Chapter 1
INTRODUCTION

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Rapid industrialization of India led to geometrical rise in the level of air, water, noise and land pollution. Increasing levels of land pollution is one of the major concerns of India which is largely due to the uncontrollable disposal of industrial solids and hazardous wastes. With rapid industrialization, the generation of industrial solid and hazardous waste has increased appreciably and the nature of waste generated has become complex. Their impacts on the ecological bodies are noticeable. In terms of generation, the concern is with the identification of the amounts and types of hazardous wastes developed at each source, with emphasis on those sources where significant wastes quantities are generated.

1.1   Industrial Waste Sludge: Hazardous Waste

Most of the treatment processes normally employed in industrial water pollution control yield sludge from a solid- liquid separation process (sedimentation, flotation, etc.) or produce sludge as a result of a chemical coagulation or a biological reaction. These solids usually undergo a series of treatment steps involving thickening, dewatering, and final disposal. Most of the generated waste sludges from industries are hazardous in nature due to their properties and presence of heavy metals.

Hazardous wastes is a waste that pose a substantial danger immediately or over a period of time to human, plant or animal life are classified as hazardous wastes. A waste is classified by United States Environmental Protection Agency (USEPA) as hazardous if it exhibits any of the following characteristics: (1) Ignitability, (2) Corrosivity, (3) Reactivity, or (4) Toxicity.

Total quantity of hazardous waste generated in Delhi is 5281 TPA, from which 201.30 TPA is recyclable in nature, 1740 TPA is incinerable and about 63 % of the waste is fit for land disposal which constitute quantity of 3340 TPA. One of the major hazardous waste generating industry in Delhi are the **metal surface finishing units** such as pickling, galvanizing, plating, etc., involving cleaning process to eliminate the scale, rust and dust.

1.2   Problems associated with Lime treated Pickling sludge

Metal finishing involves use of a range of different chemical and physical processes to improve either the corrosion resistance and/or appearance of metal surface. Acid Pickling involves immersing of stainless steel sheets into hot acidic solution mainly sulphuric acid or 1:3 ratio of nitric acid & hydrofluoric acid. **Lime treated pickling sludge** is generated when the spent pickling bath liquor is neutralized with lime. The sludge after the filter press is collected in water proof bags and stored usually in the premises in plastic tanks with Hazardous waste labels. Pickling solutions are listed in hazardous waste (management and handling), amendment rules 2002.

The disposal of the hazardous sludge generated pose a serious storage and disposal problem. Due to the presence of heavy metals in the sludge restricts its use on the land and thus requiring safe management and disposal to prevent ground water contamination and soil pollution. Such wastes can be sent to the hazardous wastes landfills only if they meet the prescribed waste acceptance criteria that are based on their leaching properties and heavy metal content and toxicity. In normal practice, this sludge is being stored in leak proof bags and no proper disposal technique is being employed by small and medium industries.

The most severe environmental and health problems associated with these waste originate from high levels of metals such as chromium and nickel due to its potential risk of metal leaching to ground water and surface water and reach in the food chain. Iron exists naturally in the water and has low toxicity. Chromium can exist in many oxidation forms, although, its hexavalent (Cr^{6+}) state is the most toxic one and together with oxygen it forms compounds such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). Human and animal exposure of high nickel dosages and in a certain form is toxic.

1.3   Solidification/ Stabilization with Cementitious binders

Most commonly used technology for disposal of metal sludges and other hazardous wastes is **Stabilisation/solidification (S/S) with cementitious binders**. When cement and other pozzolanic materials are mixed into the waste, they form a network of hydration products that bind and encapsulate the waste into a new monolithic material. Combination of physical and chemical immobilization effects locks the hazardous contaminants, which significantly reduces its leaching potential (cheeseman, 2005).

In the present study, the lime treated acid pickling sludge containing various heavy metals is studied for its utilization and S/S with cement and other pozzolanic material like fly ash to minimize the leaching of heavy metals and to produce a optimum strength concrete. The effect of

1.4   Objectives of the study

The objectives of this study are:

1. To characterize stainless steel pickling sludge.
2. To study the possibility of utilization of lime treated pickling sludge with concrete so as to minimize the leaching of heavy metals present in the sludge as well as to provide optimal strength to the concrete.
3. To study the effect of change of various factors like grade of cement, particle size grading of sludge and percent of cement replaced by sludge and flyash on the leaching and compressive strength of concrete.

Chapter 2
LITERATURE REVIEW

Chapter 2

LITERATURE REVIEW

The volume of wastewater sludges generated by various industries in India has been increasing over the past years. Previously, these sludges were improperly disposed off (illegal dumping). An increase in environmental concerns would not allow an illegal dumping of these wastes which comes in the category of hazardous waste. Thus proper treatment and disposal methods are necessary. Incineration, solidification, and secure landfilling are among common technologies that have been used. Apart from these technologies, waste can also be used for treating other wastes and also for resource recycling and recovery (Gordon, 1994).

The Ministry of Environment & Forests, Government of India, notified the Hazardous Waste (Management & Handling) Rules in 1989 under the provisions of the Environment (Protection) Act, 1986, which was further amended in the year 2000 and 2003 for effective management of hazardous waste (HW). Hazardous waste has been defined in Rule 3 of the Hazardous Wastes (Management and Handling) Amendment Rules, 2003, as any waste, which by reason of any of its physical, chemical, reactive, toxic, flammable, explosive or corrosive characteristics causes danger or is likely to cause danger to health or environment.

2.1   State of Delhi at a Glance

The National Capital Territory of Delhi is spread over an area of 1483 square kilometers. It has a maximum length of 51.9 kilometer and the maximum width of 48.48 kilometer. Out of the total area, 783 square kilometer is rural and 700 square kilometers is urban. It is surrounded on 3 sides by Haryana and to the east, across the river Yamuna by Uttar Pradesh. The major part of the territory lies on the western side of the river Yamuna, only some villages and the urban area of Shahdara lie on the eastern side of the river. Yamuna's greatest length in Delhi is around 33 miles and the greatest breadth is 30 miles. Delhi's altitude ranges between 213 to 305 metres above the sea level.

Delhi houses several small and medium scale industrial clusters which are the major root cause of pollution in river Yamuna. Present study deals with the hazardous pickling waste generated from stainless steel pickling units in Wazirpur industrial area. This industrial area houses about 1800 small scale units mainly dealing with Pickling, rolling, annealing, electroplating, fabrication, etc.

2.2   Hazardous waste generation in Delhi

Total quantity of waste generated in Delhi is around 5281 TPA, from which 201.30 TPA is recyclable in nature, 1740 TPA is incinerable and about 63 % of the waste is fit for land

disposal which constitute quantity of 3340 TPA. (DPCC, 2007). Table 2.1 enlists the sector specific break up of industries in Delhi.

Table 2.1 Sector-Specific Break-up of Industries in Delhi

Sr. No.	Sector	No. of Industries			
		Large	Medium	Small	Total
1.	Printing units	-	-	423	423
2.	Dyeing units	-	-	86	86
3.	Thermal power plant	4	-		4
4.	Metal surface treatment units	-	-	574	574
5.	Wire drawing units	-	-	258	258
6.	Chemical units	-	-	10	10
7.	Adhesives and Paints unit	-	-	24	24
8.	Engineering works	-	-	22	22
9.	Gas manufacturing industry	-	-	2	2
10.	Pharmaceuticals and cosmetics units	-	-	47	47
11	Service station	-	-	239	239
13	Power distribution	2	-	-	2
14	CETP	11	-	-	11
15	Other	-	-	293	293

(Source: DPCC, 2007)

Maximum hazardous waste generating streams are from printing, **metal surface finishing units** and CETPs Waste and residues generated through printing units. Printing residues are incinerable in nature, while sludge generating from metal surface finishing units and the CETP sludge need proper disposal techniques. Table 2.2 gives the quantity of waste generation in Delhi of some type of hazardous wastes.

Table 2.2 Quantity of generation in Delhi of some types of hazardous waste

S.No	Type of waste	Quantity generated (TPA)
1.	CETP Sludge	1424
2.	Chemical sludge form waste water treatment (metal treatment)	20.05
3.	ETP sludge	564.422
4.	Plating metal sludge	261.364
5.	Process waste sludge	125.13
6.	Sludge from staining bath	429.157
7.	Spent acid from batteries	11.7
8.	Spent bath	223.744

(Source: DPCC, 2007)

In Wazirpur Industrial area, maximum amount of hazardous waste of about 790 TPA (15 % of total HW generated) is found to be generated from around 203 industries including CETP plant. Out of 790 TPA of waste generated, around 26 TPA is recyclable, 52 TPA is incinerable and rest is sent for land disposal i.e. around 712 TPA. Major types of industries

located are Metal finishing, dyeing, service station, printing, CETP and dyeing units. (DPCC, 2007)

2.3   Pickling industry- Process

A material needs to go through several processes of manufacturing and finishing before it is finally put to use. These intermediate operations between a raw material and finished product involve use of huge quantities of water which ultimately takes form of waste water after use.

When stainless steel is manufactured, it goes through several metal finishing operations like pickling. Pickling process is carried out prior to galvanizing, electroplating and metal preparation before it is put to use. The aim of this operation is to remove oxide layers (rust and scales) from the stainless steel surface as well as a from the chromium depleted zone underneath. The pickling solution normally consists of a mixture of nitric (HNO_3) and hydrofluoric acid (HF) but sometimes only Sulphuric acid (H_2SO_4) is also taken by industries. During pickling treatment, apart from the oxides removal, metals such as iron, chromium, nickel and molybdenum are also released in the pickling bath solution where they form different complexes with the acids. It is beneficial economically and environmentally to recover and recirculate as maximum as possible of the acids back to the pickling bath. Alloys can also be recovered and reused in the steel making process.

Lagerberg (2011) described how pickling process plays an important role in providing strength and anti-corrosive properties to the stainless steel. Pickling process is aids in the removal of oxide layers and chromium depleted zone on the SS surface which gives the steel deficient strength properties and lower resistance towards corrosion. Pickling can be performed in many ways. The most common pickling methods are electrolytic and acid pickling.

There is a unique and important role of pickling bath acids HNO_3 and HF. Nitric acid removes the oxides and the chromium depleted layer. It is also a very strong oxidant which results in the formation of Fe^{3+}, Cr^{3+} and Ni^{2+} ions. More HNO_3 will therefore be consumed as the metal concentration increases in the bath. Hydrofluoric acid prevents the formation of new oxide layers and the fluorides will form complexes with the Fe^{3+}, Cr^{3+} and Ni^{2+} ions which will precipitate as sludge. It also contributes to the formation of new HNO_3 by providing hydrogen ions (H+). The composition of the bath will thereby change with use during pickling process (Lagerberg, 2011).

2.3.1   Waste water from the pickling process

The pickling process involves the use of large quantities of water for its various operations, thus in turn producing large quantities of waste waters (Fig. 2.1). In general, there are three main waste water streams which can be identified for any pickling operation:

1. Waste Acid stream: water used for achieving the right acid concentrations in the pickling bath and waste water will be generated during regeneration or dumping of

the pickling bath solutions. This stream is usually called waste acid or pickling waste. The flow of the stream will be relatively small but contain a large quantity of metal and acid.
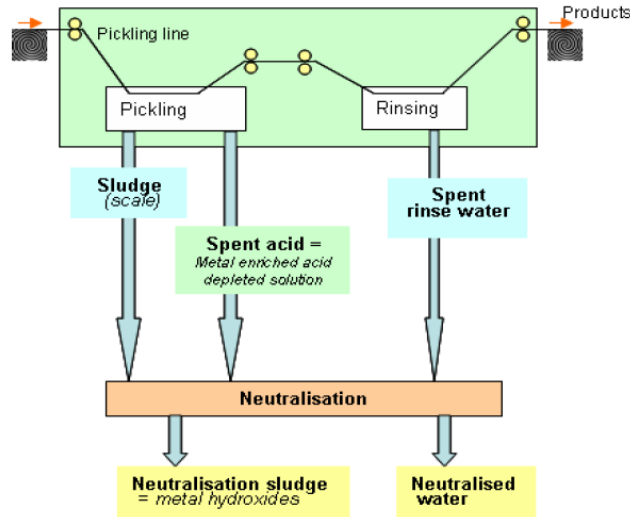

Fig 2.1 Wastewater and sludge generated in the pickling process

2. Spent Rinsing wastewater: water used for rinsing of the stainless steel surface after pickling treatment for removing acid residues and particles. Smaller acid and metal concentration than in waste acid stream from pickling bath but this stream is of larger quantity.

3. Water used for scrubbing of gases generated during pickling (nitrogen oxides and fluorides). An exhaust gas cleaning system/ wet scrubber is employed where a scrubber washes out the fluorides.

The pickling waste acid stream and spent rinse water contain high amounts of metals and are very acidic; therefore they cannot be discharged directly to the river or any water body (Schneiker, 2001).

2.3.2 Lime treated pickling sludge

In this process of pickling of stainless steel sheets, following wastes get generated:

1. Pickling bath waste sludge- It generally settles at the bottom of the tank and is mainly consisting of metal scales, rust, oxides and dust.
2. ETP Sludge- Sludge is generated in the effluent treatment plant where the pickling wastewater is treated with lime or caustic solution. This sludge contains gypsum and metal oxides.

The traditional method for treatment of spent pickling liquor is the neutralisation where pH is raised which leads to chemical precipitation of metals as metal hydroxides. The output from neutralization treatment is sludge with high metal content. For an optimal process management of the generated sludge, it is important to have good measure of the acid concentrations of the waste acid discharged and the appropriate amount of added chemicals for the neutralization of the pickling liquor. If neutralizing agents are added in excess, volume of sludge generated increase considerably with free lime present in sludge with metal oxides. Singhal (2006) undertook a study to minimize the sludge generated during the treatment with lime and sodium hydroxide.

Ito *et al.* (1998) investigated the characteristics and production mechanism of sulfuric acid and nitric- hydrofluoric acid pickling sludge produced in manufacturing of stainless steel. As per this study, stainless steel pickling sludge consists largely of surface scale from stainless-steel strips, i.e. mainly composed of Cr oxides. Also, they showed that the sludge contained twice the Cr concentration that is present in ordinary stainless steel. They had also studied the particles size distribution of H_2SO_4 sludge and HNO_3-HF acid sludge which were reported to be 0.325 and 9.2 mm, respectively. It was also found that HNO_3-HF acid sludge tends to coagulate faster while sulfuric acid sludge essentially takes time to coagulate. The study found the main components of sulfuric acid sludge and nitric–hydrofluoric acid sludge as $FeCr_2O_4$ and Cr_2O_3. The sludge precipitation in the pickling process has been suggested to be that acid penetrates cracks in the scale and dissolves part of scale and the substrate. They further reported that undissolved scale then losses the ability to bond with other scale and the substrate, and settled out in the pickling tanks.

Masahiko *et al.* (1998) determined the characteristics of sulphuric acid sludge and nitric hydrofluoric acid sludge of stainless steel Pickling. For neutralization of the Sulfuric acid sludge and the nitric acid-HF sludge, slaked lime was added up to an equivalent ratio of 1:4. Sulfuric acid sludge after neutralization contained $CaSO_4.2H_2O$, $Ca(OH)_2$, $FeCr_2O_4$ and Cr_2O_3 and nitric acid-HF sludge contained $Ca(OH)_2$, $FeCr_2O_4$, CaF_2 and Cr_2O_3.

The major concerns in electroplating and metal pickling units are discharge of heavy metals in dissolved form, release of untreated toxic gases and suspended solids which if not adequately removed pose great threat to water, air and environment. In treatment process a huge quantity of sludge is generated which contains heavy metals. These sludges cannot be dispose as open land filling because it pollutes land, surface water and groundwater pollution due to leaching property of heavy metals (Vijay & sihorwala, 2002).

Richard & Lewis (1945, 1947, 1948 & 1949) studied the Spent Pickling Liqour treatment with Limestone and limes. They found out that the limestone vary widely in their rate of reaction with pickle liquor, and the rate depends upon particle size, chemical analysis, and a specific reactivity peculiar to a particular limestone. They observed that the rate at which limestone removes iron from pickle liquor is a function of the rate at which ferrous iron oxidizes. In 1948, he also evaluated various neutralizing agents (caustic soda, soda ash, ammonia, high calcium lime, dolomite lime, pulverized high calcium limestone and dolomite lime precipitated chalk, cement dust, acetylene sludge and magnesia) by comparing their

cost, reactivity and settling characteristic of sludge and found out that substantial economy can be realized by high calcium limestone. In 1949, he investigated a new technique for Spent Pickling Liquor neutralization. The alkaline agents used in this investigation were magnesia, high calcium quicklime, and dolomite quicklime. The process consist of feeding pickle liquor at a predetermined constant rate to a bath in a reaction where the temperature was maintain above 750 ℃ and means was provided for efficient aeration, whereby a substantial reduction in sludge volume effected, settling complete in less than an hour, and the vacuum filtration rate increased markedly.

2.4 Disposal Techniques of Heavy Metals Containing Sludge

Improper storage, handling, transportation, treatment, and disposal of hazardous wastes results in an adverse impact on the ecosystem including the human environment. When discharged on land, heavy metals and certain organic compounds are phototoxic and, at relatively low levels of concentration, can adversely affect soil productivity for an extended period of time. Discharge of acidic and alkaline waste affects the natural buffer capacity of surface waters and soils and may result in reduction of the number of species as a whole. Safe and environmentally sound technique of disposal of such wastes needs to be employed to avoid any kind of environmental hazard.

2.4.1 Strategies to be adopted for safe disposal of Hazardous wastes

Today, it is widely recognized that even strict controls on land disposal coupled with modern treatment technology cannot fully solve the nation's hazardous waste problem. It is imperative that the amounts of hazardous waste generated in the first place be reduced and wherever feasible, completely eliminated.

Several options are available for hazardous waste management and disposal. In order of preference, these can be summarized as follows:

1. Eliminate or reduce waste quantities at their source by modifying industrial processes and other techniques.
2. Reclaim and recycle the waste, using it as a resource for some other industrial or manufacturing processes.
3. Stabilize the waste, rendering its non hazardous, by using appropriate chemical, biological, or physical processes.
4. Incinerate the waste, at temperature high enough to destroy or detoxify it.
5. Apply modern land disposal methods, preferably after providing some form of containerization or appropriate treatment.

2.4.2 Illegal dumpsites for hazardous waste in Delhi

Out of 47 dump site in Delhi, 23 are said to be contaminated with Hexavalent chromium whose concentrations are found to be higher than the limit as prescribed in the schedule 2 of Hazardous waste (Management and Handling) Rule, 2003. Waste, found illegally dumped on these locations are mainly containing waste and residues from printing, dyeing, metal finishing, textile, chemical and plastic and paint manufacturing industries. Fig. 2.2 is the news article published in the recent newspaper regarding pollution from pickling industries.
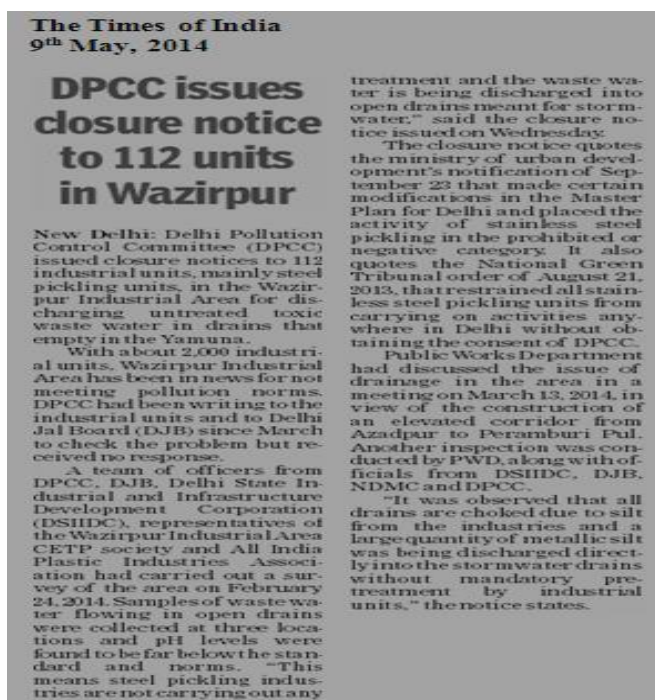

Fig.2.2 News article regarding pollution from pickling units

2.5   Environmental Effects

The most severe environmental and health problems associated with waste water from the steel industry originate from high levels of metals such as chromium and nickel. Iron exists naturally in the water and has low toxicity.

The safe disposal of the chromium wastes generated from steel and other alloy's production, chrome plating, pigments and leather tanning industries to protect human health and environment is an issue of concern (EPA, 1994 & James, 1996).

Chromium concentration up to 130,000 mg/kg has been reported (Bolto, 1984 & Katz, 1994). Among many forms of chromium, Cr(VI) is the most important one because of its toxicity, solubility, and mobility characteristics (Bartlett, 1991 & Bolto, 1984).

2.5.1   Chromium:

Chromium is widely used within different production processes. Out of the total usage, 60-70 % is used for alloys such as in stainless steel and 15 % for chemical industrial process such as pigments and in leather tanning. Due to the extensive utilisation of chromium, it has become a pollutant of air, soil and water (Cervantes, 2001).

Chromium can exist in many oxidation forms, although, the most stable and therefore most common forms are the trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) states, although, they exhibit quite different chemical properties. The Cr^{6+} is the most toxic one and together with oxygen it forms compounds such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). These are the most mobile, toxic and water soluble Cr^{6+}-compounds. Chromate is easily transported across biological membranes in plants and animals and once the compound has enter the cell, Cr^{6+} is reduced to the more stable Cr^{3+} form. The Cr^{3+} state is on the other hand insoluble and thus immobile and in the form of oxides and hydroxides, Cr^{3+} exists mainly bound to organic matter in soil and aquatic environment (Cervantes, 2001).

The Cr^{6+} compounds have shown to induce tumours in animal experiments. Cr^{6+} is more toxic than Cr^{3+} since Cr^{6+} easily enters the cells by the sulphate anion transport system. Exposure to high levels of chromium has been shown to have toxic and carcinogenic effects (Sugiyama, 1992).

2.5.2   Nickel:

Nickel (Ni) can be found in oxidation states from Ni^{-1} to Ni^{+4}; the most common form is the Ni^{+2} state. Nickel compound are used in industry such as electroplating, nickel-cadmium batteries production and stainless steel production. Nickel as contaminants in the environment originates from nickel production, recycling of nickel containing products and waste disposal. Nickel can be found in soil in both soluble and insoluble form. Nickel emitted from anthropogenic sources is mainly in the form of soluble compounds, oxides and sulphides and to a lesser extent in metallic form. In aquatic sources, divalent nickel (Ni^{2+}) is the dominating form of nickel present. The existence of other nickel compounds depends on the pH and possible other binding-partners (Denkhaus, 2002).

Human and animal exposure of high nickel dosages and in a certain form is toxic. Humans are mainly exposed to nickel trough inhalation and ingestion. Vegetables such as cocoa, spinach and nuts have shown to contain high amount of nickel. The metabolism of nickel in the human body has not been totally understood, but the impact on human health is obvious with nickel allergy as a well known reaction. Nickel has also been shown to have carcinogenic effects during long-term exposure, but it might also lead to lung fibrosis and kidney diseases (Denkhaus, 2002).

2.6 Solidification and stabilization of hazardous sludge containing heavy metals with cement/concrete

Orville and Scali (1987) examined the use of fly ash in concrete. They reported that fly ash from coal-fueled thermal power plants are used in concrete primarily because of its pozzolanic and cementitious properties. Most commonly used technology for disposal of metal sludges and other hazardous wastes is Stabilisation/solidification (S/S) with cementitious binders. Solidification is the act of tying up free water in a waste to improve its handling characteristics or to make it acceptable for landfill disposal—''landban restrictions'' (Weitzman, 1990).

Cocke (1990) illustrated the mechanism of stabilization hazardous waste and their chemical binding in cement. He described that the waste components may chemisorb, precipitate, or form a surface compound to any of several cement component surfaces, or it may form inclusions or be chemically incorporated into the cement compounds.

Singh and Garg (1999) studied the blending of cementitious binder materials like fly ash and other industrial wastes. They formulated cementitious binder by judicious blending of fly ash as well as by admixing fly ash with calcined phosphogypsum, flourogypsum, lime sludge and chemical activators of different finenesses. They reported that the development of binder takes place through formation of ettringite, C–S–H gel and C4AH13. The study suggested that the binders are eminently suitable for partial replacement (up to 25% of the cement in concrete) without any detrimental affect on the strength. The results showed that the fly ash can be used in the range from 45% to 70% in formulating these binders along with other industrial wastes to help in mitigating environmental pollution.

Cement based on solidification and stabilization has been effectively demonstrated as treatment technique to isolate hazardous wastes from the environment. Conversion of metal containing solid waste into binding material by S/S has been recommended by Vijay and Sihorwala (2003).

S/S of electroplating sludge was studied by Asavapisit and Chotklang (2004). They used alkali-activated pulverized fuel ash (PFA) as cementitious binder. Their work included the potential for utilization of alkali-activated PFA as solidification binder to treat electroplating sludge. The sludge was solidified by them using 30 wt% of lime and 70 wt% of PFA. Two alkali activators, Na_2SiO_3 and Na_2CO_3 were added by them at 0, 4, 6 and 8 wt%. The results showed that early strength development of lime- PFA cements with Na_2SiO_3 and Na_2CO_3 were considerably higher than those without it. They found that the addition of electroplating sludge had resulted in a reduced strength. They also found that the strength reduction was greater when 4% Na_2SiO_3 activator is used as compared to 8% Na_2CO_3 activator.

When cement and other pozzolanic materials are mixed into the waste, they form a network of hydration products that bind and encapsulate the waste into a new monolithic material. Combination of physical and chemical immobilization effects locks the hazardous contaminants, which significantly reduces its leaching potential (cheeseman, 2005).

Oner *et al.* (2005) conducted a study on strength development of concrete containing fly ash and optimum usage of fly ash in concrete. In this study, the fly ash was added according to the partial replacement method in mixtures. They added fly ash approximately 15%, 20%, 33%, 42%, 50% and 58% of the rest of the cement content as partial cement replacement. It was reported that the efficiency and the maximum content of fly ash that gives the maximum compressive strength were obtained by using Bolomey and Feret strength equations.

Singhal *et.al.* (2007) examined use of the sludge from lime treated spent liquor of pickling unit in the cement concrete and its leaching characteristics. They also undertook a study for using fly ash of thermal power plant with treated spent liquor sludge (TSLS) of pickling unit. They found that with the increase of sludge, the leaching test indicated toxicity and compressive strength of cubes is less than required strength so a sludge amount 7.5% is taken and fly ash content is varied to get the optimum strength.

2.7   Toxicity Characteristic Leaching Procedure (TCLP) Test (USEPA Method 1311)

2.7.1   Scope & Applications:

The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

2.7.2   Method & Apparatus:

TCLP comprises four fundamental procedures:
- Sample preparation for leaching
- Sample leaching
- Preparation of leachate for analysis
- Leachate analysis

For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

Apparatus and Materials required for TCLP:

1. **Bottle Extraction Vessel**- When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste. It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than poly-tetra-fluoro-ethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device is used for initial liquid/solid separation and final extract filtration

2. **Filter Holder**: Filtration device is used for initial liquid/ solid separation and final extract filtration. When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered. These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration.

3. **Filter**: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 μm, or equivalent. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4. **pH Meter**: The meter should be accurate to + 0.05 units at 25 EC.

5. **Laboratory Balance**: Any laboratory balance accurate to within + 0.01 grams may be used (all weight measurements are to be within + 0.1 grams).

Extraction fluid: <u>Glacial Acetic Acid</u>

Dilute 5.7 mL glacial CH_3CH_2COOH with reagent water to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 + 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

Sample Preservation And Handling:

Preservatives shall not be added to samples before extraction. Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs. Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods.

2.7.3 Leaching test by TCLP of waste stabilized with cement/concrete

At present, TCLP is used by the US EPA to evaluate whether a particular S/S process is effective in treating a given waste. Daniali (1990) had conducted a study on S/S inorganic waste (lead and chromium) with latex-modified cement. In this work, efficiency of the S/S technique using latex modified portland matrices containing lead or chromium was investigated. The preliminary results of the physical tests (setting time, compression, freeze/thaw) and TCLP of specimens made of latex modified portland cement indicated considerable improvement relative to those made of regular portland cement.

Factors such as waste form, binder system, curing time and cement-to-waste ratio have been identified to affect the leachability of a waste after an S/S treatment (Bishop 1991, Wang 1996 & Lin 1996). Most treatment methods had aimed to reduce the leaching of chromium to meet the toxicity characteristics leaching procedure (TCLP) extraction limit of less than 5 mg/l because of the complexity of chromium chemistry (Jacobs, 1992 and Vipulanandan, 1997).

Zhang *et al.* (1999) studied the leachability of trace metal elements from fly ash concrete. Their study dealt with the effect of leaching conditions on the leachability of trace metal elements from concrete incorporating two fly ashes. The data from the column-leaching tests to simulate wetting and drying, and batch-leaching tests using buffered acetic acid and synthetic acid rain as leachants, are discussed by them. The United States EPA Regulatory Method 1311-TCLP was used as a reference. The results indicated that, regardless of the type of the fly ash used, the percentage of fly ash, and the water–

cementitious ratio of the concrete, none of the trace metals analyzed (As, Cd, Cr, Cu, Pb, Se and Zn) in the leachates from the fly ash concrete samples exceeded the regulated concentration levels specified in the toxicity characteristic leaching procedure (TCLP) leaching test.

Wang *et.al.* (2000) studied the toxicity characteristic leaching procedure (TCLP) for hexavalent chromium and found out that the leachability of Cr6+ during TCLP test is dependent on the initial Cr^{6+} concentration and the leaching time.

Leaching of heavy metal in the S/S can be considered as a pH dependent and corresponding metal hydroxide solubility controlled process (Li et. al. 2001).

Singhal et.al. (2008) studied the uutilization of pickling sludge with flyash in cement concrete (M20). They found out that 7.5% of sludge and 15% flyash produces better compressive strength and reduced leaching. The reason described for this is the formation of C-S-H gel and reduced leaching due to adsorption on flyash.

2.8   Grades of cement

There are many types of cement in the market to suit every need. Some of them which are included in the revised IS: 456-2000 are as follows:

- Ordinary Portland Cement 33, 43, 53 grade (OPC), 53-S (Sleeper Cement)
- Portland Pozzolana Cement (PPC), both Fly Ash and Calcined Clay based
- Rapid Hardening Portland Cement
- Portland Slag Cement (PSC)
- Sulphate Resisting Portland Cement (SRC)
- Low Heat Portland Cement
- Hydrophobic Cement

Ordinary Portland Cement is graded according to strength as 33, 43 and 53 grade which indicates the compressive strength of cement after 28 days when tested as per IS: 4031-1988, eg, 33 Grade means that 28 days of compressive strength is not less than 33 N/mm2 (MPa). Similarly for 43 grade and 53 grade the 28 days compressive strength should not be less than 43 and 53 MPa respectively. 43 and 53 grade are also being introduced in PPC and PSC shortly by the Bureau of Indian Standards (BIS).

Table 2.3 gives some of the important requirements to be fulfilled by various types of cements. Basic components of cement are given in Table 2.4.

Table 2.3 Some important requirements to be met by various types of cement

S no	Type of cement	IS Code	Fineness (m2/kg) (min)	Setting Time in minutes		Soundness		Compressive Strength in MPa		
				Initial (min.)	Final (max.)	Le Chatelier (mm)	Auto Clave (%)	3 days	7 days	28 days
1	OPC 33	269 : 1989	225	30	600	10	0.8	16	22	33
2	OPC 43	8112 : 1989	225	30	600	10	0.8	23	33	43
3	OPC 53	12269 : 1987	225	30	600	10	0.8	27	37	53

(Source: Ultratech Cements)

Table 2.4 Basic components of Cement

1.	SiO_2	17-25 %
2.	Al_2O_3	4-8%
3.	Fe_2O_3	0.5-0.6 %
4.	CaO	61-63 %
5.	MgO	0.1-4.0 %
6.	SO_3	1.3-3.0 %
7.	$Na_2 + K_2O$	0.4-1.3 %
8.	Cl	0.01-0.1%

There are four major compounds in cement and these are known as C_2S, C_3S, C_3A & C_4AF, and their composition varies from cement to cement and plant to plant.

In addition to the above, there are other minor compounds such as MgO, TiO_2, Mn_2O_3, K_2O and N_2O. They are in small quantity. Of these K_2O and Na_2O are found to react with some aggregates and the reaction is known as Alkali Silica Reaction (ASR) and causes disintegration in concrete at a later date.

The silicates C_3S and C_2S are the most important compounds and are mainly responsible for the strength of the cement paste. They constitute the bulk of the composition. C_3A and C_4AF do not contribute much to the strength., but in the manufacturing process they facilitate combination of lime and silica, and act as a flux. In a typical Portland cement, the composition of mineralogical compounds could be as given in Table 2.5.

Table 2.5 The extent of chemical compounds in cement

S no	Compound	Composition as %
1	C_3S	48-52 %
2	C_2S	22-26 %
3	C_3A	6-10 %
4	C_4AF	13-16 %
5	Freelime	1-2 %

Table 2.6 Role of compounds on properties of cement

Characteristic	C_3S	C_2S	C_3A	C_4AF
Setting	Quick	Slow	Rapid	-
Hydration	Rapid	Slow	Rapid	-
Heat Liberation (Cal/gm) 7 days	Higher	Lower	Higher	Higher
Early Strength	High up to 14 days	Low up to 14 days	Not much beyond 1 day	Insignificant
Later Strength	Moderate at later stage	High at later stage after 14 days	-	-

Hydration of Cement:

When water is added to cement, the paste is formed due to chemical reaction, which hardens into rock like mass over a period of time. Compounds like C_3S and C_2S react in the presence of moisture and fully hydrated reaction can be expressed as

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3Ca(OH)_2$$
$$2C_2S + 4H \rightarrow C_3S_2H_3 + Ca(OH)_2$$
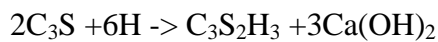
$C_3S_2H_3$ (Calcium Silicate Hydrate) becomes a hard mass over a period of time and normally called as C-S-H gel. While C_3S contributes to most of the strength development during the first two weeks, C_2S influences gain of strength after two weeks. However, in the long term (over a year) the contribution to strength is same for equal individual weight.

Table 2.7 Cements with their uses

S no	Type of cement	End Use
1	OPC 33	Used for general civil construction works under normal/mild environmental conditions. OPC 33 grade is normally not used where high grade concrete is required due to limitations of its strength. Nowadays this variety is not generally produced
2	OPC 43	Nowadays 43 grade is being used widely for general construction work. However, 43 grade OPC is gradually being replaced by blended cements.
3	OPC 53	Used in RCC and pre-stressed concrete of higher grades, cement grouts, instant plugging mortars etc. where initial higher strength is the criteria

(Source: Ultratech Cements)

Chapter 3

MATERIALS AND METHODS

Chapter 3

MATERIALS AND METHODS

3.1   MATERIALS

3.1.1 Lime treated Pickling Sludge

The lime treated pickling sludge is taken from a factory (small scale industry) situated in Wazirpur Industrial Area, New Delhi. The stainless steel (SS) sheets are pickled in an Acid Pickling Tank **(Fig. 3.1 (d))** containing Sulphuric Acid (98% purity) usually after 8 times dilution. The sheets are immersed in the hot acidic solution for about 4-5 minutes. **Fig. 3.1 (b)** shows the stainless steel sheet before and after the pickling process. This steel finishing operation cleans the sheet's surface by removing the scales, rust and dust. The SS pickling line consist of a pickling tank containing hot acidic solution, a rinsing tank containing normal water and a drying unit which dries the sheets (**Fig. 3.1 (c)).**

Lime treated pickling sludge is generated in the factory's ETP where they neutralize the generated wastewater from pickling and rinsing tank with lime. The sludge after the filter press is collected in water proof bags and stored in the factory premises in plastic tanks with Hazardous waste labels. Slight alkaline sludge is obtained in the process (**Fig. 3.1 (e & f)**).

Sludge was collected in a water proof bag from the factory and taken to college laboratory for further study and analysis.

3.1.2 Cement

Ordinary Portland cement of three different grades was used in the study i.e. OPC Grade 33 of Ambhuja Cements, OPC Grade 43 of Shree ultra cements and OPC Grade 53 of Binani cements. The cements were obtained a day before the experimentation and cube making so as to maintain its quality and characteristics.

3.1.3   Fly ash

Fly ash used in the study is collected from a CPWD construction site which indicated the source as Dadri, Thermal Power Plant. An unopened bag of Flyash was taken for the study.

3.1.4   Coarse and fine aggregates

Coarse and fine aggregates were obtained from a local building materials shop. Badarpur and Yamuna sand were not preferred for the study. Fine Sand from Bhiwadi, Rajasthan was taken for the experimental work. Coarse aggregates of 90% lying in size range of 20mm-10mm was taken.

Fig 3.1 Industrial Visit to the Stainless Steel Pickling Industry in Wazirpur Industrial Area. (a) Industry premises, (b) Stainless steel sheet before and after pickling, (c) Pickling Line, (d) Pickling bath, (e) Filter press of ETP and (f) Field analysis of pH of sludge using filter paper.

3.2   RESEARCH METHODOLOGY

Following research methodology/ steps have been followed in conducting this study. This methodology fulfills the objectives listed in Section 1.4 of this report.

The steps followed are:

1. Material collection
2. Sludge characterization
3. Design of experiments by Taguchi Methodology
4. Making of M20 concrete mixed with sludge and flyash
5. Testing of Cubes for their compressive strength after 7 and 28 days of curing.
6. Toxicity Characteristic Leaching Procedure (TCLP) test of designed concrete cubes after 28 days of curing and Testing of heavy metal concentration in leachate extract obtained.
7. TCLP test on sludge and test for heavy metal concentrations
8. Multi-response optimization by Taguchi Methods:
   a. Computation of results by Analysis of Means (ANOM) for estimating the optimal levels of control factors (type of cement, % of sludge, % of flyash and particle size grading of Sludge) which provides optimum response i.e. high compressive strength and maximum heavy metal immobilization in concrete matrix.
   b. Computation of results by Analysis of variance (ANOVA) for determining the percent contribution of each factor.

3.3   METHODS

3.3.1   Sludge Characterization

Sludge (Fig. 3.2) was characterized as per the standard methods for the examination by APHA.

Fig 3.2 Dried Lime treated pickling sludge

3.3.1.1 pH

pH estimation was done using pH meter.

3.3.1.2 Moisture Content

Moisture content was analysed by gravimetric analysis. Following steps are involved:

1. Weigh a crucible and record the weight as W1.
2. Weigh 10 gm of sludge into crucible and record weight as W2.
3. Dry for 5 hrs at $100 \pm 5°$ C in an oven.
4. Allow to cool in a desicator and weigh and record weight as W3.
5. Percent moisture content is calculated by following formula:

$$\% \text{ Moisture content} = \frac{W2 - W3}{W2 - W1}$$

3.3.1.3 Specific Gravity

Specific gravity of the sludge was determined by the following steps:

1. Weigh a volumetric flask (W1)
2. Fill water in it. Weight the flask and the water. (W2)
3. Empty the flask and add sludge sample. Weigh the flask and the sludge (W3)
4. Add water and weigh (sludge + flask + water) (W4)

$$\text{Specific Gravity} = \frac{W3 - W1}{(W2 - W1) - (W4 - W3)}$$

3.3.1.4 Sieve Analysis

Sludge was dried in the oven at $100 \pm 5°$ C. Sludge was sieved on standard sieves (Fig. 3.3) of 4.75mm, 3.26mm, 1.18mm, 0.6mm, 0.3mm and 0.075mm. The sieves are shaken for 15 -20 min.

Fig. 3.3 Sieve analysis of sludge

3.3.1.5 Heavy Metal Analysis

Heavy metals are analysed in the sludge using two techniques:
1. Atomic Absorption Spectrometer (AAS)
2. Colorimetric and Spectrometer method

Atomic Absorption Spectrometer (AAS)

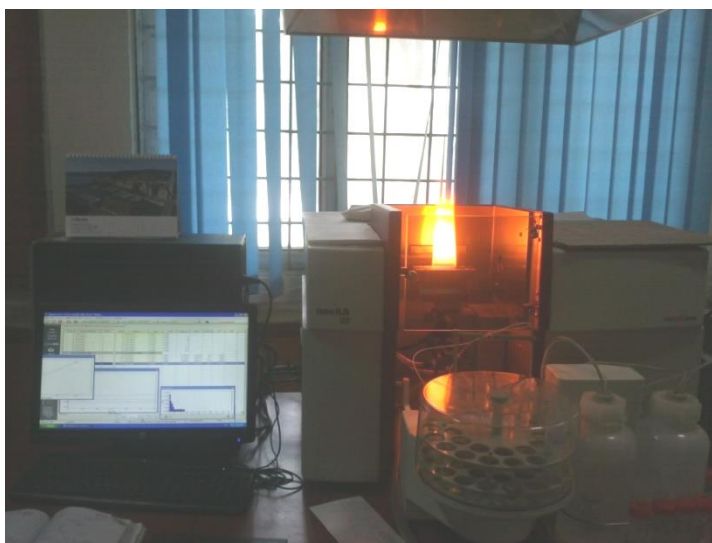AAS (NOVAA 350) (Fig. 3.4) has been used for testing of Iron, Chromium and Nickel concentrations in the sludge.

Fig 3.4 AAS (NOVAA 350)

Preparation of Acid digested extract for heavy metal determination in sludge:
0.1g sludge sample was accurately weighed and was dissolved in 2-3 ml HCl and 1-2 ml HNO3 and was heated till all the acid is removed and only ash like precipitate is left in the beaker. This residue is then filtered and transferred to reagent bottle by volume make up to 50 ml. The extraction liquid is then kept in reagent bottles (Fig.3.5) for further analysis.

Fig. 3.5 Extracted sample after acid digestion kept in reagent bottles

Fig. 3.6 Analysis on AAS

Standard solution of each heavy metal (Fe, Cr & Ni) was prepared. 10 ppm standard was prepared. Salt was selected. Its percent purity and metal content is checked.

Preparation of standard solution:

Amount of salt required to prepare 10ppm of standard solution= (10ppm x 100 ml x MW of salt x 100) / (1000 x AW of Fe x percent purity)

This salt is then added with 1 ml HCl and 3 ml HNO3, and allowed to dissolve. Then volume make up upto 100 ml is done in volumetric flask.

Analysis on AAS:

Samples are kept on the sample tray (Fig.3.6). Distilled water and 10ppm standard solution are kept was the instrument to calibrate itself. Suitable cathode lamps are selected.

Analysis by Spectometer:

1. Total Dissolved Iron:

Measurement of Total Dissolved Iron (TDI) by spectrometer:

1) Take 5 ml of the sample solution in a 50 ml volumetric flask.
2) To the 5 ml standard, add 1 ml of hydroxylamine. Shake it well.
3) To the previous solution add 5 ml of the sodium acetate solution and shake it well.
4) To the previous solution add 5 ml phenanthroline solution and mix it well. Red or orange colour will start to develop (Fig 3.7).
5) Now make the volume of the solution to 50 ml by using distilled water.
6) Wait for 10 minutes.
7) Take the absorbance of the solution at 510 nm wavelength and 100 % transmittance.
8) Multiply graph factor with the absorbance to get the concentration of the total dissolved iron.

Fig 3.7 Colorimetric analysis for Iron

Absorbance is obtained= A
Concentration of Iron in sample= A x Slope of calibration curve x dilution factor

3.3.2 Design of M20 concrete with Sludge and Fly Ash

Cement-Sludge- flyash concrete cubes are designed by using Taguchi method of design of experiments (L9 orthogonal array). Four factors are varied for the preparation of concrete cubes and each factor is varied on three levels (Table 4.1). Nine experiments are conducted as per Taguchi Methodology with variations in factor levels (Table 4.3).

Mix proportions of concrete:

Standard Mix design of M20 is used as per IS: 10262 (1982) and given in Table 3.1.
M20 Standard Mix design= Cement: Fine aggregates: Coarse aggregates:: 1: 1.5: 3
Water: binder ratio is taken as 0.5.

Table 3.1 Mix proportions of concrete used in the present study

Experiment No.	Different amounts of components for standard cube size of 15x15x15 cm3					
	Cement (kg)	Sludge (kg)	Fly Ash (kg)	Water (l) w/b=0.5	Fine Aggregates (kg)	Coarse Aggregates (kg)
1.	1.463	0.077	0	770	2.31	4.635
2.	1.1935	0.1155	0.231	770	2.31	4.635
3.	1.078	0.154	0.308	770	2.31	4.635
4.	1.232	0.077	0.231	770	2.31	4.635
5.	1.1165	0.1155	0.308	770	2.31	4.635
6.	1.386	0.154	0	770	2.31	4.635
7.	1.155	0.077	0.308	770	2.31	4.635
8.	1.4245	0.1155	0	770	2.31	4.635
9.	1.155	0.154	0.231	770	2.31	4.635

Standard Size cubes are prepared in the laboratory (Cube Size: 15 cm X 15 cm X 15 cm).

For each set of experiment, 6 cubes are cast.

Steps for preparing a concrete as per the experimental design:

1. Weigh the quantities of Cement, sludge, flyash, coarse and fine aggregates as per Table 3.4 for 6 cubes each (Fig 3.8 a).
2. Mix the contents with water in a roller drum for 2-3 min (fig 3.8 b).
3. Place the tightened standard size cubes on the vibration table and prepare the concrete cubes. (Fig 3.8 C)
4. Keep the cube in the cube holder for 24 hrs to initial set (Fig. 3.8 D). Then remove the cube holder and carefully place the cube in the curing tank for 7 days and 28 days. (Fig. 3.8 e)
5. Test the cubes for their 7 day and 28 day compressive strength on a UTM machine (Fig.3.8 f).

Fig. 3.8 (a) to (d) Preparation of concrete cubes
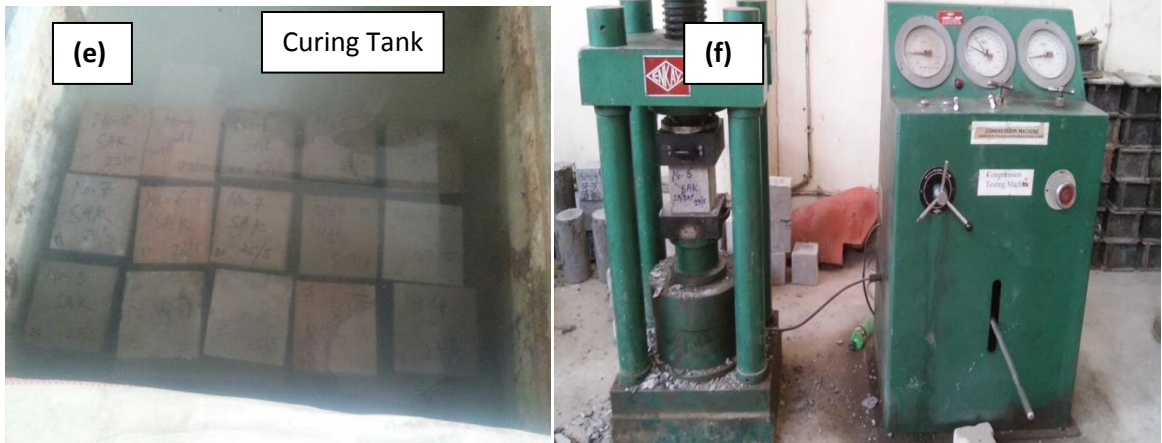
Fig. 3.8 (e) to (f) Curing of concrete cubes and their testing.

Fig 3.9 Concrete cubes with different sludge and flyash contents as per L9 Orthogonal Array

.

3.3.3 Toxicity Characteristic Leaching Procedure (TCLP) Test

STEPS:

TCLP test (18 h) is conducted as per US EPA (Method 1311).

1. After 28 days of curing, a slice of concrete approximately 9.5mm thick was cut from the mid-height of the cube. A part of each slice weighing approximately 100 g was crushed carefully using a hammer so that all particles were 9.5 mm, but the variation on the particle size distribution was not significant.
2. Each crushed concrete sample was treated with an acetic acid solution of pH 2.88 at a liquid to-solid ratio of 20:1 for a period of 18 h in the bottles.
3. The bottles were shaked at 28–30 rpm in a horizontal shaker at room temperature for 18 h.
4. At the end of the extraction, the leachates were filtered with through a 0.45 mm membrane filter to remove suspended solids (Fig. 3.10).
5. The pH of the filtrate was measured and the leachate was analyzed on AAS for Fe, Cr and Ni.

Fig. 3.10 Filtering of TCLP extract after 18 hours of shaking.

Chapter 4

TAGUCHI METHODOLOGY

Chapter 4

TAGUCHI METHODOLOGY

4.1 Introduction

To plan and conduct experiments so as to obtain sufficient and relevant data inferring the science behind the observed phenomenon, several techniques can be adopted. The conventional method of studying the effect of various factors on a particular phenomenon (e.g. Trial and error approach) is carried out by performing experiments where one parameter is varied at a time and other parameters are kept constant. This increases the quantum of work which needs to be performed as well as the exact picture of the effects, particularly the interactive effects of the parameters cannot be obtained. Therefore, conventional approach is often considered as an expensive, time consuming and arduous task. In order to overcome this issue, optimization studies done using design of experiments technique proves a better way-out.

Studies where large number of experiments cannot be done either due to high cost or fractional availability of raw materials, a number of designs/techniques available in literature are particularly useful. With the advent of new statistical methodologies involving orthogonal arrays, process optimization has become an easy, cheaper and faster option. For the optimization of experimental designs for performance quality and cost, Taguchi's method of experimental design provides a simple, efficient and systematic approach (Shaji & Radhakrishnan, 2003).

The distinct characteristics of Taguchi methodology are:

1. Its ability to study the main effects of each factor, and to model some of the important interactions by one primary experiment (Ballantyne et al., 2008).
2. The methodology optimizes the process by minimizing the variation in the process output caused by uncontrollable factors like ambient temperature, pH and temperature of curing tank, dimensional tolerances, etc.
3. It takes into account the positive effects of possible interactions between controllable process variables and uncontrollable factors (Tjantele, 1991).

The above features make it a robust methodology for design of experiments and hence, it is used for optimization in variety of scientific fields like nano-technology, waste water treatment, biotechnology, etc. Robust design methods are particularly important when one is interested in designing a system that gives consistent outputs despite the variation of uncontrollable factors (Theodore, 2006).

4.2 Taguchi Method

Dr. Taguchi of Japan has developed this method based on orthogonal arrays which gives much reduced variance for the experiments with optimum levels of control parameters.

4.2.1 Basic concept

Taguchi has envisaged a new technique of designing of experiments based on well defined guidelines. It uses a special set of arrays called orthogonal arrays which stipulates the way of conducting the minimal number of experiments which could give the full information of all the factors that affect the performance parameter. The accuracy and validation of results of the orthogonal arrays method lies in choosing the level combinations of the input design variables for each experiment.

4.2.2 Orthogonal arrays

An orthogonal array is a type of experiment where the columns for the independent variables are "orthogonal" to one another.

Benefits:
1. Conclusions valid over the entire region spanned by the control factors and their settings
2. Large saving in the experimental effort
3. Analysis is easy

To define an orthogonal array, one must identify:
1. Number of factors to be studied
2. Levels for each factor
3. The specific 2-factor interactions to be estimated
4. The special difficulties that would be encountered in running the experiment

4.2.3 Properties of an orthogonal array

The orthogonal arrays have the following special properties that reduce the number of experiments to be conducted.

1. The vertical column under each independent variables of the above table has a special combination of level settings. All the level settings appears an equal number of times.
2. All the level values of independent variables are used for conducting the experiments.
3. The sequence of level values for conducting the experiments shall not be changed.

4.2.4 Determining Parameter Design Orthogonal Array

The effect of many different parameters on the performance characteristic in a condensed set of experiments can be examined by using the orthogonal array experimental design proposed by Taguchi. Once the parameters affecting a process that can be controlled have been determined, the levels at which these parameters should be varied must be determined.

Determining what levels of a variable to test requires an in-depth understanding of the process, including the minimum, maximum, and current value of the parameter. If the difference between the minimum and maximum value of a parameter is large, the values being tested can be further apart or more values can be tested. If the range of a parameter is small, then les values can be tested or the values tested can be closer together.

Knowing the number of parameters and the number of levels, the proper orthogonal array can be selected. Using the array selector table shown below, the name of the appropriate array can be found by looking at the column and row corresponding to the number of parameters and number of levels. Once the name has been determined (the subscript represents the number of experiments that must be completed), the predefined array can be looked up. (Fraley S, 2006)

		Number of Parameters (P)																													
		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Number of Levels	2	L4	L4	L8	L8	L8	L8	L12	L12	L12	L12	L16	L16	L16	L16	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32
	3	L9	L9	L9	L18	L18	L18	L18	L27	L27	L27	L27	L27	L36	L36	L36	L36	L36	L36	L36	L36	L36	L36								
	4	L'16	L'16	L'16	L'16	L'32	L'32	L'32	L'32	L'32																					
	5	L25	L25	L25	L25	L25	L50	L50	L50	L50	L50	L50																			

Fig 4.1 Array Selector (Source: Fraley S, 2006)

4.2.5 Generic procedure adopted under each experimental investigation

The general steps involved in the Taguchi Method (Fraley S, 2006) are as follows:

1. Define the process objective, or more specifically, a target value for a performance measure of the process. This may be a flow rate, temperature, etc. The target of a process may also be a minimum or maximum; for example, the goal may be to maximize the output flow rate. The deviation in the performance characteristic from the target value is used to define the loss function for the process.
2. Determine the design parameters affecting the process. Parameters are variables within the process that affect the performance measure such as temperatures, pressures, etc. that can be easily controlled. The number of levels that the parameters should be varied at must be specified. For example, a temperature might be varied to a low and high value of 40 C and 80 C. Increasing the number of levels to vary a parameter at increases the number of experiments to be conducted.
3. Create orthogonal arrays for the parameter design indicating the number of and conditions for each experiment. The selection of orthogonal arrays is based on the number of parameters and the levels of variation for each parameter, and will be expounded below.
4. Conduct the experiments indicated in the completed array to collect data on the effect on the performance measure.

5. Complete data analysis to determine the effect of the different parameters on the performance measure.

4.2.6 Analyzing Experimental Data

Once the experimental design has been determined and the trials have been carried out, the measured performance characteristic from each trial can be used to analyze the relative effect of the different parameters.

In the present study where maximum strength and heavy metal immobilization is desired, Taguchi quality loss function of the ith quality characteristic in the jth experimental run (l_{ij}) is defined in mathematical terms as per the Eq. 1(Dubey, 2011)

$$l_{ij} = \left[1 \Big/ n \sum_{x=1}^{n} \left[y_{ij}^2 \right]_x \right]$$

Eq 1

Where y_{ij} is the observed value of the ith quality characteristic in the jth experimental run; n is the number of trials / repetitions under the same experimental conditions;

Subsequently, normalized quality loss ($\hat{l}_{ij}$) is evaluated using Eq. 2 as sometimes, simultaneous optimization of more than one quality characteristics may involve quality characteristics with different units (Aslan and Unal, 2011).

$$\hat{l}_{ij} = l_{ij} \Big/ l_{i\max}$$

…. Eq. 2

Where $\hat{l}_{ij}$ is the normalized quality loss for the ith quality characteristic at the jth experimental run; $l_{i\max}$ is the maximum quality loss for the ith quality characteristic among all the experimental runs. The previous step is followed by computation of total normalized quality loss function for the jth experimental run L_j using Eq. no. 3 (Aslan and Unal, 2011). This step requires assigning of appropriate weightage factors 'w_i' for each of the quality characteristics based on their relative importance.

$$L_j = \sum_{i=1}^{p} w_i \hat{l}_{ij}$$

.Eq. 3

Finally, multiple S/N ratio (MSNR) is evaluated using Eq. 4 provided below, as it represents the quality index at each experimental run.

$$\eta_j = -10 \log_{10}(L_j)$$

Eq.4

Where η_j represents multiple S/N ratio (MSNR) at the jth experimental run.

Analysis of Mean approach to optimize the process conditions:

The analysis of mean (ANOM) statistical approach is adopted to determine the optimum process conditions for maximum simultaneous yield of duckweed biomass and its starch and protein contents. This approach begins with computation of average MSNR of all the experimental runs in which a process variable is at same distinct level using the following formula:

$$(K) \, {}^{Level=i}_{Factor=F} = \frac{1}{n_{Fi}} \sum_{j=1}^{n_{Fi}} \left[\eta \, {}^{Level=i}_{Factor=F} \right]_j$$

Eq. 5

Where $K \, {}^{Level=i}_{Factor=F}$ represents mean of the MSNR of all the experimental runs in which factor F at level i,

$\left[\eta \, {}^{Level=i}_{Factor=F} \right]$ represents MSNR value against the experimental run in which factor F is at level i and the MSNR value against the experimental run in which Factor F at level i is in its pth appearance sequence in Table 5 is the jth value in Table 6 where p = 1,2.....n_{Fi} and and n_{Fi} represents the maximum number of appearances of factor F in level i among all the experimental runs. Thus the mean values of the MSNR of the experimental runs in which different factors are same distinct levels can be determined. Finally, the average MSNR response table was constructed from which the optimum condition for a particular factor was found by identifying the factor level at which average MSNR has the maximum value.

Prediction of optimum MSNR value

The predicted value of MSNR value at the optimum parameter levels is evaluated by following formula:

$$\eta_{opt} = \bar{\eta} + \sum_{i=1}^{k} (\bar{\eta}_{mi} - \bar{\eta})$$

Eq 6

Where $\bar{\eta}$ is the average MSNR of all experimental runs and η_{mi} is the average MSNR value of the ith significant Factor 'F' at its optimum level. In the above equation, k denotes the number of significant process parameters.

Analysis of Variance to identify the percentage contribution of each factor:

ANOVA presents the comparative significance of process parameters in terms of their percentage contribution towards the nutrient removal. It is also used for estimation of variance of error and the variance of prediction error. According to ANOVA approach, total variation in all samples combined (SS_T) is the total variation between groups (SSF) and total variation within groups (SSE).

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$$SS_T = SS_F + SS_E$$

<div align="right">Eq. 7</div>

SS_T is measured by computing the sum of squared deviations between each of all data values and overall mean of all the data points and in mathematical terms, it is given by Eq 8:

$$SS_T = \sum_{j=1}^{n} (\eta_j - \bar{\eta})^2$$

<div align="right">Eq. 8</div>

SSF is evaluated by summing up the variation due to different factors and is mathematically represented as:

$$SS_F = \sum_{X=A}^{E} SS_x$$

<div align="right">Eq. 9</div>

wherein, the variation due to particular factor X, i.e., SS_x is evaluated as the weighted sum of squared deviations between the sample means at various levels and the overall mean of all the data.

$$SS_X = \sum_{r=1}^{m} l * (K \, {}_{Factor=X}^{Level=r} - \bar{\eta})^2$$

<div align="right">Eq. 10</div>

It is noted that a particular factor which has the highest sum of squares is found to have highest influence on the output quality characteristic.

The variance or mean square of each factor 'X' is evaluated by

$$MS_X = \frac{SS_X}{DoF_X \, (i.e., l-1)}$$

<div align="right">Eq. 11</div>

Subsequently, the total variation within groups, i.e., sum of squares of error (SSe) is evaluated by re-aligning Eq. 12 as

$$SS_E = SS_T - SS_F$$

<div align="right">Eq. 12</div>

Now the Variance of Error is evaluated using Eq. no 13. ..

$$V_{Er} = \frac{SS_{Er}}{DoF_{Er}}$$

<div align="right">Eq. 13</div>

4.2.7 Advantages and Drawbacks of this method

Advantages and Disadvantages

An advantage of the Taguchi method is that it emphasizes a mean performance characteristic value close to the target value rather than a value within certain specification limits, thus

improving the product quality. Additionally, Taguchi's method for experimental design is straightforward and easy to apply to many engineering situations, making it a powerful yet simple tool. It can be used to quickly narrow down the scope of a research project or to identify problems in a manufacturing process from data already in existence. Also, the Taguchi method allows for the analysis of many different parameters without a prohibitively high amount of experimentation. For example, a process with 8 variables, each with 3 states, would require 6561 (3^8) experiments to test all variables. However using Taguchi's orthogonal arrays, only 18 experiments are necessary, or less than 3% of the original number of experiments. In this way, it allows for the identification of key parameters that have the most effect on the performance characteristic value so that further experimentation on these parameters can be performed and the parameters that have little effect can be ignored.

The main drawbacks of the Taguchi method is that the results obtained are only relative and do not exactly indicate what parameter has the highest effect on the performance characteristic value. Also, since orthogonal arrays do not test all variable combinations, this method should not be used with all relationships between all variables are needed. The Taguchi method has been criticized in the literature for difficulty in accounting for interactions between parameters. Another limitation is that the Taguchi methods are offline, and therefore inappropriate for a dynamically changing process such as a simulation study. Furthermore, since Taguchi methods deal with designing quality in rather than correcting for poor quality, they are applied most effectively at early stages of process development. After design variables are specified, use of experimental design may be less cost effective.

4.3 Studies of optimum utilizations of solid wastes with Cement/Concrete using Taguchi Methodology

Taguchi's method of experimental design provides a simple, efficient, and systematic approach for the optimization of experimental designs for performance quality and cost (Shaji, 2003). To evaluate the each independent factor or their interaction effects on the process characteristics, Taguchi uses standard orthogonal arrays. A loss function is then defined to calculate the deviations between the experimental value and the desired value. This loss function is further transferred into a signal-to noise (S/N) ratio, η (Hascalik, 2008).

The effect of experimental parameters on compressive strength and leaching of heavy metals was evaluated statistically and the level of significance of the parameters affecting the leaching and compressive strength of the concrete mixed with sludge was determined by using Taguchi Methodology. Table 4.1 gives the literature review of the studies involving the use of Taguchi methodology for design of experiments for the utilization of various types of wastes.

Table 4.1 Studies of design of experiments of utilization of various types of wastes by Taguchi method.

S.No.	Author	Waste utilised	Type of orthogonal array used	Control factors taken and parameter optimized
1.	Oguzhan Kelestemur et. al. 2014	Marble dust	L16 (4^3) (3 factors , 4 levels)	Control factors taken are Percentage of marble dust, amount of glass fiber and degree of temperature. Optimizing factors for Compressive strength and porosity.
2.	Ali Bagheri, Ali Nazari 2014	Blast furnace slag	L-9 array (3^4) (4 factors and 3 levels)	Control factors taken are aggregate content, sodium hydroxide concentration, curing time and curing temperature. Optimizing factors for Compressive strength
3.	Mohammed Nadeem, Arun D. Pofale 2012	Iron and Steel industry waste Slag	L-9 array (3^3) (3 factors and 3 levels)	Control factors taken are water to cementitious materials (w/c) ratio, % replacement of natural course aggregate and fine aggregate with slag aggregates. Optimizing factors for Compressive, split and flexural strength.
4.	Shadi Riahi et. al. 2012	Fly ash and Rice husk ash	L-9 array (3^3) (3 factors and 3 levels)	Control factors taken are curing temperature, oven curing time and sodium hydroxide (NaOH) concentration. Optimizing factors for Compressive strength.
5.	Chieh-jen chang et.al. 2012	MSWI ash- mix slag (modified) and CMP sludge	L-9 array (3^4) (4 factors and 3 levels)	Control factors taken are total cementitious materials (wt %), modified ash-mix slag substitution (wt %), CMP sludge substitution (wt %) and water to cementitious materials (w/c) ratio. Optimizing factors for Compressive strength.
6.	C.Y. Chang et.al. 2011	Construction waste or Demolition Waste (recycled aggregate)	L-16 array (2^5) (5 factors and 2 levels)	Control factors are water/cement ratio, volume ratio of recycled coarse aggregate, replacement by river sand, content of crushed brick, and cleanliness of aggregate. Optimizing factors for slump, slump-flow, resistivity, ultrasonic pulse velocity and compressive strength.
7.	Tzen chin lee 2009	Municipal incinerator fly-ash slag and semiconductor waste sludge	L-9 array (3^4) (4 factors and 3 levels)	Control factors are % cement, % slag, % chemical sludge and water to cementitious materials (w/c) ratio. Optimizing for Compressive strength.
8.	Erdogan Ozbay et.al. 2009	Fly ash	L-18 array (3^6) (6 factors and 3 levels)	Control factors are water to cementitious materials (w/c) ratio, water content (w), fine aggregate to total aggregate (s/a) percent, flyash content (FA), air entraining agent (AE) content and superplasticizer content (SP). Optimizing mix for maximum ultrasonic pulse velocity, compressive strength, splitting tensile strength and for minimizing air content, water permeability and water absorption values.
9.	Ibrahim Turkmen et.al. 2008	Blast furnace slag	L-16 array (4^5) (5 factors and 4 levels)	Control factors are % mineral admixture, water to binder ratio (w/b), curing regime and pH and curing time (in days). Optimizing for Compressive strength and finding most durable mixture by optimizing capillarity and porosity.

10.	Prabir Kumar Chaulia and Reeta Das 2008	Fly Ash	L-9 array (3^4) (4 factors and 3 levels)	Control factors are water to binder ratio (w/b), % flyash, % coarse sand and % stone dust. Optimizing for Compressive strength.
11.	Gordon C.C. Yang, Kai-Lun Kao 1994	Electroplating sludge and a calcium carbonate sludge	L-9 array (3^4) (4 factors and 3 levels)	Control factors are weight percent of cement replacement by the heat-treated material, total weight of the binding agent(s), weight ratio of water to binding agent(s), and weight ratio of binding agent(s) to electroplating sludge Optimizing for Compressive strength.

4.4 Present Study: L9 orthogonal array

Design of experiments using Taguchi parameter design

Four different controllable factors each at three different levels were considered during the study, the details of which are presented in **Table 4.2**. **Table 4.3** presents the standard Taguchi L9 orthogonal array. The experimental runs tabulated in **Table 4.4** were planned according to Taguchi L9 orthogonal array to identify the optimum process parameters for maximum simultaneous yield of process estimates namely, biomass and its starch and protein contents.

Table 4.2 Control factors and their levels

S.No.	Parameters	Level 1	Level 2	Level 3
1.	Type of Cement	OPC- 33 grade	OPC- 43 grade	OPC- 53 grade
2.	Sludge (% of cement)	5	7.5	10
3.	Fly ash (% of cement)	0	15	20
4.	Particle size grading of sludge	< 0.075 mm	0.60- 0.075 mm	2.36- 0.3 mm

Table 4.3 L9 orthogonal array

Experiment	P1	P2	P3	P4
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 4.4 Experimental Design as per L9 orthogonal array

Experiment	Type of Cement	Sludge (% of cement replaced)	Fly ash (% of cement replaced)	Particle size of sludge
1.	OPC- 33 grade	5	0	< 0.075 mm
2.	OPC- 33 grade	7.5	15	0.60- 0.075 mm
3.	OPC- 33 grade	10	20	2.36- 0.3 mm
4.	OPC- 43 grade	5	15	2.36- 0.3 mm
5.	OPC- 43 grade	7.5	20	< 0.075 mm
6.	OPC- 43 grade	10	0	0.60- 0.075 mm
7.	OPC- 53 grade	5	20	0.60- 0.075 mm
8.	OPC- 53 grade	7.5	0	2.36- 0.3 mm
9.	OPC- 53 grade	10	15	< 0.075 mm

Chapter 5

RESULTS AND DISCUSSIONS

Chapter 5

RESULTS AND DISCUSSIONS

The industrial sludge was obtained from a small scale pickling industry in Wazirpur Industrial area. The industry manufactured stainless steel pickled sheets which are further processes to make Utensils. Sludge was tested for its physical and chemical properties. Based on study, following results were obtained:

5.1   CHARACTERISTICS OF S.S. PICKLING SLUDGE

Various physical, chemical & morphological characteristics of lime treated pickling sludge has been analyzed and the results obtained are reported and discussed as follows:

5.1.1 Physical and chemical properties of sludge

The physical and chemical properties of sludge are determined as per standard methods of APHA and are presented in Table 5.1.

Table 5.1 Characteristics of lime neutralized pickling sludge

S.NO.	PROPERTIES	RESULTS
1.	Moisture content of wet sludge	58%
2.	Colour	Brownish grey but when exposed to air, it turns to brownish red
3.	Loss on ignition at 1050˚C	13%
4.	Specific Gravity	2.09
5.	pH	8.9

Lime treated pickling sludge seemed to have clayey texture with large water absorbing capacity. Due to presence of iron, the sludge changes it color from brownish grey to brownish red when exposed to air (formation of iron oxides). As the sludge is treated with lime for neutralization, alkaline pH was observed.
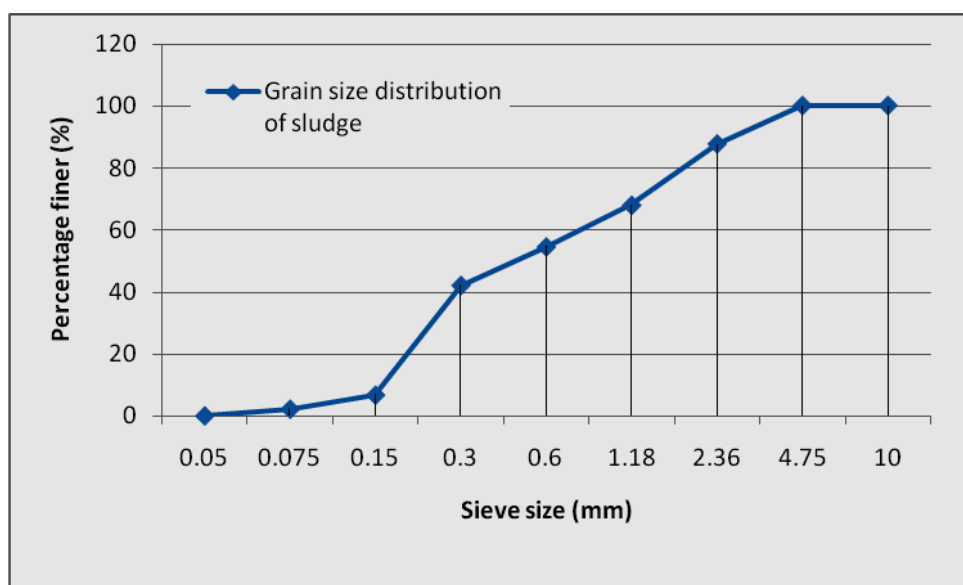
5.1.2 Sieve analysis of sludge

Particle size testing of sludge was carried out using oven dried sample of weight of 600g. Coarsest sieve of 4.75mm was placed at the top and finest sieve of 0.075 at the bottom. Weights of sludge retained on the sieves were determined. The results of sieve analysis are presented in Table 5.2.

Table 5.2 Sieve analysis of sludge

S.No	IS Sieve size (mm)	Weight retained (g)	Cumulative weight retained (g)	% cum. Weight retained	Percentage finer (%)
1.	4.75	0	0	0	100
2.	2.36	74.2	74.2	12.36667	87.633
3.	1.18	118.7	192.9	32.15	67.85
4.	0.600	80.4	273.3	45.55	54.45
5.	0.300	74.5	347.8	57.96667	42.033
6.	0.150	212	559.8	93.3	6.7
7.	0.075	27.3	587.1	97.85	2.15
8.	<0.075	12.9	600	100	
	TOTAL	**600**		**439.1833**	

Fineness modulus of sludge= 4.39

Fig.5.1. Grain size distribution of sludge

Figure 5.1 shows the grain size distribution of sludge.

Fig 5.2 Standards sieves for analysis of sludge

5.1.3 XRD of Pickling sludge

Sludge was characterized by X- Ray Diffractometer (XRD) analysis (Fig. 5.3). Room-temperature powder X-ray diffraction data were collected on a Burker D8 Advance diffractometer using Ni-filtered Cu Kα radiation. Data were collected with a step size of 0.02° and at count time of 0.2 sec per step over the range 10° < 2θ < 70°. Various 2Θ values for XRD analysis of pickling sludge and the identified compounds are given in Table 5.3.
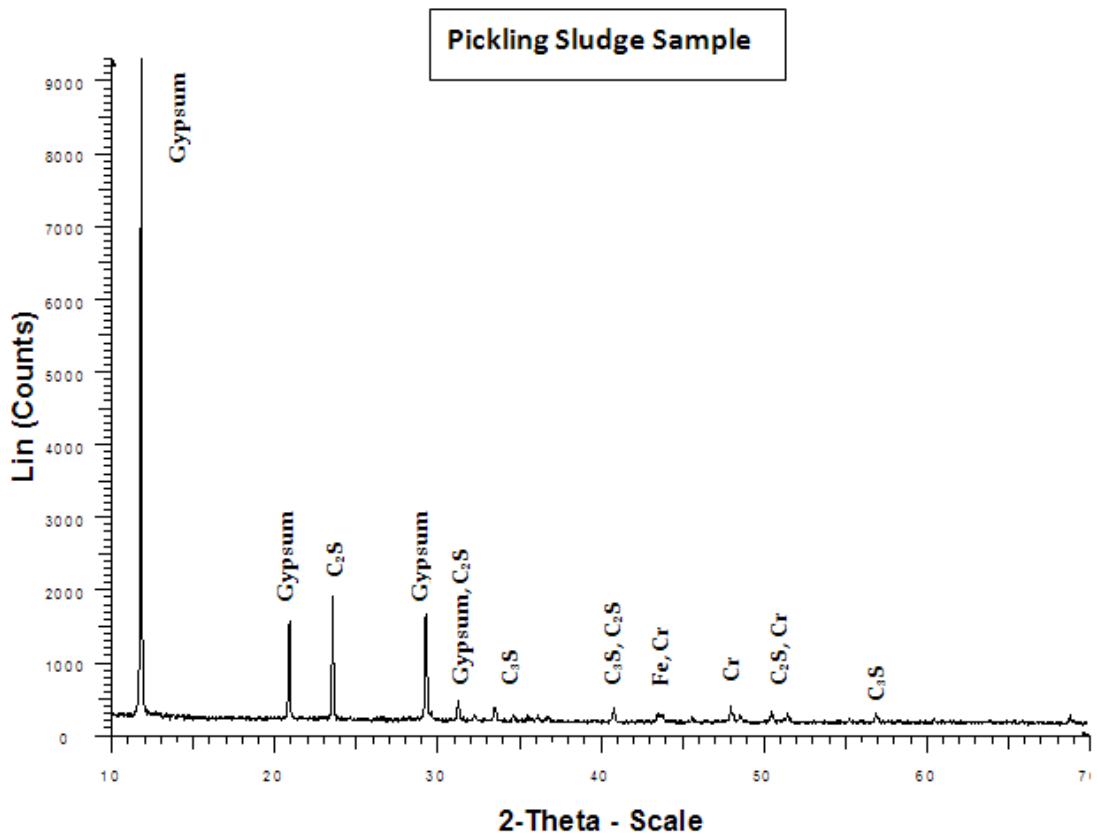

Fig. 5.3 XRD of pickling sludge

Table 5.3 Various 2Ө values for XRD analysis of pickling sludge and the identified compounds

S.no.	2 Ө value in ˚	Name of the compound
1.	11.61, 20.77, 29.19, 31.31	**Gypsum**
2.	23.46, 29.19, 40.86,	**Di-calcium silicates (C_2S)**
3.	33.39, 40.86,51.38, 56.38	**Tri- calcium silicates (C_3S)**
4.	43.678	**Iron (Fe)**
5.	43.678, 47.995, 48.52, 50.46	**Chromium (Cr)**

XRD analysis of lime treated pickling sludge indicates the presence of gypsum, C_2S and C_3S. Singhal et.al. (2008) also discusses the presence of gypsum in the pickling sludge. Formation of gypsum could have been by the following reactions:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4.\ 2H_2O$$
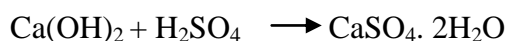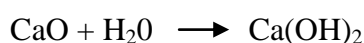
Since the pickling sludge is treated using lime (70-75% purity) which contains silica and its compounds. Gypsum may be formed by the reaction of calcium hydroxide and sulphuric acid.

Di-calcium silicates (C_2S) and Tri- calcium silicates (C_3S) are also present in this sludge as slight peaks were observed in XRD pattern. They are formed by the reaction of calcium oxide and silica present in the lime.

Presence of Chromium and Iron was also indicated in Fig 5.3. As the sludge is produced by the neutralization of spent pickling liquor which is generated due to the treatment of stainless steel sheets by pickling process, the presence of iron and chromium is due to this acid treatment which removes the scales and rust from the surface of the sheets.

5.1.4 EDX of Pickling sludge

Energy Dispersive X-Ray spectroscopy (Figure 5.4) was performed to obtain quantitative information i.e. elemental analysis or chemical characterization of the sludge sample. Analysis parameters: Acc.Voltage: 15.0 kV Take Off Angle: 69.0 deg
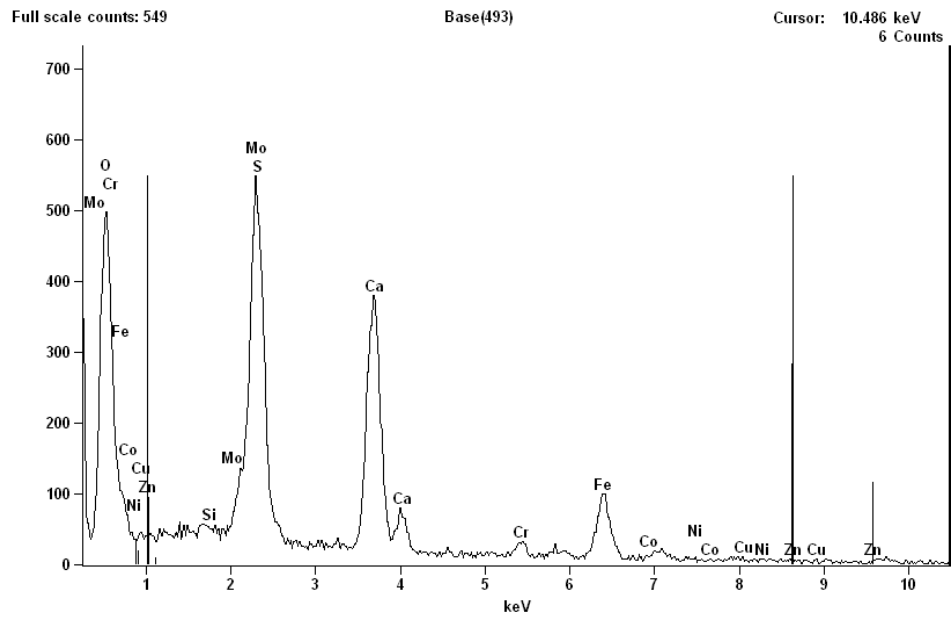
Fig 5.4 EDX analysis graph of lime treated pickling sludge

The relative proportions of the elements identified in the sludge with their respective percentage weights are presented in Table 5.4.

Table 5.4 Weight percent of elements identified in Pickling sludge by EDX analysis

Quantitative Results for: Base(493)

| Element Line	Net Counts	Int. Cps/nA	Weight %	Weight % Error	Atom %	Atom % Error	Formula
O K	0	---	0.00	---	0.00	+/- 0.00	O
Si K	224	---	0.68	+/- 0.15	1.02	+/- 0.22	Si
Si L	0	---	---	---	---	---	
S K	7982	---	23.78	+/- 0.66	31.09	+/- 0.87	S
S L	210957	---	---	---	---	---	
Ca K	6928	---	37.30	+/- 1.02	39.01	+/- 1.06	Ca
Ca L	0	---	---	---	---	---	
Cr K	401	---	4.47	+/- 0.48	3.60	+/- 0.39	Cr
Cr L	8662	---	---	---	---	---	
Fe K	1885	---	31.92	+/- 2.00	23.96	+/- 1.50	Fe
Fe L	1141	---	---	---	---	---	
Co K	0	---	0.00	---	0.00	+/- 0.00	Co
Co L	407	---	---	---	---	---	
Ni K	70	---	1.84	+/- 0.87	1.32	+/- 0.62	Ni
Ni L	0	---	---	---	---	---	
Cu K	0	---	0.00	---	0.00	+/- 0.00	Cu
Cu L	228	---	---	---	---	---	
Zn K	0	---	0.00	---	0.00	+/- 0.00	Zn
Zn L	63	---	---	---	---	---	
Mo L	0	---	0.00	---	0.00	+/- 0.00	Mo
Mo M	6644	---	---	---	---	---	
Total			100.00		100.00		

Energy-dispersive X ray spectrometers (EDS or EDX) indicate the pulse height analysis. A detector used in this gives output pulses proportional in height to the X-ray photon energy used in conjuction with a pulse height analyzer. A solid state detector is used because of its better energy resolution.

The relative proportions of the elements in the pickling sludge sample is indicates the dominance of Iron and calcium with slight percentages of Chromium, Silica and Nickel.

Heavy metal content was also analysed using AAS and Colorimeter techniques and are presented in the Table 5.5

5.1.5 SEM of Pickling sludge

Scanning Electron Microscope (SEM) micrographs in Fig 5.5 illustrates the microstructure characteristics of pickling sludge sample at different magnifications. Sludge seem to have a flaky, glassy texture.
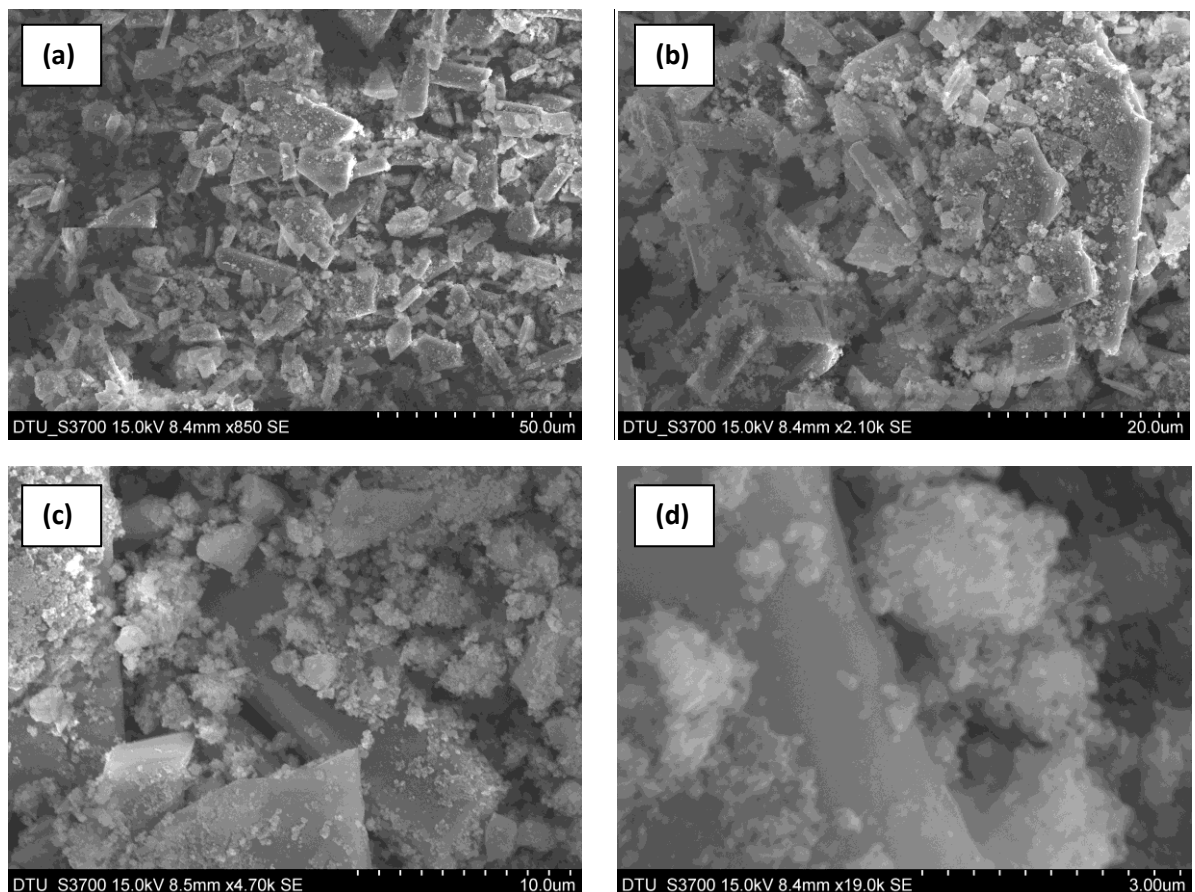
Fig.5.5 SEM micrographs of the pickling sludge at different magnifications (a) 50µm, (b) 20µm, (c) 10 µm and (d) 3 µm.

Table 5.5 AAS results of heavy metal content in sludge (Analysed from acid digested extract of 0.1g sludge sample)

S.No.	Element	Atomic Absorption Spectroscopy (AAS) (conc. in mg/l)	Colorimetric analysis by Spectrometer (conc. in mg/l)
1.	**Iron**	-	0.1306
2.	**Total Chromium**	2.723	0.5563
3.	**Nickel**	2.436	-

5.2 FLY ASH CHARACTERISTICS

Fly ash used is collected from a CPWD construction site which indicated the source as Dadri, Thermal Power Plant. The analysis of flyash is as per IS: 1727-1967 and its chemo-physical properties are presented in table 5.6:

Table 5.6 Fly Ash characteristics

	Parameters	Value %
1.	Specific gravity	2.25
2.	SiO_2	60.27
3.	Al_2O_3	25.46
4.	Fe_2O_3	6.02
5.	MgO	0.29
6.	CaO	3.68
7.	SO_3	0.12
8.	Surface area (cm_2/g)	3980
9.	LOI	1.10

Table 5.6 shows that sum of three ingredients i.e SiO_2, Al_2O_3 and Fe_2O_3 is greater than 70%, therefore as per ASTM C-618 Mineral admixture class, this ash is considered as Class F and according to IS: 3812-2003, since reactive lime content is less than 10%, it is called siliceous pulverized fuel ash. Such flyash is produced from burning anthracite and bituminous coal (type of coal available in India) and has pozzolanic properties.

As per clause 5.2 of IS 456-2000 Plain and Reinforced cement concrete code of practice, fly ash (conforming to IS 3812 part 1) up to 35% can be used as part replacement of OPC in the concrete.
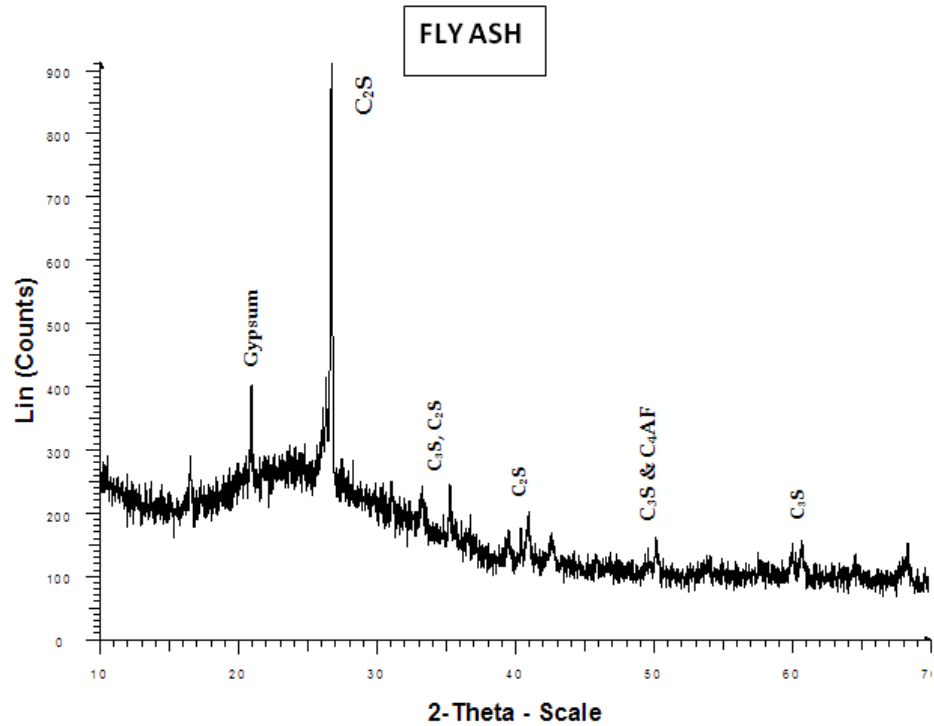
5.2.1 XRD analysis of fly ash

Fig. 5.6 XRD of Fly ash

The XRD pattern of Flyash indicates the presence of Gypsum, Dicalcium silicates, Tri-calcium silicates and C_4AF. This shows that the fly ash has strong pozzolanic properties. That is the reason why fly ash has been added as a cementitious binder material in combination with sludge to produce better pozzolanic compounds resulting in improved strength of concrete.
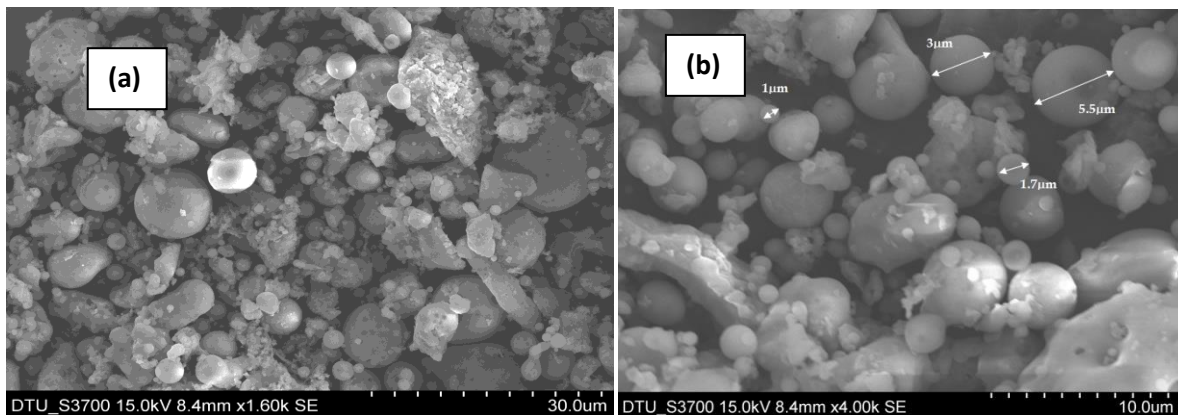
5.2.2 SEM of Fly ash

Fig.5.7 SEM micrographs of the flyash at different magnifications (a) 30μm and (b) 10μm.

Micrographs in Fig 5.7 indicate the morphology of the fly ash. Fly ash suitable for use in concrete consists mostly of glassy, hollow, spherical particles which are actually cenospheres. Variations are seen in the shape (rounded to angular), surface texture (smooth and dence to highly porous) and presence and absence of surface coating (e.g. magnetite). In contrast, cement particles are generally angular.

5.3 FINE AGGREGATE SIEVE ANALYSIS

Fine aggregate is analyzed as per IS- 383-1970 and sieve analysis of the fine aggregates is given in Table 4.6. The sieve analysis of this type of aggregates seems to conform to **Grading Zone (2)** of Table 4 of IS: 383-1970. Fineness modulus is calculated and is obtained as 4.7 for this quality of fine aggregate.

Table 5.7 Sieve analysis of fine aggregates

S.No	IS Sieve size (mm)	Weight retained (g)	Cumulative weight retained (g)	% cum. Weight retained	Percentage finer (%)
1.	4.75	15.2	15.2	1.52825256	98.472
2.	2.36	159.4	174.6	17.5547959	82.445
3.	1.18	234	408.6	41.0818419	58.918
4.	0.6	163.6	572.2	57.5306656	42.469
5.	0.3	123	695.2	69.8974462	30.103
6.	0.15	173.8	869	87.3718078	12.628
7.	0.075	75.5	944.5	94.9627991	5.0372
8.	<0.075	50.1	994.6	100	-
	TOTAL	**994.6**		**469.927**	
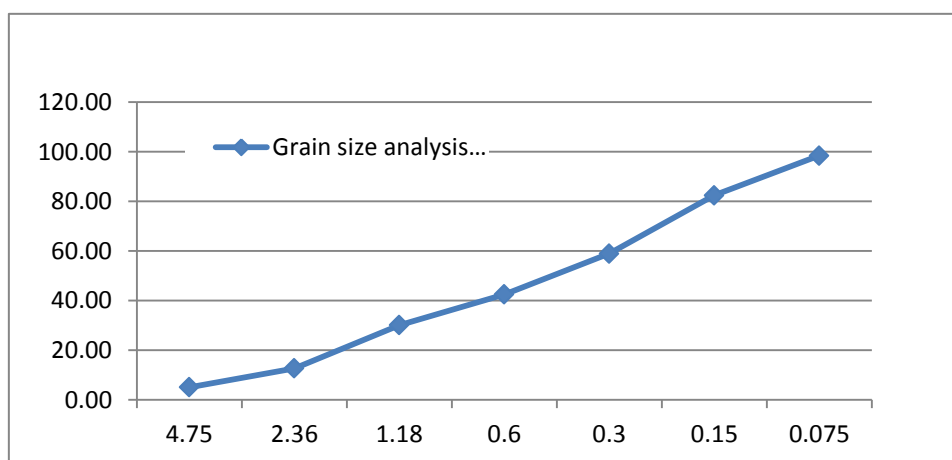
Fig 5.8 Grain size distribution curve for fine aggregates

5.4 COARSE AGGREGATE SIEVE ANALYSIS

Course aggregate is analysed as per IS-383-1970 and sieve analysis was conducted. The results of sieve analysis are presented in Table 5.8. As per the results obtained, the coarse aggregate used in this study is conforming to Table 2 of IS: 383-1970.

Table 5.8 Sieve analysis of course aggregates

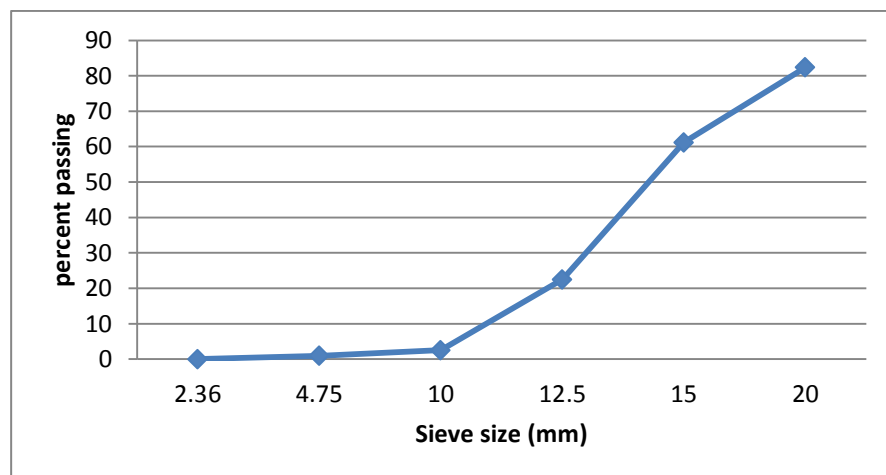| S.No	Sieve size (mm)	Weight retained (g)	Cumulative weight retained (g)	% cum. Weight retained	Percentage finer (%)
1.	20	511	511	17.621	82.379
2.	15	614	1125	38.793	61.207
3.	12.5	1122	2247	77.483	22.517
4.	10	580	2827	97.483	2.517
5.	4.75	46	2873	99.069	0.931
6.	2.36	27	2900	100.000	
	TOTAL	**2900**			

Fig. 5.9 Sieve analysis of course aggregates

Fig.5.10 Standard Sieves for particle size analysis for coarse aggregates

5.5 Leaching and Compressive strength of concrete after addition of sludge

5.5.1 Compressive strength of cement-sludge-flyash concrete cubes after 7 and 28 days of curing

Concrete cubes are designed on the basis of L9 orthogonal array (Table 4.3). M-20 concrete is prepared by addition of Lime treated pickling sludge and flyash as cement replacements. Table 5.9 shows the total percent of cement replacement in each of 9 experiments.

Table 5.9 Cement replacement by sludge and flyash

Experiment No.	% Sludge	% Fly ash	Total % cement replacement
1.	5	0	5
2.	7.5	15	22.5
3.	10	20	30
4.	5	15	20
5.	7.5	20	27.5
6.	10	0	10
7.	5	20	25
8.	7.5	0	7.5
9.	10	15	25

The compressive strength of concrete cubes of nominal mix design M20 (1:1.5:3) was tested after 7 and 28 days of curing. The results are represented in Table 5.10

Table 5.10 Results of compressive strength (in MPa) after 7 days of curing

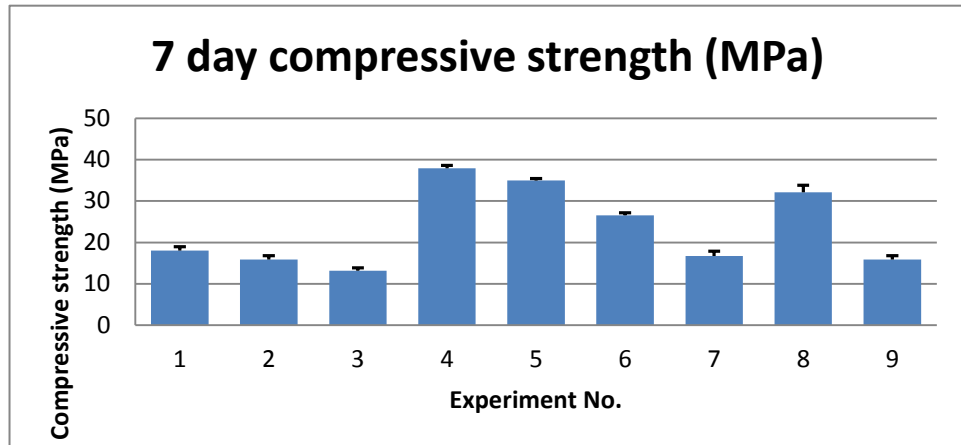| Experiment No.	7 day compressive strength (MPa)				
	1	2	3	Mean	Std. Dev. (±)
1.	17.78	17.33	19.11	**18.07**	0.93
2.	15.56	16.89	15.11	**15.85**	0.93
3.	12.44	13.78	13.33	**13.19**	0.68
4.	37.78	37.33	38.67	**37.93**	0.68
5.	34.67	35.56	34.67	**34.96**	0.51
6.	25.78	26.67	27.11	**26.52**	0.68
7.	16.89	15.56	17.78	**16.74**	1.12
8.	33.33	30.22	32.89	**32.15**	1.68
9.	15.11	15.56	16.89	**15.85**	0.93

Fig. 5.11 Compressive strength of concrete cubes after 7 days of curing

Experimental cubes no. 4, 5, 8 and 6 shows higher strength as compared to others (Fig. 5.11). 33 grade cement cubes i.e. Experiment cube no. 1, 2 & 3 shows low strength with increase in sludge and flyash content. Exp Cube 8 has no flyash but only sludge and shows higher strength. 53 grade cement seemed to show low strength with fly-ash.

Table 5.11 Results of compressive strength of concrete cubes after 28 days of curing

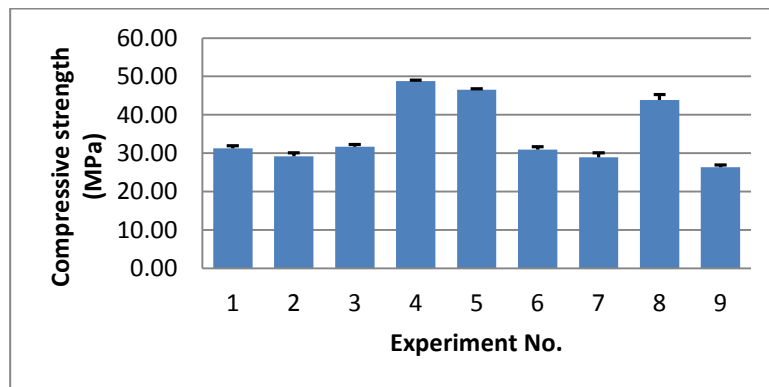| Experiment No.	28 day compressive strength (MPa)				
	1	2	3	Mean	Std. Dev. (±)
1.	30.67	32.00	31.11	**31.26**	0.68
2.	28.89	30.22	28.44	**29.19**	0.93
3.	32.00	31.11	32.00	**31.70**	0.51
4.	48.44	48.89	48.89	**48.74**	0.26
5.	46.22	46.67	46.67	**46.52**	0.26
6.	30.22	31.56	31.11	**30.96**	0.68
7.	29.78	27.56	29.33	**28.89**	1.18
8.	44.89	42.22	44.44	**43.85**	1.43
9.	25.78	26.67	26.67	**26.37**	0.51

Fig. 5.12 Bar graph representing variation in compressive strength after 28 days of curing

Maximum strength cement-sludge-flyash concrete was observed in the Experimental cube No- 4 (43 grade OPC, 5% sludge, 15% flyash and sludge particle size ranging in 0.3-2.36 mm) with total cement replacement of 20%. Experimental cube no- 5 also observed high strength (43 grade OPC, 7.5% sludge, 20% flyash and sludge particle size less than 0.075 mm). Total cement replacement on Exp-5 was 27.5 %. Formation of C-S-H gel is the reason for the increase in compressive strength.

Exp-8 observed high strength which might be due to large content of cement present in it. It has 7.5 % sludge as cement replacement with no flyash, only 7.5% total cement replacement.

10 % sludge as cement replacement shows decreased strength as compared to others. Low strength was observed in Exp-9 and 7. This might be due to presence of 10% sludge replacing cement.

Experimental cubes with 33 grade OPC showed compressive strength (after 28 days) in the range of 29-32 MPa, whereas 43 grade OPC showed 30-49 MPa and 53 grade OPC showed in the range of 26-45 MPa.

5.5.2 Toxicity characteristic leaching procedure (TCLP) Test

TCLP test was conducted on cement-sludge –flyash concrete cubes which has been cured for 28 days. The results of TCLP for Iron, chromium and nickel are presented in Table 5.12.

Table 5.12 Concentration of heavy metals in the leachate * after TCLP (18hrs) of cement-sludge-flyash concrete cubes at 28 days curing

S.No	Experiment No.	IRON	TOTAL CHROMIUM	NICKEL
1.	1.	BDL	0.0124	BDL
2.	2.	BDL	0.01042	BDL
3.	3.	BDL	0.05026	BDL
4.	4.	BDL	0.03024	BDL
5.	5.	0.0706	0.03859	BDL
6.	6.	0.0357	0.06525	BDL
7.	7.	BDL	0.02152	BDL
8.	8.	0.1093	0.04715	BDL
9.	9.	0.269	0.03757	BDL
	Drinking water Standard (as per BIS) (mg/l)	**0.3**	**0.05**	**0.2**

BDL- Below Detectable Limit
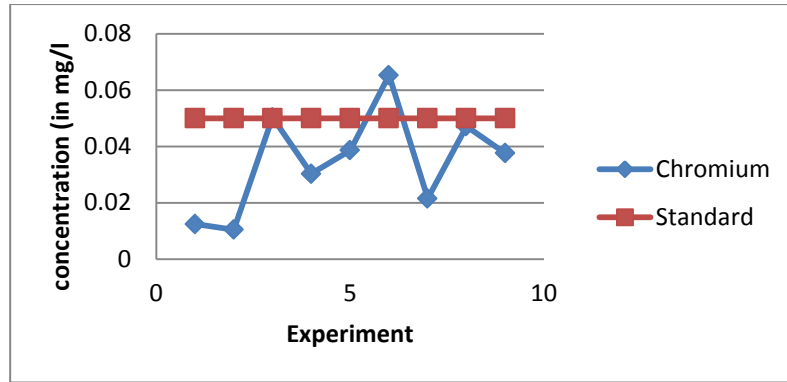*average of results of 2 analysis by AAS

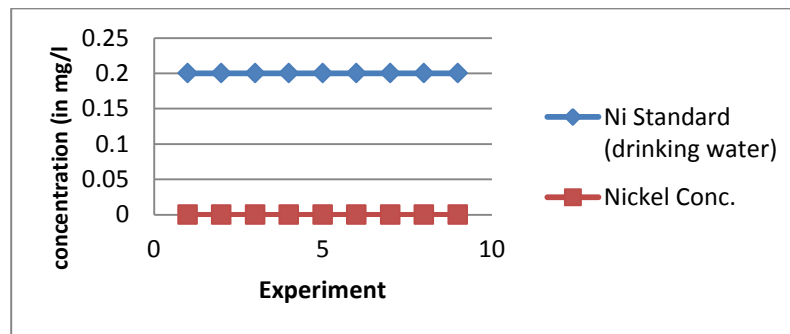Fig.5.13 concentration of Chromium in TCLP leachate
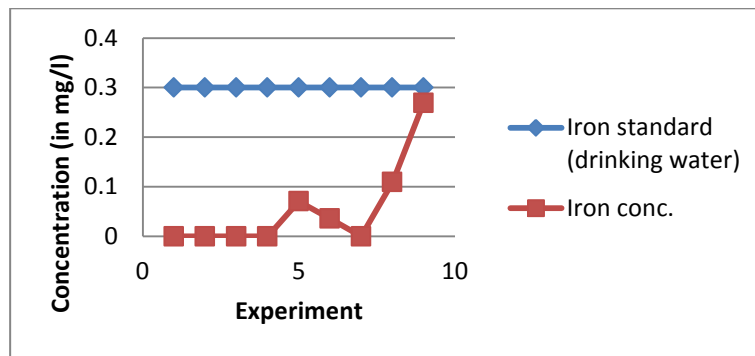

Fig.5.14 concentration of Nickel in TCLP leachate

Fig.5.15 concentration of Iron in TCLP leachate

Table 5.12 shows that the Ni was absent in the leachate and Iron was only observed in few of the Experiments. Chromium was observed in very little concentrations i.e. below the prescribed ground water standard of 0.05mg/l. Experimental cubes 3 & 6 observed slight above concentrations, which might be due to the presence of 10% sludge in them. Decrease in the metal concentrations in the leachate may be due to the formation of hydration product matrices and also dur to the presence of active sites on the surface of flyash. This has also been explained by Zhang et. al (1999).

5.6 ANALYSIS BY TAGUCHI METHODOLOGY

For multi-response analysis of results wherein it is required to optimize the design, Compressive strength obtained after 28 days of curing (Table 5.11) and heavy metal concentration in TCLP leachate (% concentration within limits) is analysed. Both the responses can be analysed for "Higher the better" simultaneously as higher strength and high percent concentrations within limits is desired.

5.6.1 Combined heavy metal Concentration (% Conc. Within limits)

In order to obtain a single parameter representing the concentration of heavy metals (Cr, Ni and Fe) in TCLP leachate in accordance with their permissible standards, percent concentration within limits is calculated and added in accordance with the heavy metal toxicity. Chromium being highly toxic and a parameter of maximum concern with respect to pickling sludge is given 70% factor, Nickel 20 % and Iron 10%.

Table 5.13 Percentage concentrations within limits and meeting standards

Experiment.No.	Concentration(in mg/l) in TCLP leachate			Percent concentrations within limits for each heavy metal			Combined % conc. Within limits
	IRON	TOTAL CHROMIUM	NICKEL	IRON	TOTAL CHROMIUM	NICKEL	
1.	0	0.0124	0	100	100	100	100
2.	0	0.01042	0	100	100	100	100
3.	0	0.05026	0	100	99.48	100	99.636
4.	0	0.03024	0	100	100	100	100
5.	0.0706	0.03859	0	100	100	100	100
6.	0.0357	0.06525	0	100	69.5	100	78.65
7.	0	0.02152	0	100	100	100	100
8.	0.1093	0.04715	0	100	100	100	100
9.	0.269	0.03757	0	100	100	100	100

Table 5.14 represents the summary of the final results obtained for further analysis by taguchi methodology.

Table 5.14 L9 orthogonal array and experimental results

Experi ment	Type of Cement	Sludge (% of cement)	Fly ash (% of cement)	Particle size of sludge (mm)	28 day compressive strength (MPa) R1	Percent concentrations Within limits in leachate R2
1.	OPC- 33 grade	5	0	< 0.075	31.26	100
2.	OPC- 33	7.5	15	< 0.60	29.19	100

	grade					
3.	OPC- 33 grade	10	20	<2.36	**31.70**	**99.636**
4.	OPC- 43 grade	5	15	<2.36	**48.74**	**100**
5.	OPC- 43 grade	7.5	20	< 0.075	**46.52**	**100**
6.	OPC- 43 grade	10	0	< 0.60	**30.96**	**78.65**
7.	OPC- 53 grade	5	20	< 0.60	**28.89**	**100**
8.	OPC- 53 grade	7.5	0	<2.36	**43.85**	**100**
9.	OPC- 53 grade	10	15	< 0.075	**26.37**	**100**

5.6.2 Data analysis of S/N ratios:

S/N ratios are calculated as per equations given in chapter 4. Loss functions, multi-response S/N ratios gives data which on further analysis by ANOM and ANOVA gives useful results.

Table 5.15 Tabulation of measured responses and computed values of S/N ratio

	Compressive strength (R1)	Percent conc. within limits in leachate (R2)	Quality loss values		Normalized Quality Loss values		Total loss function	Multi response Signal-to-noise ratio
	R1	R2	L1	L2	N1	N2	TNQL	Ŋ (dB)
1.	31.26	100	0.001023	0.0001	0.71	0.62	0.66	1.775283593
2.	29.19	100	0.001174	0.0001	0.82	0.62	0.72	1.446506358
3.	31.7	99.636	0.000995	0.000101	0.69	0.62	0.66	1.824912454
4.	48.74	100	0.000421	0.0001	0.29	0.62	0.46	3.419810347
5.	46.52	100	0.000462	0.0001	0.32	0.62	0.47	3.285394209
6.	30.96	78.65	0.001043	0.000162	0.73	1.00	0.86	0.646428575
7.	28.89	100	0.001198	0.0001	0.83	0.62	0.73	1.395189239
8.	43.85	100	0.00052	0.0001	0.36	0.62	0.49	3.102716364
9.	26.37	100	0.001438	0.0001	1.00	0.62	0.81	0.922308241
		AVG	0.000919	0.000107			0.65	1.97983882
		MAX	0.001438	0.000162				

Two responses (R1 and R2) needs to be optimized. A loss function is calculated to evaluate the deviation between experimental value and the desired value. As each quality characteristichas different units of measurement, it is essential to normalize quality loss. 50% each of weighting factors is given to both the responses and thus, total loss is calculated. The weighting factors are decided as per the priorities of the responses which needs to be simultaneously optimized.

Taguchi loss function for multiresponse optimization requires the maximization of multi-response signal to noise ratio (MRSN ratio) (Gaitonde, 2006). MRSN varied from 0.65 to 3.42 with average of 1.98. High S/N ratios depict better signals then noise, thus to better optimization of responses.

5.6.3 Results of Analysis of Mean (ANOM)

The main effects of each factor can be estimated using Analysis of Means (ANOM). The effect of a level of the factor is the deviation caused by it from overall mean response.

Table 5.16: Response table mean multiple response

Symbol	Control factor	Mean Multiple response S/N ratio for each factor and level		
		Level 1	Level 2	Level 3
A	Type of Cement	1.68	**2.45**	1.81
B	% of Sludge	2.20	**2.61**	1.13
C	% of Flyash	1.84	1.93	**2.17**
D	Particle Size grading of sludge	1.99	1.16	**2.78**

Total mean S/N ratio: 1.98

The optimum level of a factor is the level that gives the highest Signal to noise ratio. Based on the data presented in Table 5.16, the optimal performance for compressive strength and heavy metal immobilization values of the cement-sludge-flyash concrete cubes is obtained at:

Table 5.17 Optimal settings of the control factors

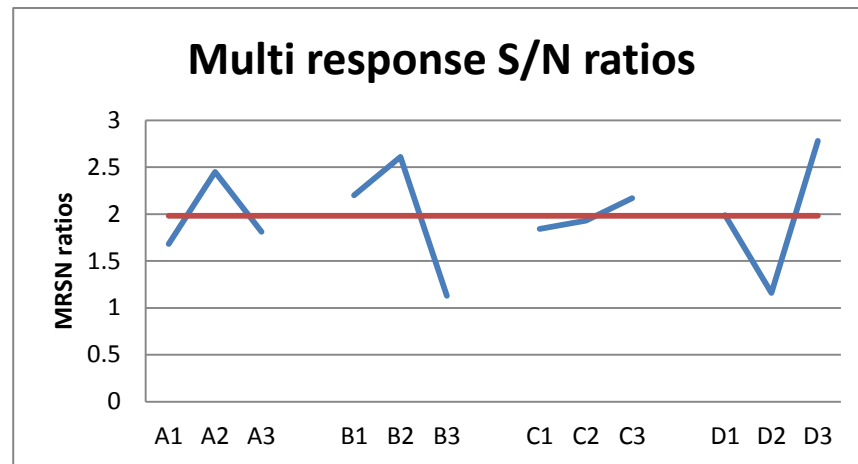| S.No.	Control factor	Level	Optimal value
1.	Type of Cement	A2	43 Grade OPC
2.	Percentage of sludge added	B2	7.5 %
3.	Percentage of flyash	C3	20%
4.	Particle size grading of sludge	D3	sludge with 60% particles in the range of 0.300 to 2.36 mm

Fig. 5.16 Multi response S/N ratios for 4 control factors and their respective 3 levels

Verification of predicted optimal levels of various factors and their suggested performance improvement can be judged by either conducting a confirmation experiment or by calculating the Multi response S/N ratio (η_{opt}) of the optimal parameters. By equation, the η_{opt} was calculated to be 4.07. Since this value is greater than all the MRSN ratio values of the experiments, then the optimal parameters are said to prove to be the optimal performance parameters.

5.6.4 Results of Analysis of Variance (ANOVA)

In this study, ANOVA analysis is carried out to determine statistically significant process parameters and percent contribution of these parameters on the compressive strength and heavy metal immobilization in cement-sludge-flyash concrete cubes. Degrees of freedom

Table 5.18- Summary of analysis of variance (ANOVA)

	Factors	Degrees of freedom	Sum of Squares	Variance	Contribution of factors (%)
A	Type of Cement	2	1.020289	0.510144	11.83
B	% of Sludge	2	3.498781	1.74939	40.55
C	% of Flyash	2	0.1718	0.0859	1.99
D	Particle Size grading of sludge	2	3.936435	1.968218	45.63
	Error	0	0	-	-
	Total	8	8.627304	1.078413	100

The percentage contribution of each factor is determined by calculating sum of squares and variance in ANOVA. Investigation of ANOVA data indicates that the two most effective control factors are the particle size grading of the sludge (45.63%) and the other is the percentage of sludge as cement replacement (40.55%). Type of cement used also had a significant effect on the responses and its contribution is coming out to be 11.83%. Percentage of flyash as cement replacement is contributing 2 % to the variations in results. This may be due to the small range of variations/levels taken for flyash factor i.e. 0%, 15% and 20%.

Chapter 6
CONCLUSIONS AND RECOMMENDATIONS

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

6.1   CONCLUSIONS

The study investigations have led to the following conclusions:

1. XRD analysis of lime treated pickling sludge indicates the presence of pozzolanic materials like gypsum, C_2S and C_3S. Presence of Chromium and Iron was also indicated. The relative proportions of the elements in the pickling sludge sample analysed by EDX analysis indicates the dominance of Iron and calcium with slight percentages of Chromium, Silica and Nickel.

2. Maximum strength cement-sludge-flyash concrete was observed in the Experimental cube No- 4 (43 grade OPC, 5% sludge, 15% flyash and sludge particle size ranging in 0.3-2.36 mm) with total cement replacement of 20%. Experimental cube no- 5 also observed high strength (43 grade OPC, 7.5% sludge, 20% flyash and sludge particle size less than 0.075 mm). Total cement replacement on Exp-5 was 27.5 %. Formation of C-S-H gel is the reason for the increase in compressive strength. Experimental cubes with 33 grade OPC showed compressive strength (after 28 days) in the range of 29-32 MPa, whereas 43 grade OPC showed 30-49 MPa and 53 grade OPC showed in the range of 26-45 MPa.

3. Nickel was absent in the leachate extract of TCLP of SS Pickling Sludge. Sludge contained nickel (1.84% by weight as EDX results and 2.436 mg/l for 50 ml extract made from 0.1g sludge) which might have immobilised in the concrete matrix.

4. Iron was only observed in few of the Experiments. Chromium was observed in very little concentrations i.e. below the prescribed ground water standard of 0.05mg/l (By CPCB). Experimental cubes 3 & 6 observed slight above concentrations, which might be due to the presence of 10% sludge in them whereas the optimal content is 7.5% by the observed results. Decrease in the metal concentrations in the leachate may be due to the formation of hydration product matrices and also due to the presence of active sites on the surface of flyash.

5. The optimal performance for compressive strength and heavy metal immobilization values of the cement-sludge-flyash concrete cubes is obtained at:

   - ➢ **Type of Cement= 43 Grade OPC (level 2 or A2)**
   - ➢ **Percentage of sludge added= 7.5 % (level 2 or B2)**
   - ➢ **Percentage of flyash= 20% (level 3 or C3)**
   - ➢ **Particle size grading of sludge= sludge with 60% particles in the range of 0.300 to 2.36 mm (level 3 or D3)**

6. Percent contribution of the factors taken on the compressive strength and heavy metal immobilization in cement-sludge-flyash concrete cubes analysed by ANOVA indicates that **Particle size grading of sludge (46%)** and **Percentage of sludge added (41%)** contribute most to the variations observed in the analysis results.

6.2 RECOMMENDATIONS

1. Utilization (solidification and stabilization) of Lime treated pickling sludge in concrete is an effective method of utilization/disposal of hazardous sludge. In combination of flyash, better immobilization of heavy metals and improved strenght can be obtained.

2. Addition of 7.5 % flyash and 20% flyash can improve the strength of the concrete. It also reduces or saves the cement by its replacement with pickling sludge. It proves beneficial as cement is a costly commodity and its production generates pollution.

3. This sludge-flyash cement concrete has low metal leachability and is of considerable strength and can be used as a pavement material or used in roadbeds and or parking lots.

6.3 FUTURE SCOPE OF WORK

1. Sludge from the pickling bath which is without neutralization treatment can also be studied for the utilization with cement-concrete.

2. The levels of variations (range) can be widened more for percent sludge replaced by sludge and flyash.

3. Leaching test can be performed for the pavement blocks/ roadbeds/ etc. for ensuring the immobility of heavy metals and thus eliminating the chances of contamination of ground water.

4. Study can be conducted with other control factors and levels. Also study for the utilization of this sludge with cementitious binder materials other then flyash can be undertaken.

5. Similar studies can be undertaken for other type of hazardous waste which has disposal difficulties.

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