CHAPTER - 2

MATERIALS AND METHODOLOGY

2.1 Materials

For the stabilization/solidification (S/S) of jarosite waste, the different-different compositions of pozzolanic material (GGBS) and a pozzolanic reaction activator (hydrated lime) along with jarosite waste, were used and have been discussed in subsequent subsections.

2.1.1 Jarosite

Jarosite is a solid waste produced from hydrometallurgy operations involved in extraction of Zinc metal, in which, initially the zinc ore concentrate (contains ~ 50 % zinc) is roasted and then exposed to leaching operation where iron residual (jarosite) is produced as a waste [4-6]. In the present study, Jarosite is acquired from Hindustan zinc limited, Udaipur, Rajasthan (India) and a photograph of jarosite is shown in Figure 2.1.

Figure 2.1 A photograph of jarosite

On the basis of American Society for Testing and Materials (ASTM) the jarosite texture was found as silty, clayey loam and is yellowish-brown in color (Figure 2.1). The particle size distribution was conducted in accordance with ASTM D6913-04 (sieve analysis)

[54] and ASTM D422-63 (hydrometer analysis) and presented in Figure 2.2. [55]. The consistency limits such as liquid limit, plastic limit, and plasticity index of jarosite were determined as per ASTM D4318-10 [56]. The geotechnical index properties and results of the chemical analysis are listed in Table 2.1.
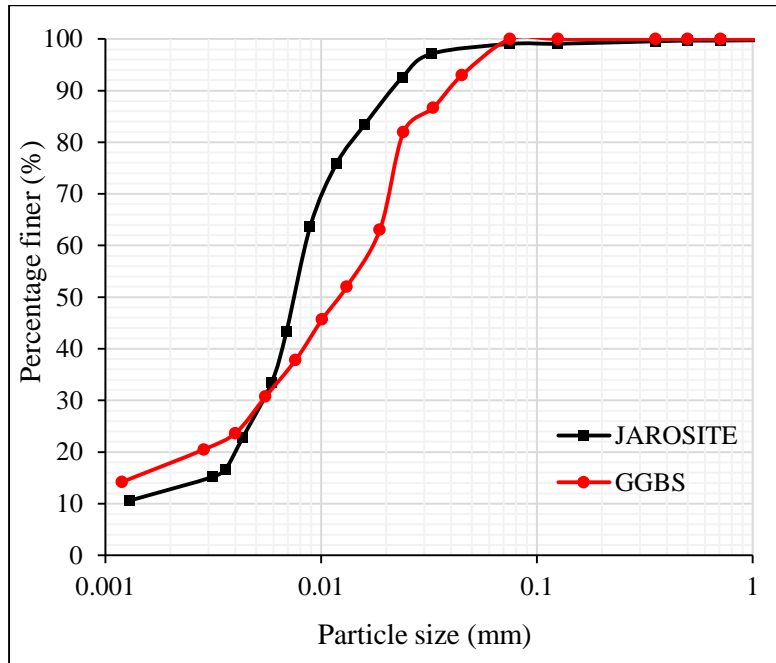

Figure 2.2 Grain size distribution of jarosite and GGBS

Based on consistency limits and guidance given in ASTM D2487-11 [57], jarosite is classified as silt with high plasticity (MH) (at the lower end of MH category, Liquid limit = 54% and Plasticity index = 22%). The specific gravity was found to be 2.77 (ASTM D854-00). The differential free swell index (DFS) of jarosite was 18%. Thus the degree of expansiveness of jarosite is characterized as low (BIS: 2911-3) [59].

Table 2.1 Geotechnical and chemical properties of jarosite

Properties			
Geotechnical	Values	Chemical compositions	Values (%)
Liquid limit (%)	54	Silica (SiO_2)	7.73
Plastic limit (%)	32	Alumina (Al_2O_3)	8.98

Properties			
Geotechnical	Values	Chemical compositions	Values (%)
Plasticity index (%)	22	Calcium oxide (CaO)	4.92
Specific gravity	2.77	Iron oxide (Fe_2O_3)	32.11
Silt size (%)	85	Potassium oxide (K_2O)	0.76
Clay size (%)	15	Magnesium oxide (MgO)	1.80
Maximum dry density (Mg/m^3)	1.13	Zinc oxide (ZnO)	9.07
Optimum moisture content (%)	42	Total sulfur (SO_3)	31.80
Hydraulic conductivity (cm/sec)	$1.75*10^{-3}$	Lead oxide (PbO)	1.91
Texture	Clayey silt	Sodium oxide (Na_2O)	0.63
pH	6.87		
Differential free swell Index (%)	18		

2.1.2 Ground granulated blast furnace slag (GGBS)

Ground granulated blast furnace slag (GGBS) is a derivative of the iron manufacturing. In this study, the GGBS (specific gravity of 2.73) is obtained from Krishna Udyog, Burdwan, West Bengal, India (Figure 2.3). The particle size distribution chart and chemical composition of GGBS are presented in Figure 2.2 and Table 2.2 respectively.

Figure 2.3 A photograph of ground granulated blast furnace slag

Table 2.2 Chemical properties of GGBS

Chemical Composition	Value (%)
Silica (SiO_2)	34.17
Alumina (Al_2O_3)	18.36
Calcium oxide (CaO)	33.78
Iron oxide (Fe_2O_3)	0.80
Magnesium oxide (MgO)	8.82
Total sulfur (SO_3)	2.91

2.1.3 Hydrated lime

The hydrated lime [$Ca(OH)_2$], used as a cementitious material in the study, was obtained commercially. The specific gravity was found to be 2.48. Hydrated lime is derived from quicklime by reacting with water. Hydrated lime is mostly used in the stabilization applications. The photograph of lime is shown in Figure 2.4 and the chemical composition is presented in Table 2.3.

Figure 2.4 A photograph of hydrated lime powder

Table 2.3 Chemical properties of hydrated lime

Chemical Composition	Value (%)
Silica (SiO_2)	4.29
Alumina (Al_2O_3)	1.48
Calcium oxide (CaO)	71.46
Iron oxide (Fe_2O_3)	0.27
Magnesium oxide (MgO)	15.48
Total sulfer (SO_3)	4.56
Lead oxide (PbO)	0.47
Sodium oxide (Na_2O)	0.03

2.2 Testing Methodology

A number of laboratory studies namely Strength (Unconfined compressive and Split tensile strength tests), Durability (Freezing-Thawing study), Mineralogical and Morphological (X-Ray Diffraction (XRD) & Scanning electron microscope (SEM) corresponding to Energy-dispersive X-ray spectroscopy (EDX) tests) and Leachate have been carried out on jarosite waste stabilized with GGBS and lime. The objective of the present study is to find out the influence of pozzolanic material (GGBS) and an activator (hydrated lime) on the characteristics of stabilized jarosite to be used as a constructional material in Civil Engineering. The GGBS has been added at a rate of 10, 20, 30 and 40% by weight of dry jarosite. For all the compositions of the jarosite-GGBS mixture, the lime content varies as 2.5, 5.0, 7.5 and 10% by weight of jarosite. Jarosite brought from the zinc industry was firstly dried in an oven for 24h at 105 °C, and after that was grinded to break all lumps. Figure 2.5 illustrate the flow diagram of testing methodology adopted.
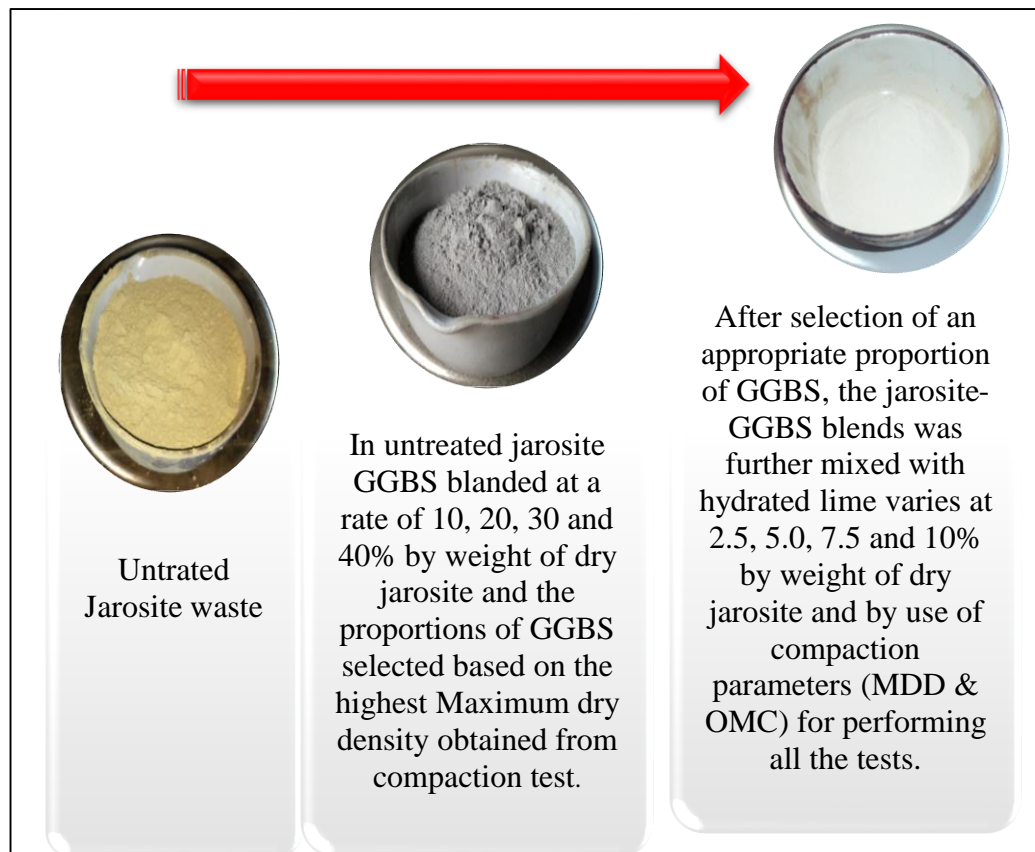
Figure 2.5 Flow diagram illustrates the methodology adopted

To prepare the samples of jarosite-lime or jarosite-GGBS-lime blends for various tests, firstly, the compaction tests were conducted to find out the compaction parameters (maximum dry density (MDD) and optimum moisture content (OMC)) of all the blends. Afterward, all the samples were compacted at MDD and OMC, and respective studies were performed.

2.3 Detailed Description of Testing Methodology Adopted

Table 2.4 shows the list of test performed and respective standards adopted as well as Figure 2.6 illustrate the flow diagram of the various studies undertaken. All the tests were conducted in laboratory as per the testing methods described in the relevant ASTM Standards. However, in the absence of ASTM Standards for a particular test, Indian Standards were followed. In addition, the leachate study is conducted in accordance with

Toxicity Leachate Procedure (TCLP), United States Environment Protection Agency (USEPA) Method 1311 [25].

Table 2.4 Standards adopted for testing

| Tests conducted	Standard adopted	
	ASTM Standard	Indian Standard
Particle size distribution (Sieve analysis)	ASTM D6913-04 [54]	BIS 2720 Part 4 [65]
Particle size distribution (Hydrometer analysis)	ASTM D422-63 [55]	BIS 2720 Part 4 [65]
Consistency limits	ASTM D4318-10 [56]	BIS 2720 Part 5 [66]
Soil classification system	ASTM D2487-11 [57]	BIS 1498 Part 2.2 [67]
Specific gravity	ASTM D854-10 [58]	BIS 2720 Part 3 [68]
Differential free swell index	-	BIS 2911 Part 3 [59]
Mini Compaction	ASTM D698- 12e1 [60]	-
Falling head permeability	ASTM D5084-03 [61]	BIS 2720 Part 9 [69]
Unconfined Compressive Strength	ASTM D2166-13 [62]	BIS 2720 Part 10 [70]
Split Tensile Strength	ASTM D3967 [63]	BIS: 10082 [71]
Freezing-Thawing	ASTM D560M-15 [64]	BIS 4332 Part 4 [72]
The standard for Unfired bricks	-	BIS 12894 [73]
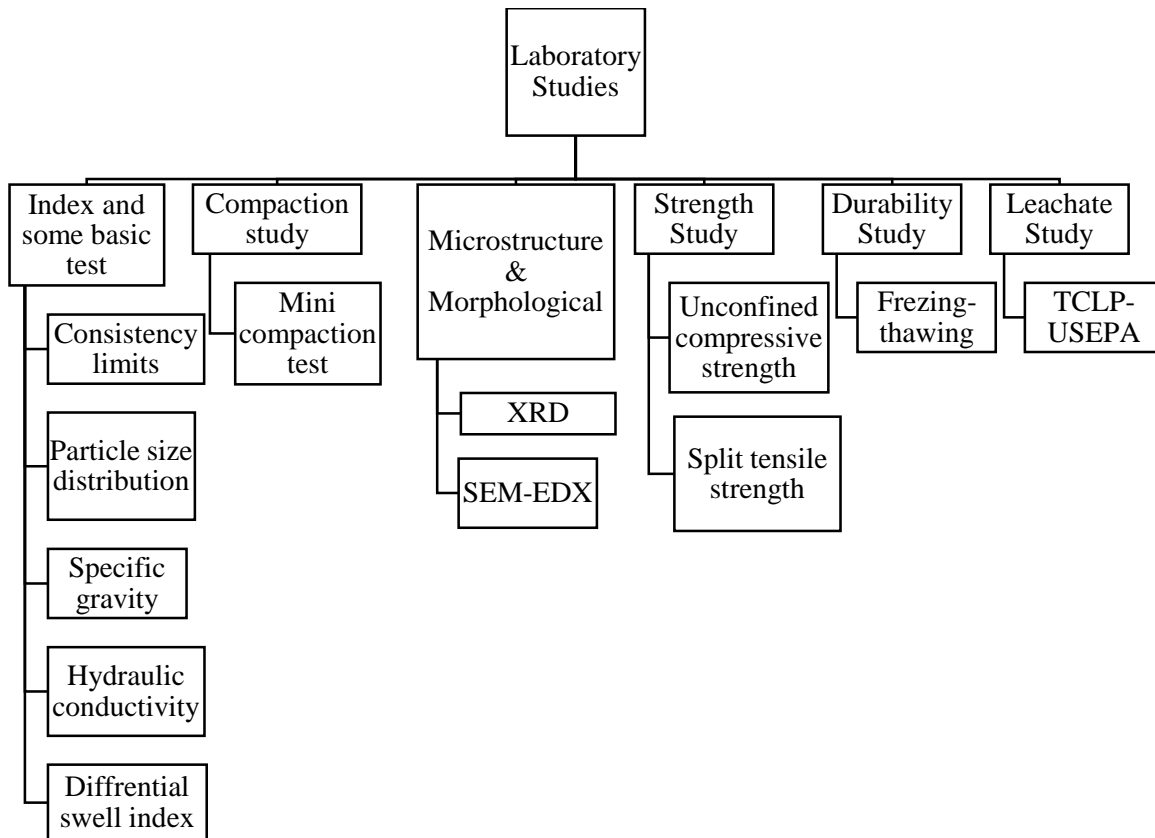
Figure 2.6 Flow diagram of the various studies undertaken

2.3.1 Specific gravity

Specific gravity test for the different basic materials such as jarosite, GGBS and marble dust used in the present study was found out with the help of density bottle of volume 50 ml (Figure 2.7). Mass of empty density bottle with stopper is recorded as M_1. About 10 to 20 g of a sample is transferred to the density bottle, and the mass of bottle and sample with stopper is recorded as M_2. Then the bottle having sample inside it is filled with water, entrapped air is removed, and then its mass is recorded as M_3. Then the bottle is emptied and is filled with water to find mass M_4. Specific gravity is calculated by the formula:

$$G = \frac{M_2 - M_1}{(M_2 - M_1) - (M_3 - M_4)}$$

Where,

M_1 = mass of bottle and dry soil in g;

M_2 = mass of density bottle in g;

M_3 = mass of bottle, soil and water in g; and

M_4 = mass of bottle when full of water only in g.

Figure 2.7 Density bottle for determination of specific gravity

The specific gravity shall be calculated at 27 ℃. If the room temperature is different than 27 ℃, the following correction shall be done:

$$G' = KG$$

Where,

G'= Corrected specific gravity at 27 ℃, and

$$\text{The } k = \frac{\text{Relative density of water at room temperature}}{\text{The relative density of water at 27 ℃}}$$

2.3.2   Grain size distribution

2.3.2.1 Sieve analysis

Grain size distribution curves for materials were obtained with the help of fine sieve analysis method because they belong to the size range of 4.75 mm to 75µ. The set of the sieve having sieves of 2 mm, 1 mm, 600µ, 425µ, 300µ, 212µ, 150µ and 75µ arranged in the order that the largest aperture sieve being kept at the top and the smallest aperture sieve at the bottom are used in this analysis. The sample is put on the top sieve, and the

whole assembly (set of sieves and bottom pan) is shaken for at least 10 minutes. The portion of sample retained on each sieve is weighed with the help of which percentage finer for each sieve is calculated. Finally, the particle size distribution curve with the percentage finer as the ordinate and the particle diameter as the abscissa is being plotted.

2.3.2.2 Hydrometer analysis

Grain size analysis for material was carried out with the help of hydrometer analysis because the substantial amount of their particles was finer than 75μ. The suspension of the sample in water with the dispersing agent is prepared. The sedimentation jar is shaken vigorously and is then kept vertical on a solid base. The hydrometer readings are taken by using a hydrometer (Figure 2.8) at ½, 1, 2, 4, 8, 15, 30 minutes and 1, 2 & 4h, etc. which are further used to compute the particle size and percentage finer to get the particle size distribution curve.

Figure 2.8 Hydrometer for particle size distribution

2.3.3 Consistency limits

The guidelines mention in relevant standards (mentioned in Table 2.4) were used for the determination of the consistency limits namely liquid limit and plastic limit.

2.3.3.1 *Liquid limit*

Liquid limit of jarosite was determined with the use of standard tool designed by Casagrande (Figure 2.9). About 120 g of the jarosite sample finer than 425µ sieve thoroughly blended with distilled water on a flat glass plate to form a homogenous paste. The paste is placed in the brass cup of Casagrande apparatus and a groove is cut with the standard grooving tool. The rotation rate of handle is kept constant i.e. about two revolutions per second, and the number of blows are counted until the bottom of the groove cut meet along a 10 mm length due to flow and not by slide. About 10 g of jarosite from near the closed groove is taken for water content determination. This process is repeated at different water contents.
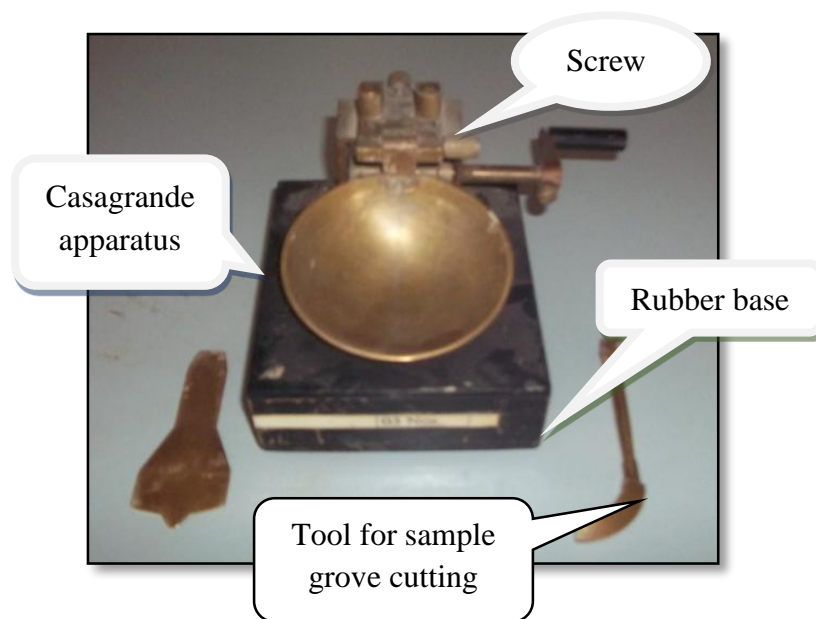

Figure 2.9 Casagrande apparatus for determination of liquid limit

After taken required observation, a flow curve was drawn on a semi-logarithmic scale, in which arithmetical scale represents water content whereas logarithmic scale represents number of drops. At least four points should be plotted to make as a nearly straight line, to drawn the flow curve. The water content equivalent to 25 drops, read from the flow curve, is recorded as the liquid limit.

2.3.3.2 *Plastic limit*

Plastic limit of clay was determined by taking the jarosite sample passing through a 425μ sieve which is mixed with water until the material becomes plastic enough to be easily remolded. A ball is formed with about 8 g of paste and rolled between fingers up to 3 mm diameter, and the sample is again remolded into a ball. This process of rolling and remolding is repeated until the thread starts just crumbling at a diameter of 3 mm. The crumbling threads are kept for water content determination. The test procedure is repeated by two or three times, and the average water content is taken which is taken as the plastic limit.

2.3.4 Mini compaction

Mini Compaction Mold, (Figure 2.10) advanced by Sridharan and Sivapullaiah [60] is used for compaction test. For every compaction test, about 200 g of the jarosite-GGBS-lime mixture is used. The required amount of moisture is added to the blend and then mixed thoroughly. Afterward, the blend is compacted in a cylindrical mold having 38.1 mm diameter in three layers, and each layer is given 36 blows from 1 kg drop hammer. After compaction, the sample is removed from the mold, and its bulk unit weight is recorded, moisture content determined and the resultant dry unit weight is calculated.
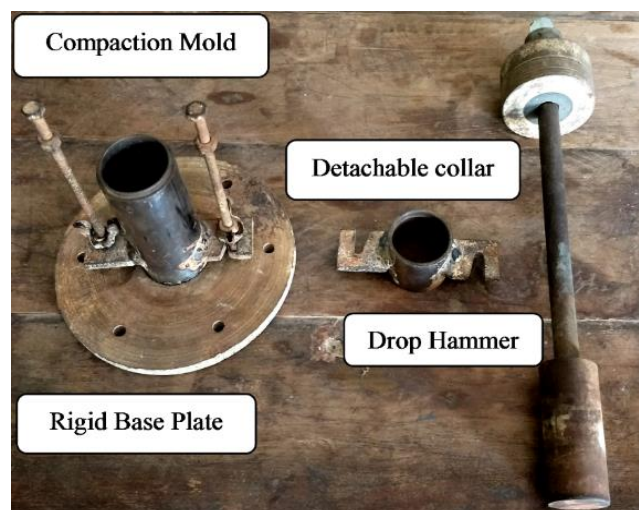

Figure 2.10 A photograph showing different parts of mini compaction equipment

2.3.5 Hydraulic conductivity

Hydraulic conductivity of jarosite was determined by conducting falling head permeability test in accordance with standards (mentioned in Table 2.4) in laboratory. As per the standard, firstly the jarosite was compacted at its OMC and MDD in three layers in the standard mold. Afterward, the compacted jarosite sample was saturated and then a standpipe of the standard cross-sectional area is fixed over the permeameter (Figure 2.11) and water is permitted to run down. Once the steady flow is achieved, reading of head corresponding to time interval was taken. After the required observations, the coefficient of permeability is calculated by the use of following formula:

$$k = \frac{2.303aL}{At} \log\frac{h_1}{h_2}$$

Where,

   a = cross-sectional area of standpipe;
   L= length of sample column;
   A= area of the soil column,
   t = time required for head drop;
   h_1=initial head; and
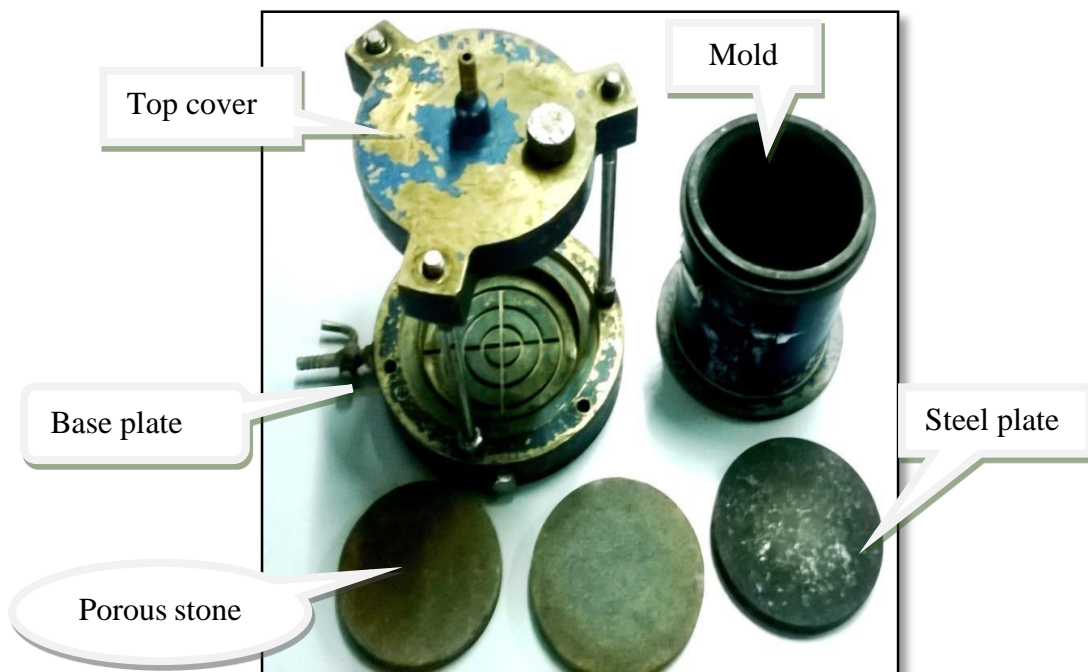 h_2= final head

Figure 2.11 Permeability test apparatus with all parts

2.3.6 Differential free swell index

The differential free swell index (DFS) was performed to determine the relative volume change in kerosene oil and distilled water, i.e., swell index of the material. 10 g of the material sample is kept in two glass tubes one containing kerosene oil and the other distilled water, for 24h (Figure 2.12). Afterward, the differential free swell index (DFS) was calculated by using the following relation:

$$\text{The DFS index} = \frac{\text{Soil volume in water} - \text{Soil volume in kerosene}}{\text{Soil volume in kerosene}} \times 100\%$$
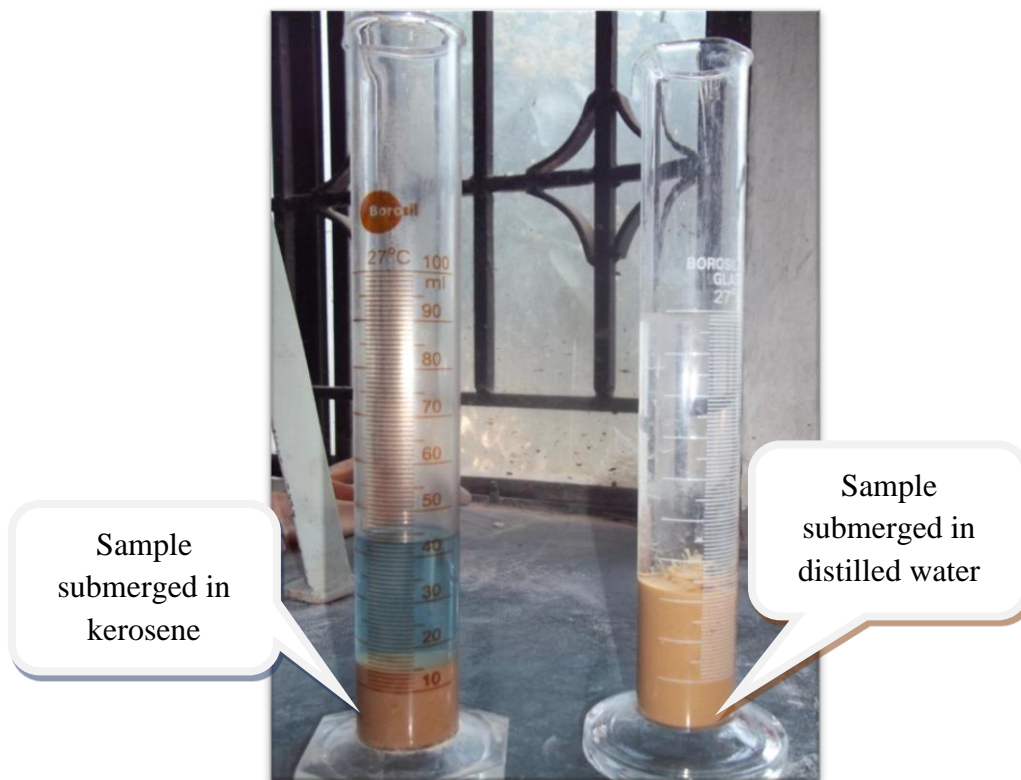

Figure 2.12 Differential free swell index test setup

2.3.7 Strength study

With the help of MDD and OMC of all the jarosite-GGBS-lime mixture, samples for strength characteristics namely unconfined compressive strength (UCS) and split tensile strength test were prepared as per relevant standards (Table 2.4) respectively.

2.3.7.1 *Unconfined compressive strength*

Unconfined compression test is reliable, quick and widely accepted experimental program for predicting the shear strength. The UCS tests were conducted on the samples of jarosite-lime-GGBS blend in accordance with relevant standards. The samples were prepared in a mold, which has an aspect ratio of 2, i.e., 38 mm in diameter and 76 mm in height (Figure 2.13) with a strain rate of 1.25 mm/min used for testing. Figure 2.14 illustrates the laboratory experimental setup for UCS test.

Figure 2.13 UCS mold with accessories

2.3.7.2 *Split tensile strength*

The tensile strength of any cemented materials is a very vital geotechnical constraint. Due to the cementing nature of the stabilized material, concerning to its longevity, the brittleness and splitting behavior should be necessarily known [74]. Vaniček [74] also revealed that the tensile strength parameter is associated with predicting the chances of

tensile cracks possible to develop in stabilized earthen constructions, for example, embankments, reinforced retaining walls or landfills.
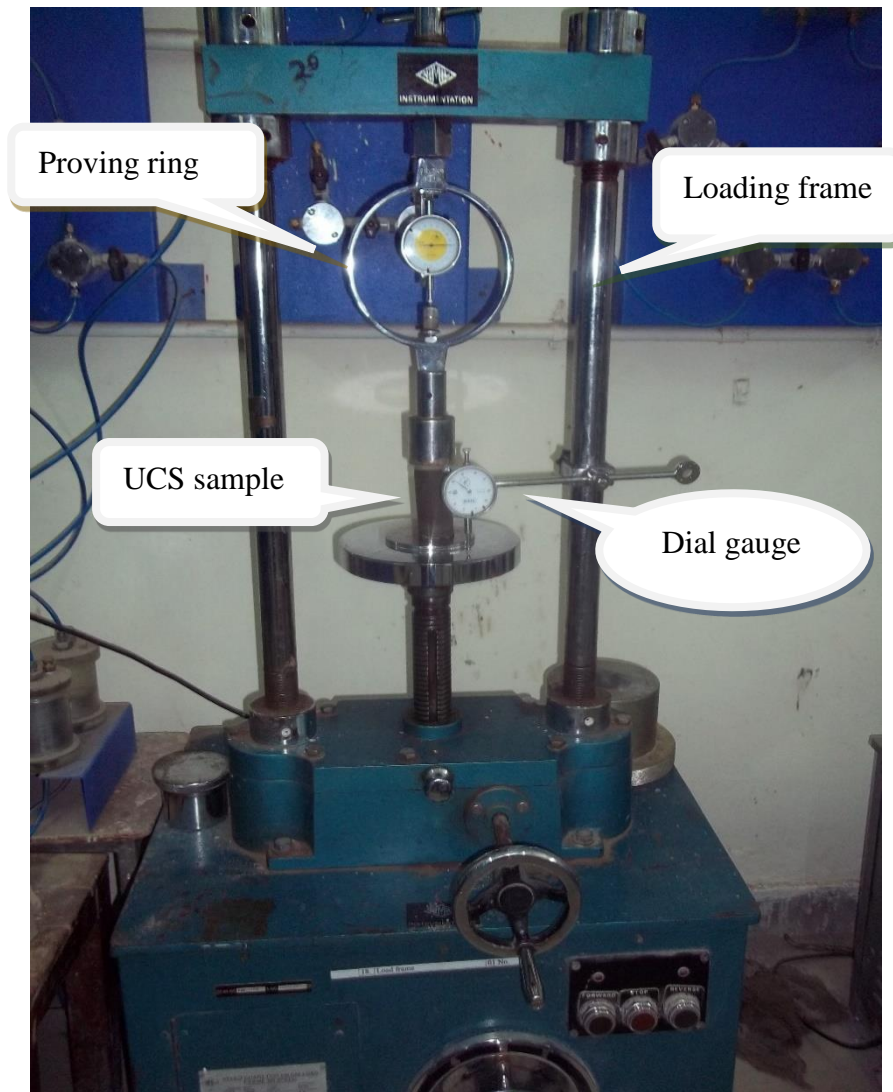

Figure 2.14 Laboratory experimental setup for UCS test

It is difficult to perform direct uniaxial tension strength tests, thus, for determination of the tensile strength of stabilized jarosite, an indirect method such as Brazilian Split tensile strength test (Figure 2.15) was conducted. The samples were prepared with an aspect ratio of 0.5, i.e., 38 mm in diameter and 19 mm in length and a strain rate of 1.25 mm/min was used for testing. By placing the cylindrical sample between the platens of Brazilian tensile strength testing apparatus, the split tensile tests were carried out. After placing the

sample, it was compressed by loading on it, leading to failing diametrically in tension, and the corresponding maximum load was recorded.
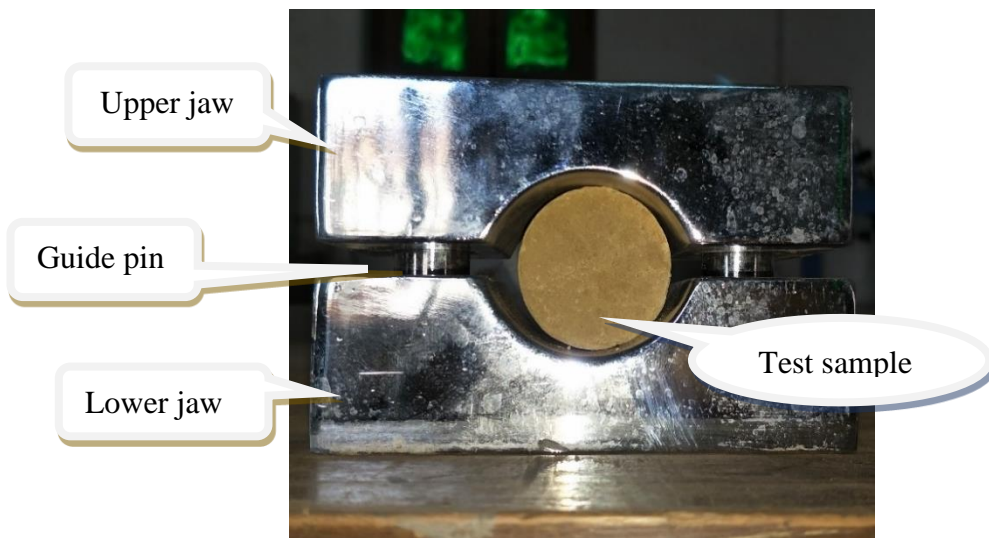

Figure 2.15 Laboratory experimental setup for Brazilian split tensile test

2.3.7.3 *Sample preparation for the strength test*

In general, the samples for strength tests were prepared by compacting the blend in three layers in the cylindrical mold having different aspect ratio with respect to the type of strength test. For UCS test, the samples prepared were 38 mm in diameter and 76 mm in height, i.e., with an aspect ratio of 2. Similarly for tensile strength test, the samples were prepared with 38 mm diameter and 19 mm length, i.e., with an aspect ratio of 0.5. The different blends of GGBS-lime stabilized jarosite were divided into three equal parts, and every part was transferred to the mold and compacted. This process was continued for each layer to obtain a thoroughly compacted sample. Before pouring blend into the mold, a thin coating of a lubricant was applied on the inner surface of the mold to diminish the friction between the mold and the blend. Thus, the chances of disturbance of sample were minimized and also reducing the possibility of developing any fracture in the sample during its removal. Also, for proper bonding between two layers, sufficient scraping of the surface was made before placing the blend for the next layer. The compacted sample

was removed from the mold using a hydraulically operated sample extractor. After removing; due to non-availability of other methods, the samples were kept in polythene bag for curing (to minimize moisture loss due to evaporation) and kept in a desiccator for curing for 7, 28, 60 and 90 days at controlled room temperature, i.e., 28 ± 3 °C. (Figure 2.16) After curing of samples for respective curing periods in a humid room, UCS and split tensile tests were carried out at a strain rate of 1.25 mm/minute. The standard deviation in the strength of three individual samples, molded at the same moisture content, would not vary by more than 10% from their mean strength, was considered as a test result.

(a)

(b)

(c)

Figure 2.16 Samples preparation for strength study, (a) USC samples; (b) Tensile samples; (c) Samples kept in a polythene bag for curing

2.3.8 Durability study

For evaluation of durability and degree of adequate hardness to resist field weathering of stabilized jarosite-GGBS-lime matrix, freezing, and thawing (F-T) test was conducted in the laboratory.

2.3.8.1 *Freezing-thawing*

The freezing and thawing test was conducted to assess the durability of stabilized jarosite-lime samples in accordance with relevant standards (Table 2.4) in laboratory. In the analysis of freezing-thawing studies, the samples were subjected to a closed-system type of freezing. In this type of system, there are no sources of moisture existing during the process of freezing except that initially present in the pores. This study is suitable in the regions where no such variation occurs in the in situ moisture content anticipated among winter and summer periods like cold regions [75-76].

For this test, the respective cured samples were placed in a deep freezer (Figure 2.17 (a)) at -20 °C for 24h and then at room temperature (23 ± 5 $^\circ$C) for 24h for thawing (Figure 2.17 (b)). These temperature ranges were selected in accordance with previous studies [77-79], which revealed that if the temperature subjected in the freezing phase is too adjacent to 0 $^\circ$C, chances of partial freezing or maybe no freezing occurs in samples because of the nonexistence of frost nucleation. Thus, to attain complete frost dispersion, a temperature of -20 $^\circ$C for 24h was chosen and similarly, for attaining complete thaw weakening, a temperature of 23 ± 5 $^\circ$C was selected for 24h in a vessel maintained at a relative humidity of 100%. Each jarosite-lime sample was subjected to 0, 1, 3 and 5 freezing-thawing cycles. The number of cycles was chosen as per available literature [80-82], which revealed that the reduction in strength usually occurs in primary few cycles, i.e., up to 5 cycles. For each F-T cycle, four UCS samples of each blend were prepared,

in which two were tested for strength study and remaining two for weight loss study (material loss). The average reading of two samples was considered as a test result.

In strength study, the percentage loss in strength of samples for each F-T cycle was measured by performing UCS test on them. Similarly, in weight loss study, after the completion of each F-T cycle, each sample was given two firm strokes on all areas with a wire scratch brush and then samples were weighed. Subsequently, comparing final sample weight with initial one (before F-T cycle sample weight), gives the percentage weight loss or material loss.

(a)   (b)

Figure 2.17 Samples preparation for durability study, (a) Deep freezer; (b) Frozen samples kept for thawing

2.3.9 Mineralogical and morphological analysis

The samples of stabilized jarosite with different lime and GGBS content and curing period were examined for their mineralogical changes using X-ray diffraction (XRD) test

and their morphological changes by utilizing scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX).

2.3.9.1 X-Ray diffraction

X-ray diffraction method is widely used in the analysis of solid solution, crystalline and particularly, with small-angle scattering, the size and, to some extent, the shape of small particles. This diffraction technique was used in present study to identify the hydration products of lime-GGBS stabilized materials. In the present study, X-Ray Diffraction (XRD) analysis was carried out by using high resolution X-Ray diffractometer (Rigaku Miniflex 600, Germany) (Figure 2.18).

Theoretically, in XRD test, X-rays homochromatic rays are concentrating onto a crystal-like surface, thus the ray's diffraction occurs. The atoms in the crystal scatter the diffracted rays lying in its path. The scattered rays reinforced only when the Bragg's law is satisfied:

$$n\lambda = 2d \sin\Theta$$

Where,

λ = wavelength of the X-ray;

d = crystal spacing characteristic of each mineral component;

Θ = angle of incidence of the X-ray; and

n = integral number

By the use of known wavelength X-rays the d spacing of the various phases in a crystal plane can be determined. In the powder X-ray diffraction test, the sample of material was grinded to a very fine powder and positioned in the path of X-rays. Thus, each particle of material was a randomly crystal oriented with concerns to the ray. Afterward, the diffracted rays were identified with their intensities and related angles. The d spacing and their related intensities form the pattern which is unique properties of the element.

Identification of a particular element is made with the help of standard tables containing crystal reflections with their intensities.

Figure 2.18 A photograph of high-resolution X-Ray diffractometer (Rigaku Miniflex 600, Germany)

2.3.9.2 *Morphological analysis (SEM-EDX)*

In the morphological (microstructural) analysis, scanning electron microscope (SEM) corresponding to energy-dispersive X-ray spectroscopy of various jarosite-GGBS-lime mixtures were carried out using high resolution scanning electron microscope (SUPRA 40, Zeiss 4.0 (Figure 2.19)). The oven dried pieces of sample collected after performing strength test were used for SEM studies. For examining the change in the packing nature (due to pozzolanic reactions) of stabilized mixtures, several SEM images were recorded at different magnifications.

Figure 2.19 A photograph of high-resolution scanning electron microscope (SUPRA 40, Zeiss 4.0)

2.3.10 Toxicity Leachate Characteristics Procedure (TCLP) Study

For evaluation of the degree of hazardous nature of raw jarosite waste and its stabilized product, the United States Environmental Protection Agency (USEPA)-Toxicity Leachate Characteristics Procedure (TCLP) [25] is widely adopted and it was also used in present study. In this procedure, the powdered sample of stabilised product is blended with a solution of acetic acid and 1N NaOH as an extraction liquid (pH 4.93), with a liquid to solid weight ratio of 20:1 and then this solution is agitated in a rotary extractor for a period of 18h at the speed of 30 RPM and 22 °C. After agitation, the solution is loaded into Zero Head Space Extractor (ZHE) and the extractor is closed airtight. In order to extract leachate fluid, a pressure of 50 psi is applied through the extractor, and up to 50 ml of expelled fluid is collected. The collected fluid is screened through a filter paper having 0.6-0.8 μm filtering capacity. This filtrate fluid is distinct as a TCLP extract, and it is analyzed further for evaluation of hazardous constituents such as Silver (Ag),

Chromium (Cr), Cadmium (Cd), Lead (Pb) and Arsenic (As). In the current study, the

Thermo Scientific iCAP6200 Duo inductively coupled plasma (ICP) spectrophotometer

(Figure 2.20) was used for evaluation of heavy metals and toxic elements.

Figure 2.20 A photograph showing Thermo Scientific iCAP6200 Duo inductively
coupled plasma spectrophotometer