline condition

Fig.41, 42 and 43 are graphical representation of elemental leaching through 1,5 cyclooctadiene modified sulfur concrete (SPC-1) and PCC specimens because of alkaline medium. Reverse Scenario observed in Alkaline medium, Leaching from SPC-1 blocks more compared to Cement Concrete. Almost all elements leached higher through SPC-1 specimens compared to Cement Concrete, theses is because cement concrete is highly durable in alkaline medium because cement is alkaline in nature. It is made up of $Ca(OH)_2$, that is alkaline base.

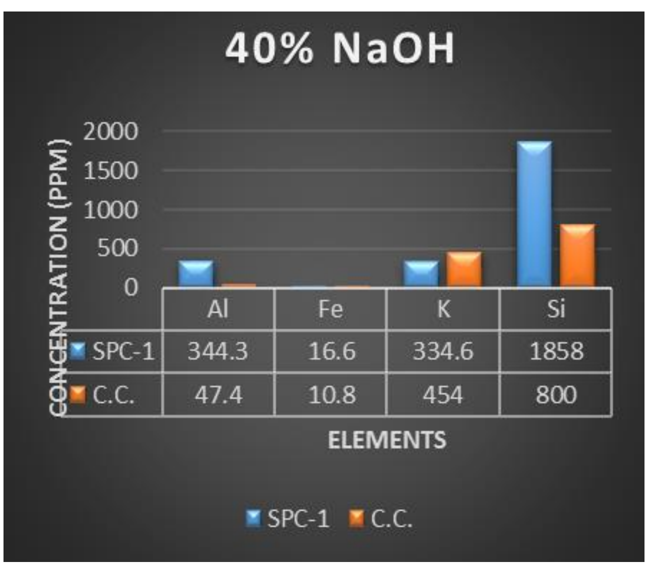


Figure 43 comparison of elemental analysis of SPC-1 and C.C. immersed in 40% NaOH

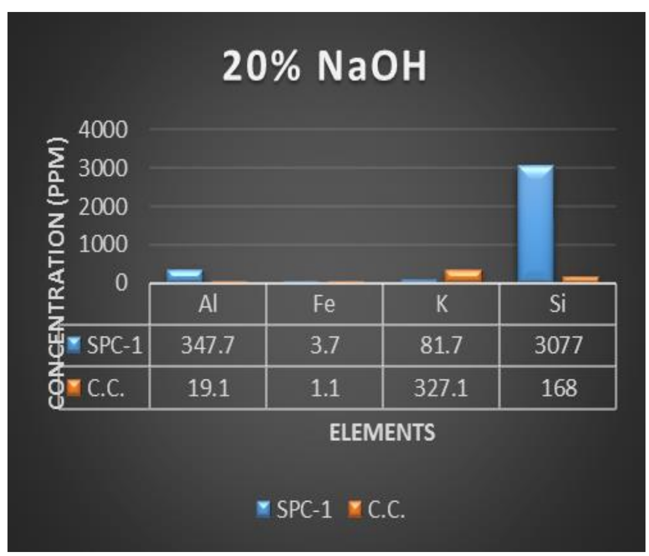


Figure 42 comparison of elemental analysis of SPC-1 and C.C. immersed in 20% NaOH

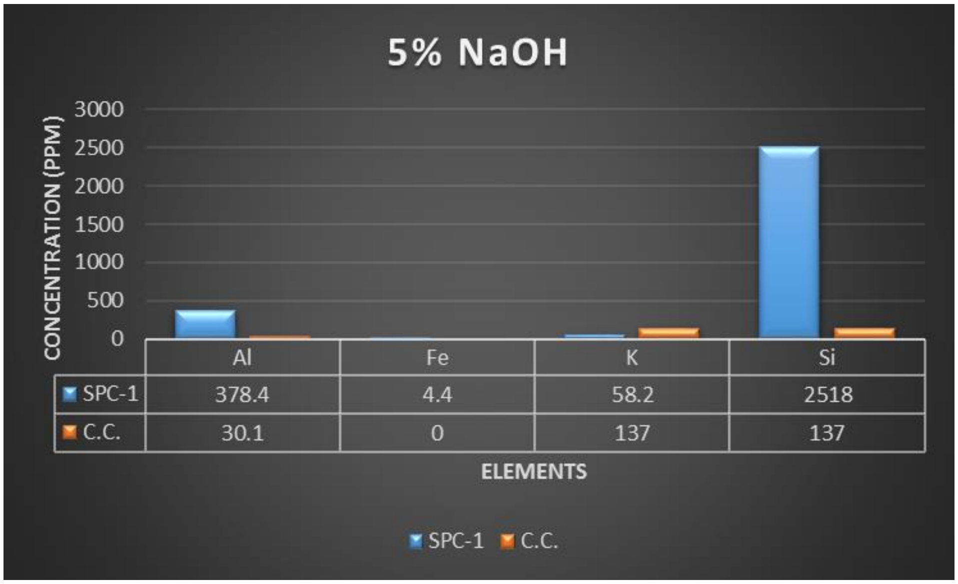


Figure 44 comparison of elemental analysis of SPC-1 and C.C. immersed in 5% NaOH

[B] Leachate analysis for SPC-2 and PCC specimens

Fig. 45, 46 and 47 represent graphical interpretation of elemental leaching through Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur concrete (SPC-2) and cement concrete. Same result obtain from the leachate test of SPC-2 and SPC-1,

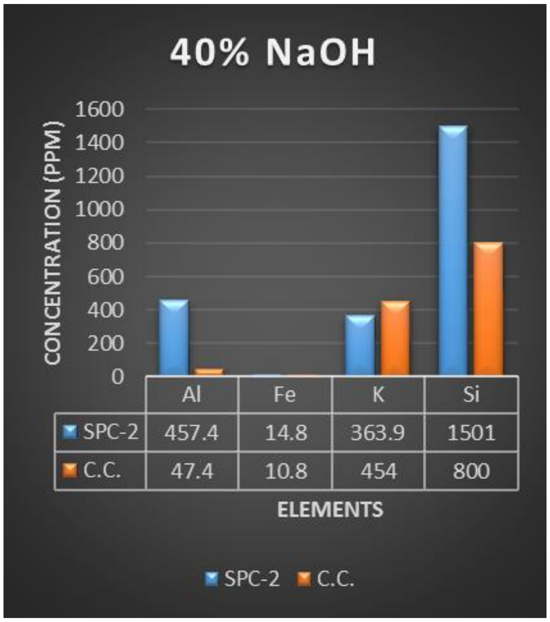


Figure 45 comparison of elemental analysis of SPC-2 and C.C. immersed in 40% NaOH

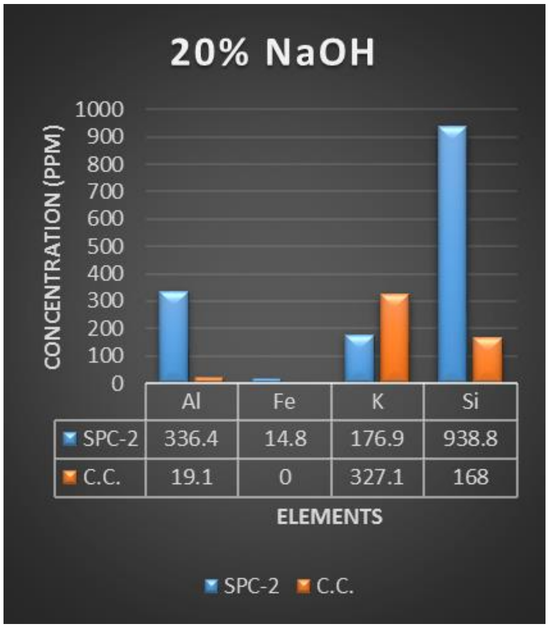


Figure 46 comparison of elemental analysis of SPC-2 and C.C. immersed in 20% NaOH

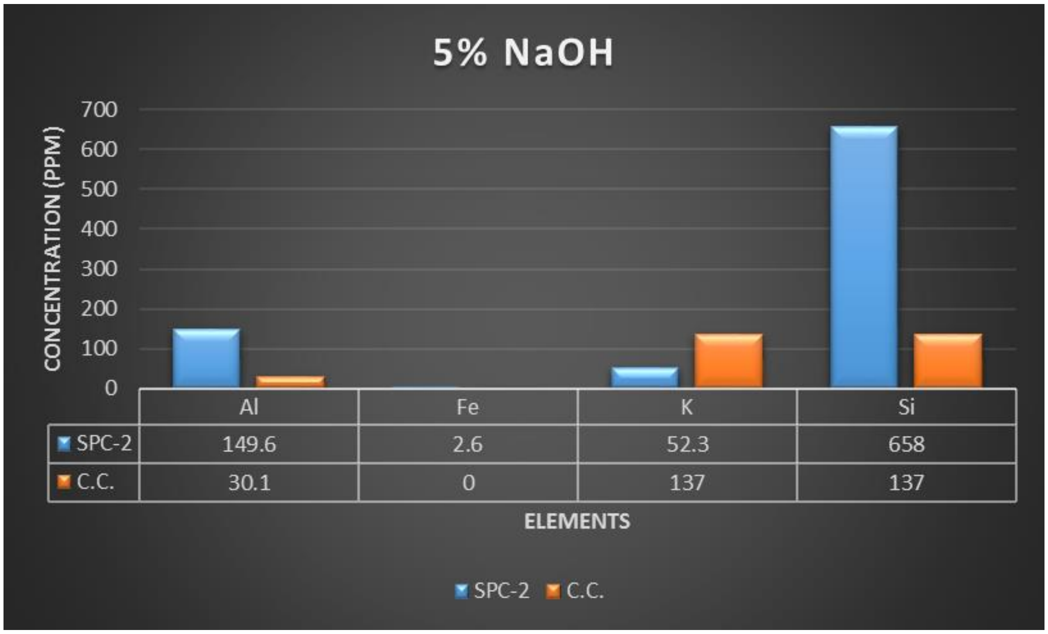


Figure 47 comparison of elemental analysis of SPC-2 and C.C. immersed in 5% NaOH

It is observed that SPC-2 specimens have maximum elemental leaching compare to cement concrete leaching. But iron leaching is same from both type of specimens that is 14.8, 14.8 and 2.6 ppm from sulfur concrete of 40, 20 and 5 % NaOH solution respectively. On the other side iron leaching from cement concrete specimen is lesser but nearer similar with sulfur concrete block. Silica leaching is very high from sulfur concrete that is 1501, 938.8 and 658 ppm form 40, 20 and 5 % NaOH solution respectively. But potassium leaching is more from cement concrete blocks that is 454, 327.1 and 137 ppm from 40, 20, and 5 % NaOH solution respectively, in the case of sulfur polymerized concrete 363.9, 176.9 and 52.3 ppm of potassium leached away from 40, 20 and 5% NaOH condition.

4.5.2.2. Physical effects after alkaline condition

Effects on Compressive strength

[A] Effects on Compressive strength of SPC-1 and PCC

Effects of alkalinity on sulfur concrete and cement concrete measured through changes of compressive strength of each specimens after immersing in NaOH solution with varying concentration. Fig. 48 gives the graphical representation of compressive strength effect. Initial strength have been calculated before immersion.

Physical durability tested according to loss or gain of compressive strength of specimens due to effect on extreme environmental condition. Compressive strength of each specimens like SPC-1 and PCC have been taken prior to immersion. Effect can be tested through % loss or gain of strength after immersion. Fig.45 represent the plot of %changes of compressive strength for SPC-1 and Cement concrete blocks. It can be observed that from fig.48 samples of sulfur concrete get affected by alkaline atmosphere but it does not shows much impact on compressive strength, because strength of blocks still increases after immersion. Where there is drastically changes over strength of cement concrete.

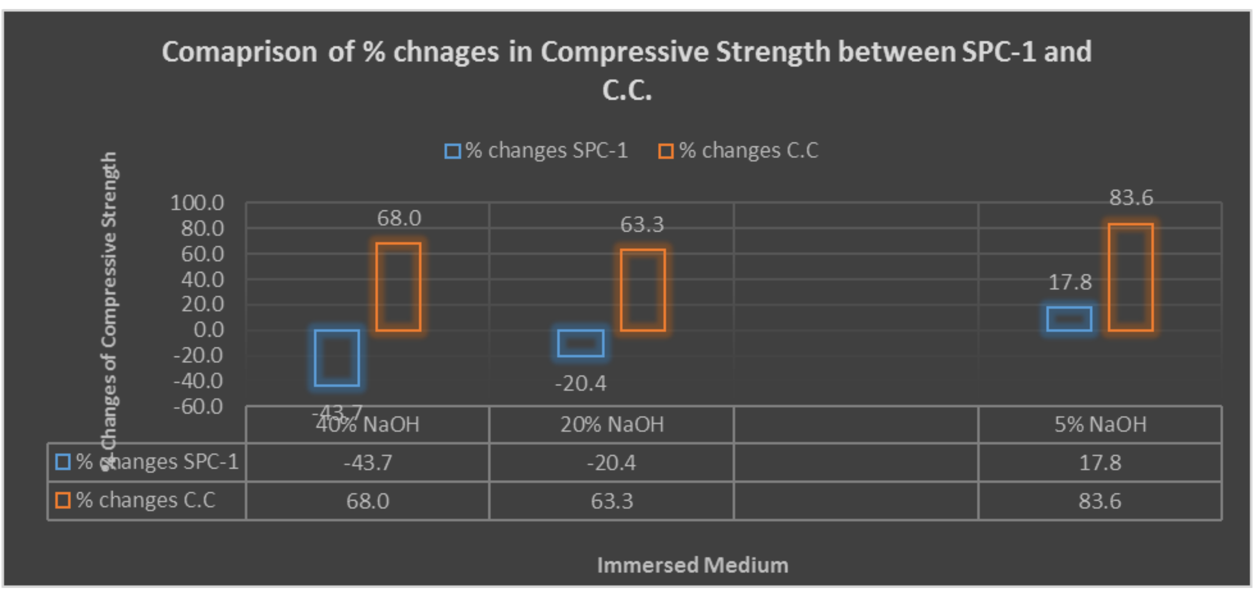


Figure 48 Effect on compressive strength of SPC-1 and C.C. in alkaline medium

Fig. 49 represent the effect on compressive strength of sulfur polymer concrete by Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur and PCC blocks. As the SPC-2 blocks also affected by alkaline conditions but that effects does not identify through compressive strength of sulfur specimens. While with the same cement concrete shows reduction of strength.

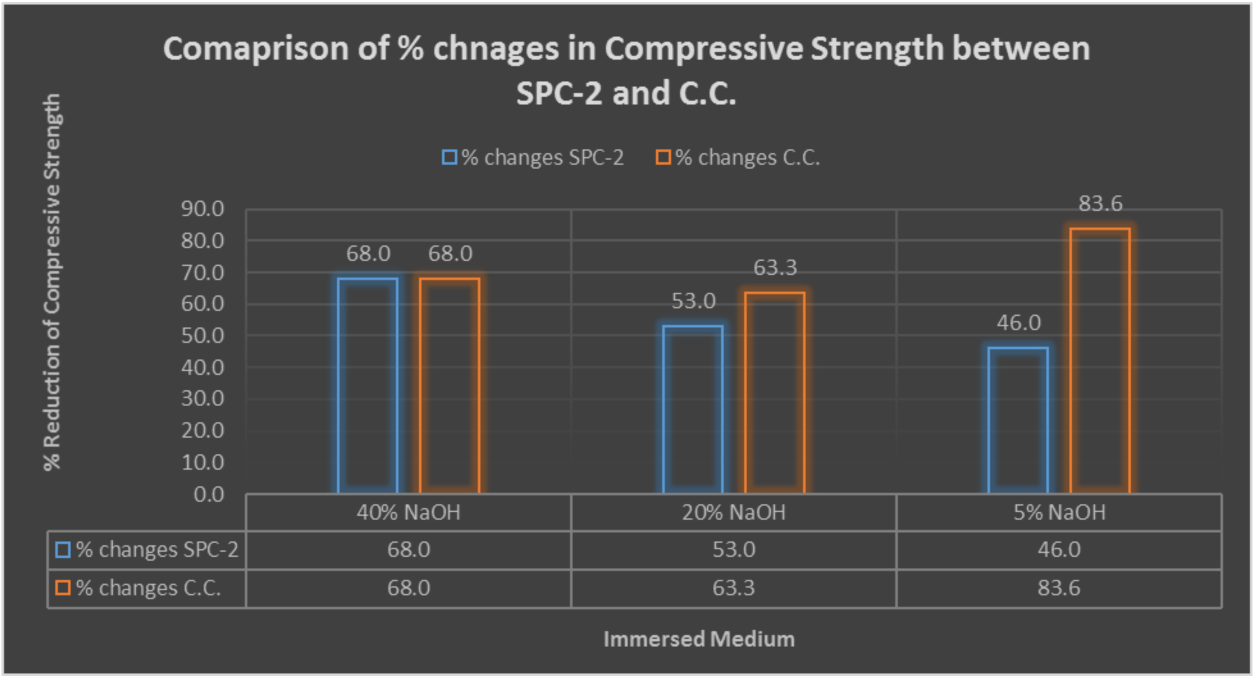


Figure 49 Effect on compressive strength of SPC2 and C.C. in alkaline medium

Effects on weight

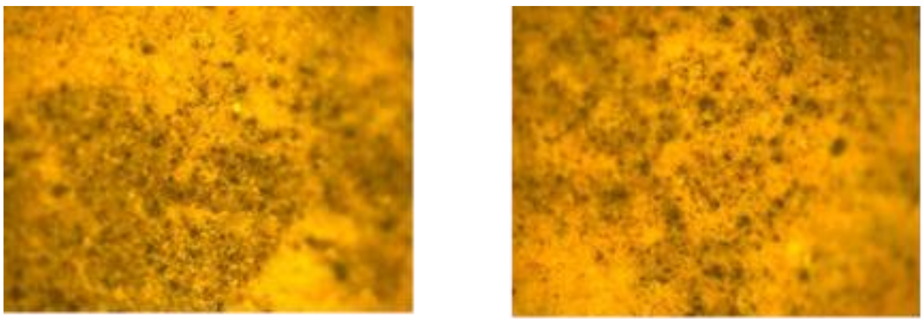
Table no. 8 gives the detail about the % weight changes of SPC-1, SPC-2 and PCC specimens after immersing in alkaline medium. Weight reduction is higher side in case of SPC-2 specimens for 40, and 20 % NaOH medium case but in 5% NaOH solution weight reduction found more from cement concrete. So sulfur concrete with both the modified sulfur shows better efficiency even though in alkaline condition.

Table 8 Table 8 effects on weight of SPC-1, SPC-2 and Cement concrete after immersion in alkaline medium

Alkaline Medium	% Weight changes in SPC-1	% Weight changes in PCC	% Weight changes in SPC-2
40% NaOH	1.58	0.33	19.41
20% NaOH	0.76	0.66	3.93
5% NaOH	0.35	1.68	0.24

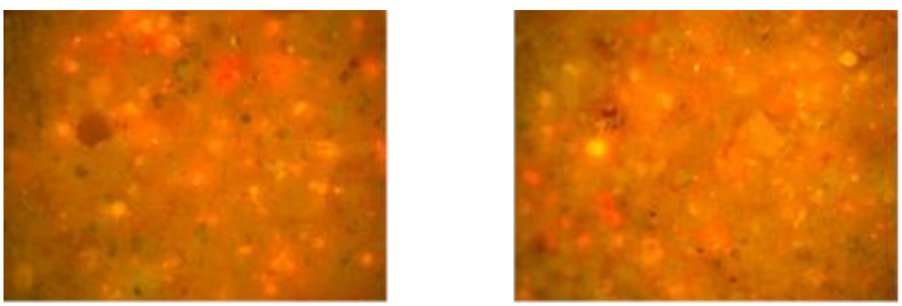
Effects on surface

Effects of alkaline medium was identified through surface damages occurred on specimens during immersion, which was analyzed through Polarized optical microscopy. Fig 50, 51and 52 give representative images of surface after alkaline treatment of PCC, SPC-1 and SPC-2 respectively. No significant changes are observed in PCC, SPC-1 and SPC-2 samples after alkaline treatment.



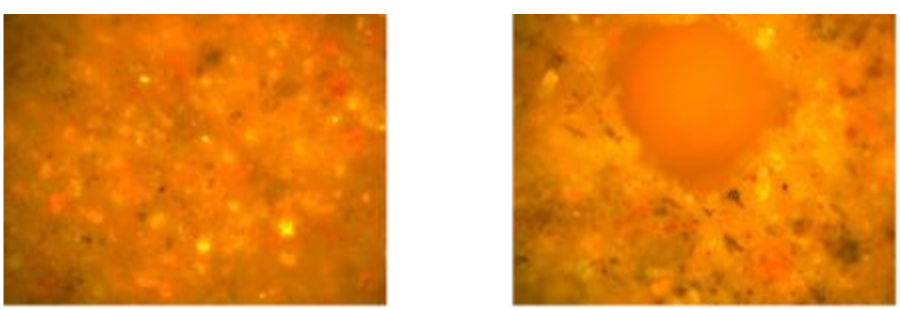
(a) (b)

Figure 50 details of PCC specimens immersed in 5% NaOH (a)-Before and (b) after immersion



(a) (b)

Figure 51 details of SPC-1 specimens immersed in 20% NaOH (a)-Before and (b) after immersion



(a) (b)

Figure 52 details of SPC-2 specimens immersed in 5% NaOH (a)-Before and (b) after immersion

4.5.3. Durability in saline condition

Salinity is very critical issue related to compatibility of cement concrete especially for saline atmosphere. Cement concrete rapidly corroded through saline medium because it corrode to reinforced steel and starts to degrade easily. Sulfur polymer concrete made up of 1,5 cyclooctadiene modified sulfur, Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur and Portland cement concrete immersed in a various saline solutions with 1, 3, 3.2, and 5 % saline solution for same immersion period of seven days. Additional condition provided is comparison with saline water made by 3.2% NaCl solution and de-ionized water. Reason behind making solution of 3.2% NaCl is that salinity of saline water is 3.2 mg/l.

Fig.53, 54 and 55 represent condition of blocks after immersion in saline water for SPC-1, SPC-2 and PCC blocks respectively.

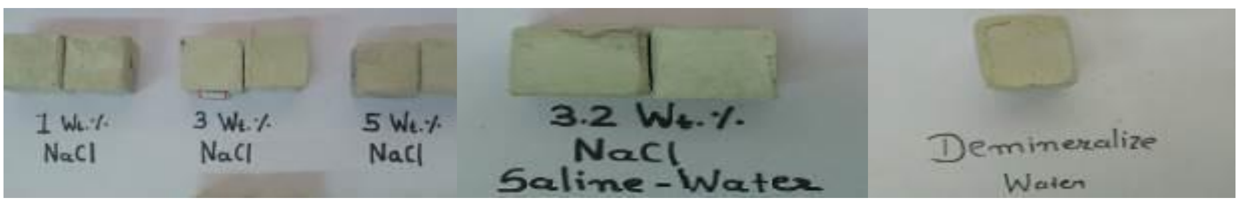


Figure 53 SPC-1,5 Cyclooctadiene modified sulfur blocks after immersion in saline and de-ionized water medium

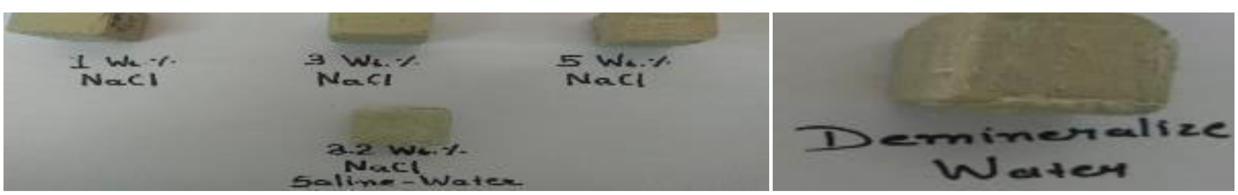


Figure 54 SPC-Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur blocks after immersion in alkaline medium

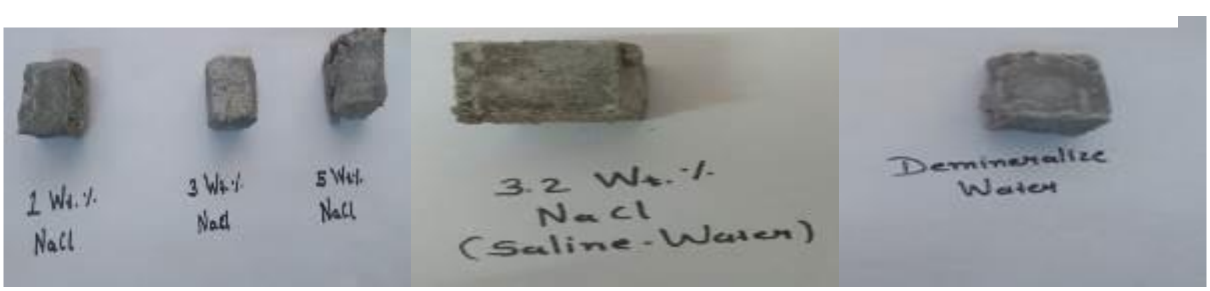


Figure 55 Portland cement concrete blocks after immersion in alkaline medium

4.5.3.1.1. Leachate test for alkaline condition

Elements leaching from specimens because of saline and de-ionized water conditions measured through ICP-OES. Elemental leaching form specimens of 1,5 cyclooctadiene modified sulfur concrete, Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur concrete and Portland cement concrete/ cement concrete immersed in a 1, 3, 3.2 and 5 % NaCl solution and for de-ionized water.

3.5.3.1. Chemical effects after salinity treatment

[A] Leachate analysis for SPC-1 and PCC specimens

Fig.56, 57, 58, 59 and 60 gives data of elemental leaching form specimens of SPC-1 (1,5 cyclooctadiene modified sulfur concrete) and C.C. (Portland cement concrete) immersed in a 1, 3, 3.2 and 5 % NaCl solution and for de-ionized water. It can be find that elemental leaching from cement concrete is maximum compare to sulfur polymer concrete made up of 1,5 cyclooctadiene modified sulfur. In case of sulfur concrete potassium leaching is almost zero ppm, while in the case of cement concrete potassium leaching is very much higher. Aluminum leaching is nearer same from both the specimens either of sulfur concrete and Portland cement concrete specimens. Silica leaching is 77.1, 69 ppm from SPC-1 and Cement concrete respectively for 1% NaCl medium that is same case with de-ionized water case where silica leaching is 31.6, 44 ppm for SPC-1 and PCC blocks.

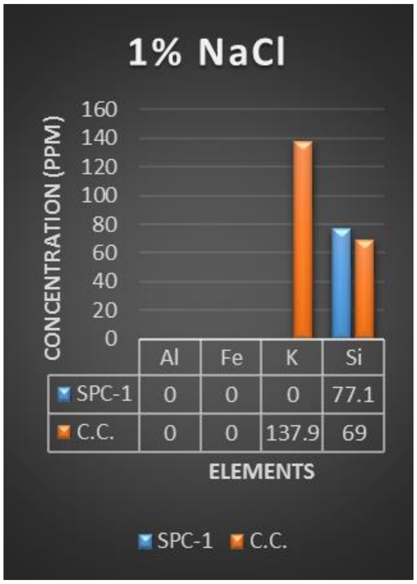


Figure 58 comparison of elemental analysis of SPC-1 and C.C. immersed in 1% NaCl

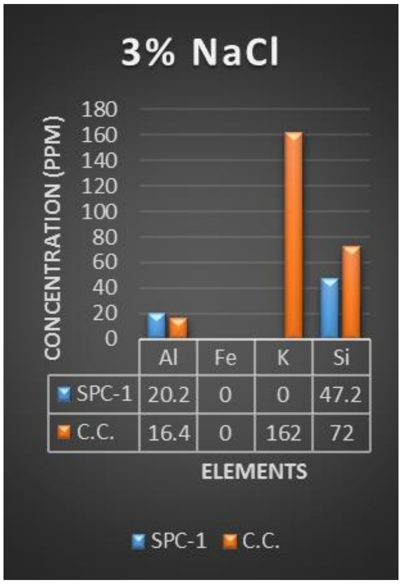


Figure 57 comparison of elemental analysis of SPC-1 and C.C. immersed in 3% NaCl

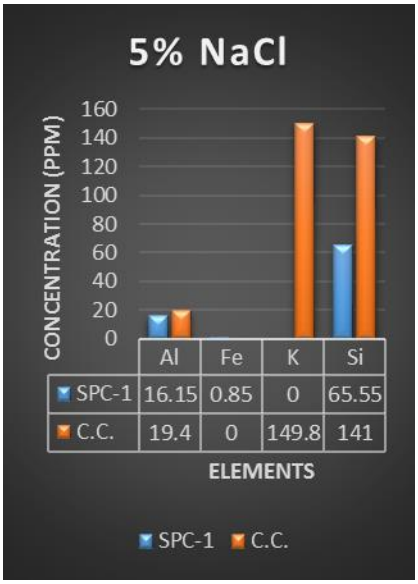


Figure 56 comparison of elemental analysis of SPC-1 and C.C. immersed in 5% NaCl

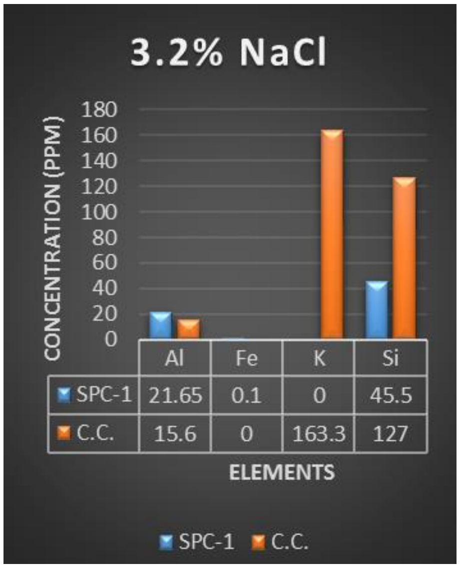


Figure 59 comparison of elemental analysis of SPC-1 and C.C. immersed in Demineralized water

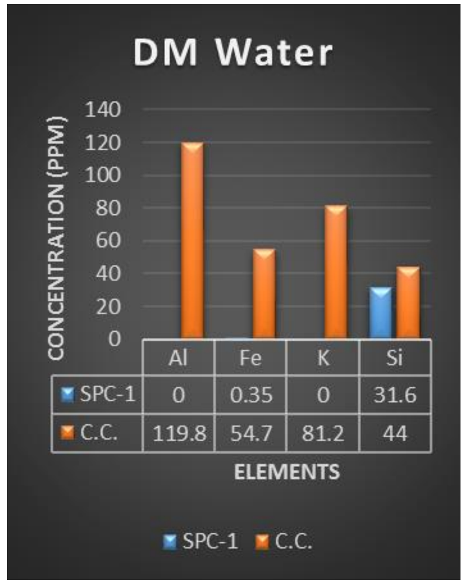


Figure 60 comparison of elemental analysis of SPC-1and C.C. immersed in 3.2% NaCl

[B] Leachate analysis for SPC-2 and PCC specimens

Sulfur polymer concrete made up of Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur concrete (SPC-2) tested for elemental analysis in comparison with Portland cement concrete (C.C.). Fig.61, 62, 63, 64 and 65 represent the graphical data of elemental leaching through SPC-2 and C.C. specimens. Iron leaching is 0 ppm for sulfur specimens and cement concrete specimens. But potassium leaching from cement concrete specimen is 151.8 ppm and 163.3 ppm from 3 and 3.2% NaCl solution, with same condition sulfur concrete shows good resistivity for potassium leaching. Also silica leaching is very much higher from cement concrete compared to sulfur polymerized concrete. Silica leaching from cement concrete is 141 ppm in case of 5 % NaCl solution and 127 ppm in case of 3.2% NaCl solution, but for sulfur concrete amount of silica leaching is very less that is only 1.85 ppm for 5% NaCl solution and 0.95 ppm for 3.2% NaCl solution, so if compare against cement concrete is almost negligible leaching. It can be conclude that sulfur concrete have good resistivity against saline conditions.

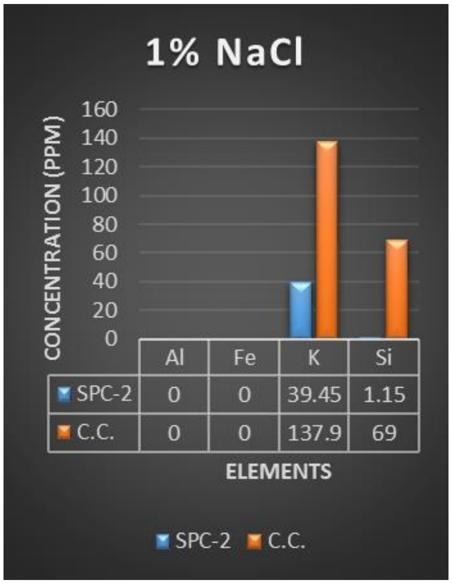


Figure 61 comparison of elemental analysis of SPC-2 and C.C. immersed in 1% NaCl

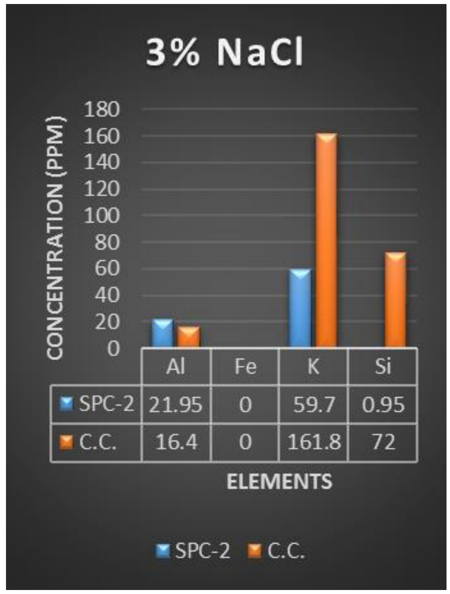


Figure 62 comparison of elemental analysis of SPC-2 and C.C. immersed in 3% NaCl

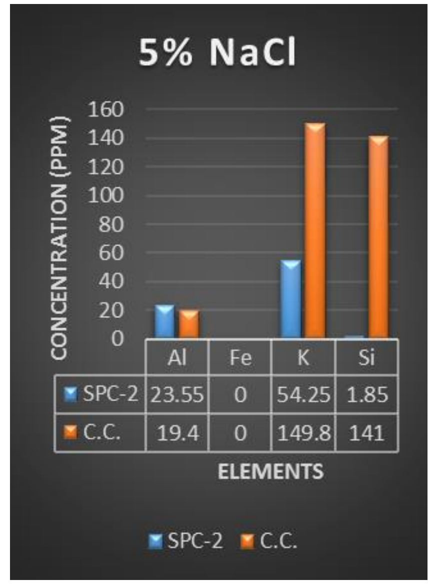


Figure 63 comparison of elemental analysis of SPC-2 and C.C. immersed in 5% NaCl

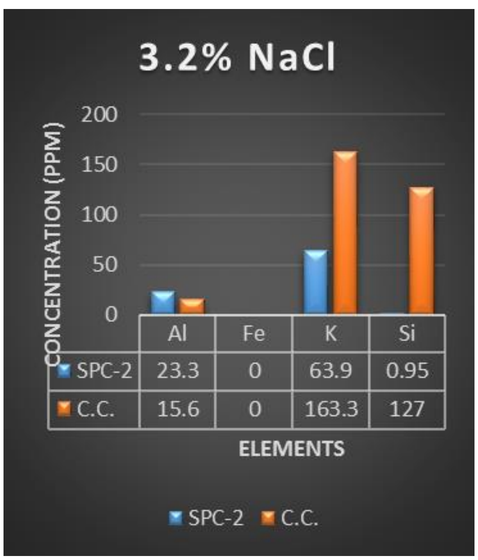


Figure 65 comparison of elemental analysis of SPC-2 and C.C. immersed in 3.2% NaCl

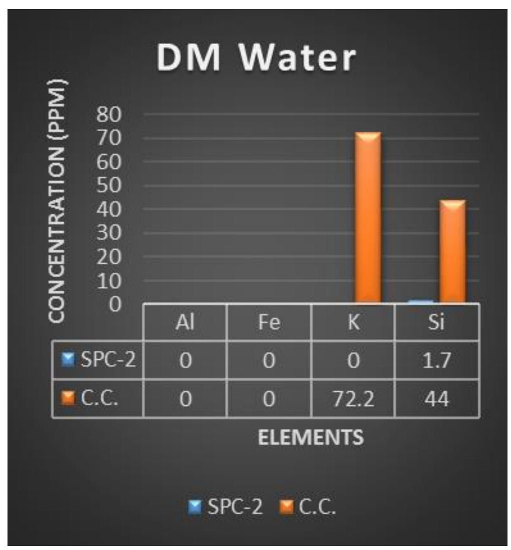


Figure 64 comparison of elemental analysis of SPC-2and C.C. immersed in DM Water

3.5.3.2. Physical effects after salinity treatment

Effects on Compressive strength

[A] Effects on Compressive strength of SPC-1 and PCC

Sulfur polymer concrete of 1,5 cyclooctadiene modified sulfur and cement concrete tested for compressive strength after immersion in saline condition. It is noted that saline water have high impact on compressive strength of cement concrete. So analyzing of compressive strength have very powerful impact on physical effect. Fig. 66 represent the graphical data about effect of compressive strength on each specimens after immersing in saline solution with varying concentration. It can be identify that strength of sulfur polymer concrete cannot very much affected in saline condition, only in case of 1% NaCl solution reduction is higher side, for rest of the medium reduction is very less. But if we compare it with cement concrete there is above 80% reduction of strength is noted for all saline and demineralized water condition, that proves that cement concrete have low resistance towards saline condition.

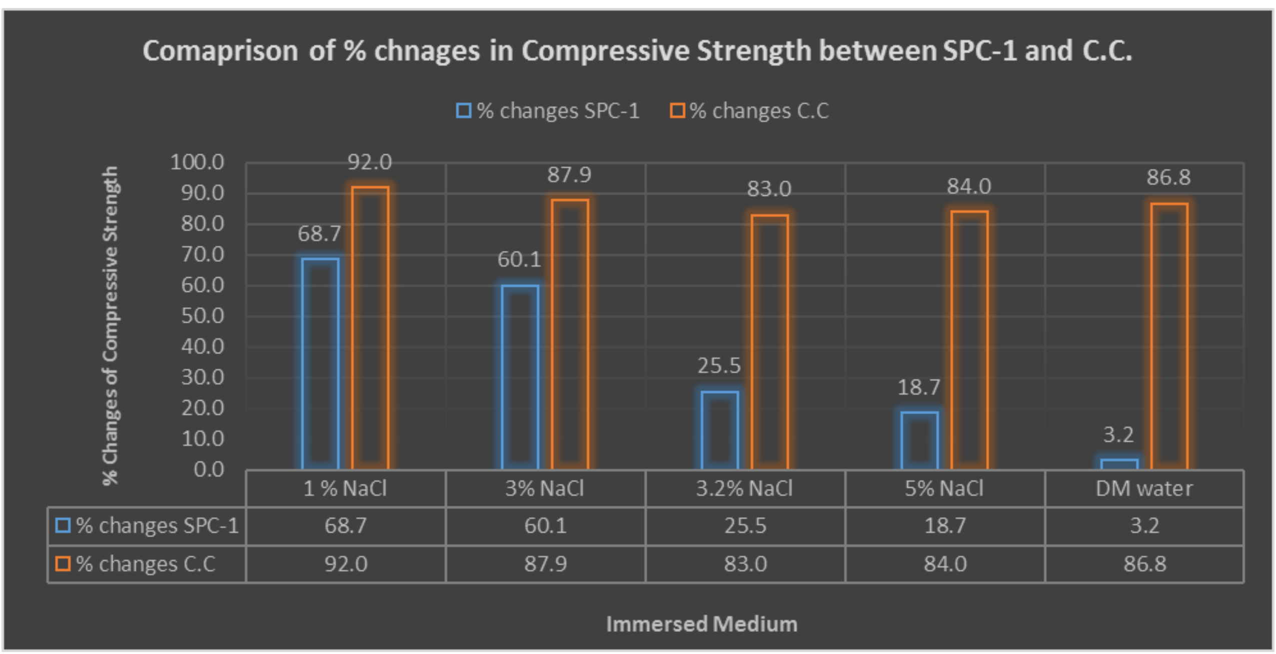


Figure 66 Effect on compressive strength of SPC-1 and C.C. in Saline medium

[B] Effects on Compressive strength of SPC-2 and PCC

Sulfur polymer concrete of Trans, trans-1,4 Diphenyl-1,3-Butadiene modified sulfur and cement concrete tested for compressive strength after immersion in saline condition. It is noted that saline water have high impact on compressive strength of cement concrete. So analyzing of compressive strength have very powerful impact on physical effect. Fig.67 represent the graphical data about effect of compressive strength on each specimens after immersing in saline solution with varying concentration. Here, strength reduction in sulfur concrete is below 50% in all case of salinity, but for cement concrete above 80% of strength is reduced for all saline cases.

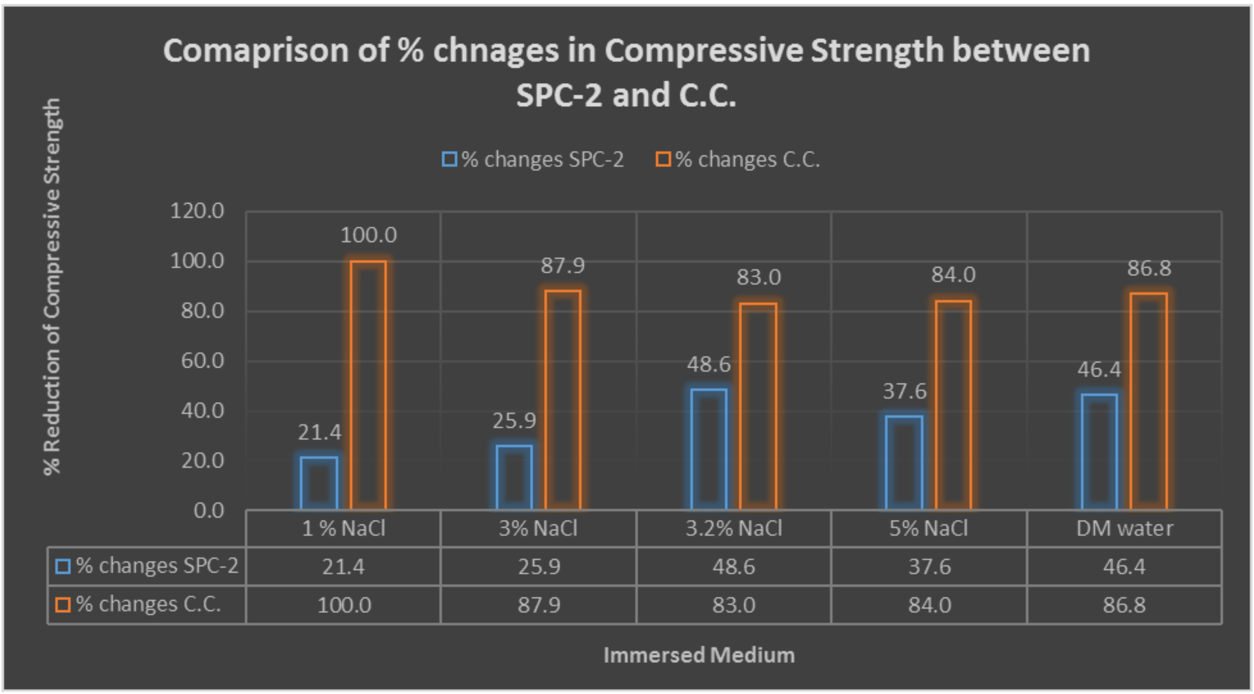


Figure 67 Effect on compressive strength of SPC-2 and C.C. in alkaline medium

Effects on weight

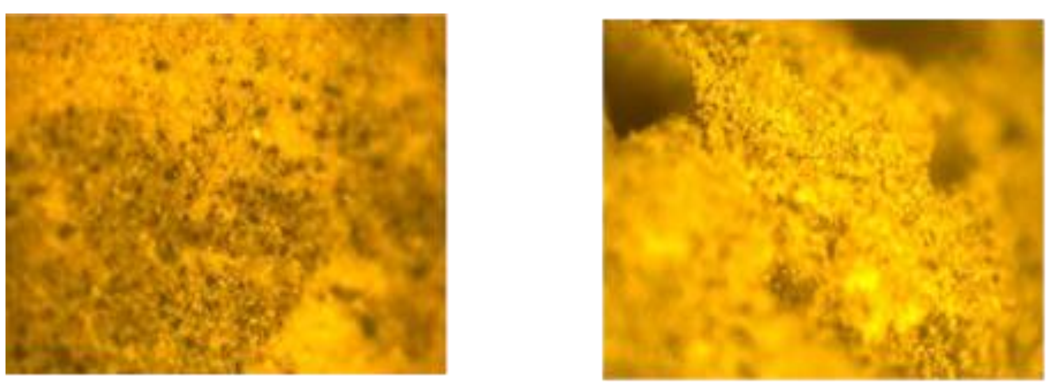
Table No. 9 gives the detail about the % weight changes of SPC-1, SPC-2 and PCC specimens after immersing in alkaline medium. Weight reduction is higher side in case of SPC-2 specimens for 40, and 20 % NaOH medium case but in 5% NaOH solution weight reduction found more from cement concrete. So sulfur concrete with both the modified sulfur shows better efficiency even though in alkaline condition.

Table 9 effects on weight of SPC-1, SPC-2 and Cement concrete after immersion in saline medium

Saline medium	% Weight changes in SPC-1	% Weight changes in PCC	% Weight changes in SPC-2
1% NaCl	-0.04	1.86	0.05
3% NaCl	-0.01	1.59	0.03
3.2% NaCl	-0.06	1.69	-0.07
5% NaCl	0.05	1.64	-2.41
DM Water	0.00	1.71	0.02

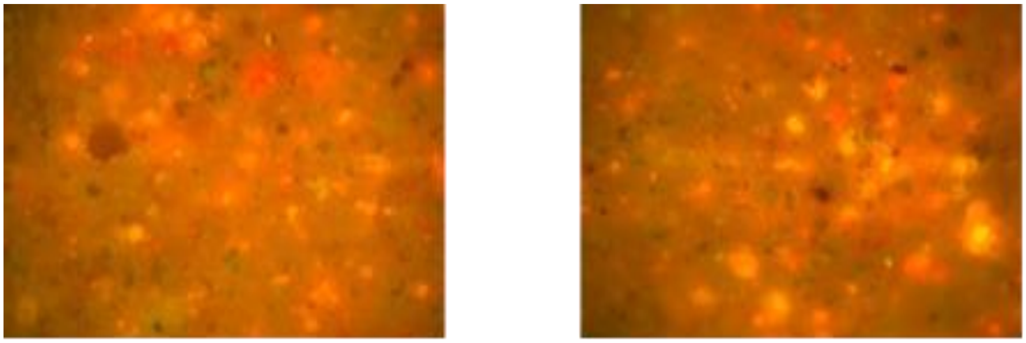
Effects surface area

Physical effects of saline medium on specimens were identified through surface damages occurred on specimens during immersion in Saline solutions, Fig. 68, 69 and 70 give the images from POM of surfaces of PCC, SPC-1 and SPC-2 specimens respectively. In case of PCC specimen more pore observed before treatment, however reduction in pore are observed after NaCl treatment. This may be deposition of salt in the pore. No significant changes are observed in SPC-1 and SPC-2 samples after saline treatment.



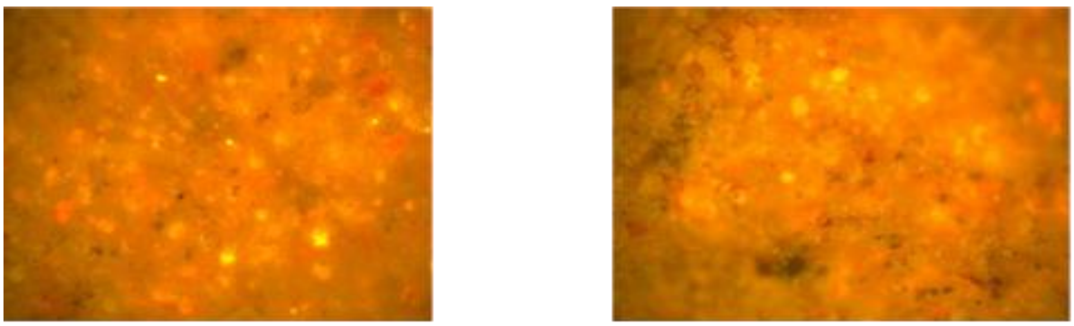
(a) (b)

Figure 68 details PCC specimens immersed in 1% NaCl (a)-Before and (b) after immersion



(a) (b)

Figure 69 details of SPC-1 specimens immersed in 3.2% NaCl (a)-Before and (b) after immersion



(a) (b)

Figure 70 details of SPC-2 specimens immersed in 1% NaCl (a)-Before and (b) after immersion

Conclusion

In this study, sulfur composites prepared from elemental sulfur and aggregates like fly ash, spent adsorbent 4A, normal clay and spent FCC. Selection of suitable aggregate through testing compressive strength of each composite. Sulfur composite with spent FCC had gain maximum compressive strength of 14 MPa, hence it was use for further experimental work.

Sulfur modification applied through use of different organic modifier, 1,5 cyclooctadiene and trans, trans-1,4 diphenyl-1,3-butadiene to resist sulfur in monoclinic phase and to increase compressive strength of composite. Strength increment of 668% and 213% for modified sulfur prepared with 1, 5 cyclooctadiene modified sulfur and trans, trans-1,4 diphenyl-1,3-butadiene modified sulfur respectively in compared to elemental sulfur.

For testing durability of prepared product against Portland cement concrete, cubical specimens of 30×30×30 mm size immersed in different extreme environment as a) Acidic medium of H_2SO_4 solutions b) Alkaline medium of NaOH solutions c) Saline condition by NaCl solutions and d) Hydrated conditions by De-ionized water. Durability of specimens tested through identifying the physical and chemical changes after immersion. Effects on compressive strength, % moisture absorption and leaching of elements included during whole study. Obtained results are summarized as follows.

- ✓ Acidic Condition: Portland cement concrete mainly affected in acidic conditions and especially in case of diluted acid condition compared to SPC. In 50% H_2SO_4 solution 595 and 295 ppm of aluminum and iron leaching occurred respectively from cement concrete specimens, where in case of SPC-1 and SPC-2 iron leaching was 33 ppm for SPC-1 and 13 ppm for SPC-2. Aluminum leaching was 1 ppm from SPC-1 and 0 ppm for SPC-2. 91% of compressive strength reduction observed in PCC specimen in 10% H_2SO_4 solutions, while in case of 39% and 30% reduction observed in SPC-1 and SPC-2 specimens respectively. This prove no diverse effect of acidic condition on prepared sulfur composites.
- ✓ Alkaline Condition: Silica leaching was more in SPC-1 & SPC-2 compared to PCC specimens. Silica leaching form SPC is mainly from spent FCC used for its preparation.

Alkaline condition did not affect mechanically to SPC specimens because very less percentage of compressive strength reduction observed compare to PCC.

- ✓ In case of saline conditions, elemental leaching of silica and potassium from PCC were more compared to SPC Sulfur concrete. Compressive strength reduction was observed more in PCC specimens compared with SPC-1 & SPC-2sulfur concrete specimens for saline environment. In 5% NaCl solutions 84% strength reduction was observed in cement concrete specimens where with same case 18.7% and 37.6% strength reduction was observed in SPC-1 and SPC-2 specimens respectively. Hence proved potential advantage of SPC over PCC in saline environment.

From all that obtained results it can be concluded that prepared SPC (sulfur polymer concrete) is more durable in terms of moisture absorption and compressive strength gain, economical (concrete material made from only refused and by-products of petroleum refinery), easy to handle, less time consuming process and environmental friendly because emission of greenhouse gases from cement production while in case of sulfur concrete no hazardous gases released. Presence of sulfur also SPC also gives hydrophobicity and antifungal activity to sulfur composite material.

Chapter 5

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