CHAPTER - 1

INTRODUCTION AND LITERATURE REVIEW

1.1 General

Currently, industrialization evolution is synonyms of any developing country, which moves on the way to become a developed country. But, advances in this process leads to engendering large extent of waste and by-products. Due to the environmental concerns, there is a vital need that all types of industrial sectors take care for safe disposal of the pollutants generated in any form of waste such as solid, liquid or gaseous state; as well as pay attention to the effective and economical management of waste [1]. Worldwide, about 20 billion tons of total wastes are produced, wherein about 12 billion tons of wastes are produced from industrial progression, 4 billion tons produced in the form of municipal solid wastes (MSW), and the remaining 4 billion tons cover natural wastes in the form of organic as well as inorganic [2]. For, the disposal of the waste, the land disposal method is one of the widely adopted conventional methods, but due to the large production of wastes, the requirement of more precious land rises, thus the scarcity in land arises mostly. For solving this precious land scarcity problem, the waste management is a general trend today.

The waste management program mainly consists of, controlled production of waste; reduce, reuse, recycle and reclaim (4-R) the waste; recovery of energy and also eco-friendly disposal of waste. In previous few decades, for the enchantment in the waste management/utilization, the various industrial wastes such as marble residuals, coal combustions residues, rice husk ash, phospho-gypsum, cement kiln dust, copper slag, blast furnace slag, bagasse ash, ceramic dust, waste steel chips, brick dust and many more, has been fruitfully exploited as stabilizing agents, with or without addition of small percentage of cementing agent such as binder.

1.2 Problem Statement

The Jarosite is a solid waste remains during the hydrometallurgical operations, involved in the extraction of zinc from the lead-zinc smelter. A German mineralogist named August Breithaupt recognized a yellowish-brown mineral at ***Jaroso*** in the southeastern coast of Spain, and was named as jarosite [3]. Mostly, the jarosite process has been widely used for zinc metal extraction in hydrometallurgy. In the process of zinc extraction, zinc ore concentrate (contains ~ 50% zinc) is firstly roasted at 900 °C and then subjected to leaching where the iron residue (jarosite) is formed as a waste material [4-6].

Due to the presence of very fine particles and also containing heavy and toxic elements in jarosite, its inadequate disposal causes an adverse impact on the environment including soil and groundwater contamination, and fine particles suspension is also dangerous to aquatic life in the sea. Also, the disposal of jarosite in lakes or ponds needs huge areas of valuable land, and the disposal of dry jarosite can also lead to chances of dust pollution which further creates serious health issues for the people living near jarosite storage sites. [2]

The zinc smelters produced about 12.60 million metric tons of zinc metal in 2016, which was increased to 13.20 million metric tons in 2017; whereas the estimated zinc resources available worldwide is about 2.3 billion metric tons (Table 1.1). In India, mainly two industries namely Hindustan Zinc Limited (HZL) and Binani Zinc Limited are contributing to the production of zinc metal. HZL has the largest multi-unit of mining and smelting industry, having an installed capacity of 3.49 MT/per year [7-8]. These zinc extraction plants released a large quantity of jarosite waste, from which about 0.25 and 0.60 million tons per annum jarosite are being released in India and the European Union respectively [8]. The major quantities of jarosite are released from China, USA, Spain, Holland, Canada, France, Australia, Yugoslavia, Korea, Mexico, Norway, Finland, Germany, Argentina, Belgium and Japan [10].

Table 1.1 Worldwide metallurgical zinc production [9]

Country	Production (Million Tons)		Reserve (Million Tons)
	In 2016	In 2017	
The United States	0.805	0.730	9.700
Australia	0.965	1.000	64.000
Bolivia	0.490	0.500	4.800
Canada	0.322	0.340	5.400
China	4.800	5.100	41.000
India	0.682	1.300	11.000
Kazakhstan	0.340	0.360	13.000
Mexico	0.670	0.680	20.000
Peru	1.330	1.400	28.000
Sweden	0.257	0.260	3.800
Other countries	1.890	1.520	33.000
World total (Rounded)	12.600	13.200	230.000

1.2.1 Production process of jarosite waste

Jarosite is formed when zinc sulfide ore is roasted at 900 °C and leached with sulfuric acid [11]. In the process of leaching with sulfuric acid, jarosite precipitates through a selective precipitation method only when pH < 2.5. Figure 1.1 shows the flow-sheet for recovery of zinc and production of jarosite waste by the roasting-leaching-electro-winning process.

The addition of alkali metal or ammonium ions, the iron compound (Fe^{3+}) type jarosite residues (X $[Fe_3 (SO_4)_2(OH)_6]$) is precipitated in the processing of zinc extraction. [5-6, 12]. The formation of jarosite waste is represented by the following equilibrium condition:

$$3Fe_2(SO_4)_3+X_2SO_4+12H_2O \longrightarrow 2XFe_3(SO_4)_2(OH)_6+6H_2SO_4$$

The general chemical formula of jarosite is X [$Fe_3(SO_4)_2(OH)_6$], (where X represents Na^+, K^+, NH_4^+, 1/2 Pb^+ etc.**)** [4-6].

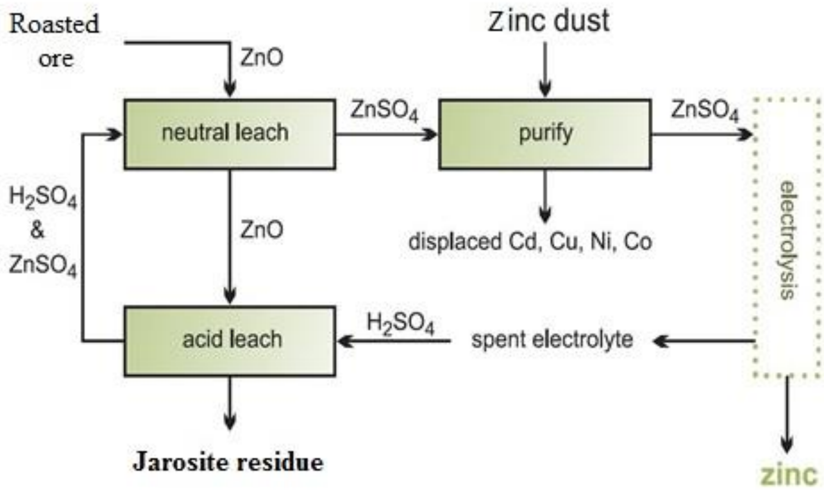

Figure 1.1 Flow-sheet for Recovery of zinc and production of jarosite waste by Roasting-Leaching-Electro-winning process [13]

As said earlier, it is summarized that jarosite is a hazardous waste containing heavy and toxic elements and has concerns towards environment and surrounding human beings, and hence, its safe management is necessary. Thus, the current study will not only make an attempt to stabilize and detoxify the jarosite but also try to use this stabilized/treated material in various application of civil engineering such as in embankment design, as a subgrade material, in brick/block manufacturing etc.

1.3 Literature Review

Substantial Research and development (R&D) projects for the safe storage, disposal, and utilization of jarosite are being carried out all over the world.

1.3.1 Disposal practice of jarosite waste and its management

The landfill is the most common disposal practice globally adopted. About 95% of generated waste is disposed of in the form of landfill worldwide [14]. The susceptibility from acid leaching of jarosite waste requires landfill sites to be lined, usually with either plastics or chemical barriers [15].

Ribet et al. [16] reported that layering a sulfide tailings dump with activated carbon (found in sewage sludge) and other types of municipal garbage leads to enhance chemical reduction in the upper layers, but this method was found ineffective when there are presence of high microbial concentrations in the waste because they increased the rate of decomposition, especially of sulfur containing compounds [17].

The jarosite waste is conquering costly land with environmental pollution concern. In India, as per safe environmental concern, involves in the disposal practice of Hindustan Zinc Limited, the jarosite waste is mixed with lime and cement and transported to the disposal area and then disposed of in lined disposal yard in form of stabilized and stable material (Jarofix)[18]. On the basis of an economical factor applied in the production cost of jarofix, the current study attempts to focus on production of more economical, immobilize and stable material from hazardous jarosite waste in compare to costly jarofix process. Figure 1.2 (a) and (b) illustrates the disposal yard and embankment of stabilized jarosite (jarofix) respectively.

(a) (b)

Figure 1.2 A pictorial view of disposal practice of jarosite (jarofix) [19], (a) Disposed yard; (b) Embankment

Another efficient method for jarosite waste storage/disposal is self-sealing protection through the addition of another waste product such as fly ash [20]. The method creates an impervious layer around the jarosite body by filling pores within the reacted layer.

Davis et al. [21], reported the utilization of deep tilling lime and limestone slurry into zinc sulfide tailing which is exposed to an abandoned mine by the flood event. This method has reportedly proven a success for both new and old jarosite dumps.

1.3.2 Application/ Utilization of jarosite

There are many motives to increase the rate of utilization of jarosite. A few of these are discussed below:

- ✓ Firstly and mainly, costs of disposal can be minimized.
- ✓ Secondly, land scarcities for disposal can be kept to a minimum, so possible to enhance other uses of the land.
- ✓ Thirdly, the by-product produces from jarosite may enable to improve financial support from the sale of the product.
- ✓ Fourthly, the by-products of jarosite can replace some unusual and costly natural resources.

Numerous researches have been completed their research in recent years for exploring the possibility to utilize zinc smelter by-products, namely jarosite as an alternative to conventional construction material and other applications. These applications can be as a form of fertilizer, ceramic and glass product, brick manufacturing, concrete products, embankment fill, roadway and sub-grade design, soil stabilization, addition to cement as gypsum, addition to construction materials as a lightweight aggregate, etc.

1.3.2.1 *Jarosite used in brick manufacturing*

Kalwa et al. [22] presented a study of sintered (fired) bricks. The sintered (fired) bricks produced from different ratios of jarosite-clay mix along with 0–45% fly ash resulted in density in the range of 1.4–1.93 g/cm^3. Furthermore, the authors concluded that the density of fired bricks increased when the jarosite clay mixes ratio increased.

Asokan et al. [8] attempted to evaluate the characteristics of Indian jarosite with objectives to potentially reducing and recycling raw waste materials for producing value-added products. In this study, the authors examined the various properties of solidifying products, with the addition of coal combustion residual (CCR) and sand in jarosite waste in different proportions. It was observed that the compressive strength, water absorption capacity and density, at a ratio of 3:1 (jarosite-sand), are as 43.4 kg/cm^2, 17.46%, and 1.51 g/cm^3 respectively, which efficiently fulfil the requirement for it's used in the construction sector as per Indian standard specification [23]. Further, the physicochemical properties indicate the utilization potential as building materials like bricks, blocks, cement, tiles, and composites.

Later on, Asokan et al. [8, 24] advocated that the detoxification and immobilization of hazardous jarosite waste was achieved through sintering and solidification process in which composite products formed by using coal combustion residues (CCRs), pond coal combustion residues (PCCRs) and marble processing residues (MPRs) as an additives with clay. Results revealed that the particle size of jarosite waste was finer than that of CCRs, PCCRs, and MPRs. That is, jarosite possesses a higher surface area and water holding capacity. Also, they observed that the composite products advanced from 1:1, 2:1 and 3:1 (jarosite: clay) with an addition of 15% CCRs, PCCRs or MPRs waste, fulfill the minimum requirement to be used for construction purposes as per Indian Standard specification [23]. It was also concluded from the toxic elements leaching test of solidification/stabilization (s/s)-sintered products that using jarosite-clay in the ratio 2:1 along with 15% CCRs confirm the United States Environmental Protection Agency (USEPA)-Toxicity Leachate Characteristics Procedure (TCLP) [25] limits and also meets the suitability requirement for various engineering applications.

Further, a work reported by Makhatha et al. [26] shows the possibility to use jarosite waste along with clay and fly ash in construction industries. The mineralogical and physical study of jarosite waste along with clay and fly ash were reported. The physical characteristic shows that the densities were 3.13, 2.67 and 2.21 g/cm^3 for jarosite, clay and fly ash respectively. An increase in density occurs with the increment in the percentage of jarosite in the mixture. However, a decrement in density was perceived with the increase in fly ash percentage in the jarosite and clay mixture.

1.3.2.2 *Jarosite used in construction work/industry*

Solidification/stabilization (s/s) technique is well-accepted worldwide and is used for the immobilization of heavy movable metals in hazardous wastes. Thus, the stabilized product can be safely utilized in the construction work. This process prevents the leaching of toxic elements and improves the physical and mechanical characteristics of the waste. Numerous experimental studies have been undertaken to stabilize jarosite in a cement type medium, creating an artificially cemented product that can be used in various civil engineering applications.

Robinson and Todd [27] filed a patent in the United States which shows the process for forming a synthetic rock with hazardous ammonium jarosite based sludge by the addition of fly ash and cement, without the necessity to remove the ammonia in jarosite. The cement alone is sufficient to neutralize the powder mix for achieving this degree of basicity, but lime could be added if required. From the experiment results, it was observed that nine parts of jarosite with the addition of two parts of fly ash and one part of Portland cement by weight were sufficient to solidify as an inert rock-like substance. The compressive strength and leachate test were conducted and concluded that the strength after 28 days curing was 0.64 MPa and the leaching rate was environmentally acceptable.

Ek [28] reported the "Jarochaux process" which involves the blending of calcium compounds such as quicklime, slaked lime, and milk of lime to stabilize the jarosite waste so that the treated material can be placed in landfills or embankments safely. Similarly, the stability of jarofix (jarosite mixed with lime and Portland cement) and the Jarochaux product has been studied indirectly by Levens et al. [29] in a report dealing with the environmental impact of cemented jarosite waste backfill. The study concluded that with the addition of cement in jarosite, great reduction comes in the exposure of sulfide to oxidizing agents. Hence, the movement of entrained toxic elements into water supplies decreased.

Chen et al. [30] reported the mineralogical study of artificially cemented jarosite material (Jarofix) for safe disposal. They concluded that stabilized cemented jarosite is impervious in nature with higher compressive strength. In jarofix products, Portland cement content was greater than 15%, which satisfies all environmental criteria for waste disposal relevant to USEPA guidelines [25]. The use of Portland cement decreases the need for storage of jarosite in large volume tailings ponds.

Similarly, Seyer et al. [31] also studied the mineralogical behavior of jarofix material. They observed that cemented jarosite was more stable material as compared to jarosite. They had also examined its long-term (5 years) behavior in the laboratory and pilot testing which was further followed by three years of successful process and environmental amenability. Finally, they concluded that the jarofix process represents a major discovery in the zinc industry for the treatment of leachable iron jarosite residues. Its chemical and physical characteristics significantly reduced the long-term problem relevant to water infiltration, and underground water-soil contamination.

Mymrin et al. [5] reported the combination of jarosite waste (JW) with dumped ferrous slag (DFS) and Al-surface cleaning waste (ASCW) with or without the addition of Portland cement resulting in a new constructional material which possesses an excellent strength and water resistance. These properties of the newly developed material prompted it to be used as a construction material for different civil engineering applications such as in base and sub-grade of roads, airfields runways and as a filler material in dams without the use of precious natural crushed stones, gravel, and sand. It can also be used to produce bricks, tiles and similar types of items. They also reported the utilization of these new materials resulting from mixtures of JW, DFS, and ASCW in large-scale and concluded that it is environmentally beneficial due to a decrease in leachability in acid and alkaline solutions, which was below the demands of environmental standards.

Later on, Mymrin et al. [32] reported the potential of new material produced from the combination of a jarosite waste (JW) with dumped ferrous slag (DFS) and Al-surface cleaning waste (ASCW) with or without the small addition of Portland cement. They examined the long-term effect of curing period on treated material. They also reported the mineralogical (X-Ray Diffraction (XRD) and Scanning electron microscope (SEM) changes observed in a treated material with time and suggested the utilization of these materials in various civil engineering applications. Hage et al. [6, 33] reported a new waste-to-waste technology as per Brite Euram program of the European Community in which pressure reduction of jarosite residual with a cellulose type waste material such as sewage sludge in an autoclave method was examined. The mobile components in the jarosite waste were stabilized with autoclave method and finally immobilized. As per Dutch regulation for construction material, the jarosite waste with its stabilized product was tested. The standard column leaching tests were conducted, in which the percolated water sample was collected to simulate raining water conditions in the field at three weeks duration. They concluded that the leachability of almost all metals is potentially decreased, but the quantities of leached zinc and cadmium still exceeded the Dutch U2 standard for building materials with restrictions. The immobilizing efficiency of an autoclave material was quite impressive. A counter current washing step of jarosite with the treated material will decrease the leachability of the solid and even increase the chances for the production of construction material.

Further, a study reported by Cheilas et al. [34] shows a feasible alternative for sewage sludge generated from urban wastewater treatment plants by blending with cement and jarosite/alunite (J/A) precipitate to produce a new construction material. Mortar prism samples 4 x 4 x 16 cm in dimensions were prepared, which composed of 50% sewage sludge, 30% cement and 20% jarosite/alunite. The autoclave and laboratory curing methods were used to prepare the samples in which they were treated for three hours at a temperature of 200 °C and a pressure of 16 bar. The samples were cured for 28 and 90 days respectively in a laboratory condition. The compressive and flexural strength tests, in addition to chemical, mineralogical, thermal and leaching analysis were conducted. The results revealed that stabilized/solidified products were suitable for construction purpose.

1.3.2.3 *Jarosite used as a sub-grade and geotechnical material*

Sinha et al. [19] reported that jarofix is a stable material which was an obtained by the addition of 2% lime and 10% cement in jarosite waste. They estimated that the annual production of jarofix material, in the form of zinc waste at Hindustan Zinc Limited, Chittorgarh, Rajasthan, was about five lacs metric tons and the unutilized accumulated material is about 15 lacs metric tons. They studied the jarofix feasibility in road construction. The jarofix waste was further blended with local soil and bottom ash in the range of 25-75% and examined for their physical and geotechnical characteristics. The potential of these different mixtures in the embankment and sub-grade layers of road pavement construction were also analyzed, and the authors concluded that jarofix and bottom ash, both having very low compression index value (0.06 and 0.04 respectively), could be effectively used in embankment design with a small settlement. Further, with a very low value of CBR, jarofix itself was unfeasible in use as a sub-grade material and hence the jarofix: bottom ash in the ratio of 50:50 and 25:75 showed potential because of very high CBR value.

Later, Sinha et al. [35] practically justified the potential of jarofix in road construction and reported an experimental study of jarofix road embankment section (300 m in length), constructed on one side of widened portion of State Highway (SH-9), Udaipur-Chittorgarh, Rajasthan, India and an embankment with conventional sub-grade section of local soil. The location of the experimental section is shown in Figure 1.3. The quality and stability of constructional section were evaluated by geotechnical field tests such as sand replacement method, plate load test, and dynamic cone penetration test. It was concluded from these studies that jarofix (100%) has the potential for the construction of road embankment. Also, a mix of jarofix: soil (50:50) may further have a potential for construction of embankment and sub-grade layer design. The stability analysis of embankment was also carried out and reported that the factor of safety was in the range of 1.83-2.66 for jarofix and 1.57-2.10 for the jarofix-local soil mix.

Figure 1.3 Location of the experimental jarofix test section (Sinha et al., 2012)

Sinha et al. [36] presented the results of various tests on jarosite waste such as grain size analysis, Atterberg limits, proctor compaction test, free swelling index, specific gravity, CBR, consolidation, and direct shear. The properties revealed that jarosite waste could be specifically recommended as a construction material for embankment and sub-grade design of road pavement.

1.3.2.4 *Jarosite used as a liner in the landfill*

Ding et al. [20] reported the geochemical process to controls the environmental problems dealing with disposal of acidic jarosite and alkaline fly ash. The jarosite mixed with fly ash may perhaps be possible to utilize as a liner in landfills because with an interception of two different chemically originate materials, a self-sealing layer was formed between the both wastes. Thus this layer could isolate and immobilize both wastes. Numerous radiotracer tests were conducted in the laboratory to find diffusion and reaction of iron (Fe^{3+}) in jarosite and fly ash system. For simulating the coupled behavior of diffusion and precipitation, a model was developed, which also explored changes in porosity due to pore filling by precipitates. The immobilization of iron (Fe^{3+}) content in jarosite was possible with the introduction of fly ash in the jarosite interface. Due to this fly ash introduction, precipitation reactions produced gypsum ($CaSO_4.2H_2O$) and ferric oxyhydroxide (FeOOH) minerals at the interface which was responsible for immobilization of iron content.

1.3.2.5 *Jarosite used as a substitute of gypsum in cement production*

Bombled [37] reported the potential of using non-calcium sulfate salts (jarosite) as a substitute in natural gypsum. They examined the rheological properties of the cement paste which was affected by non-calcium cations. The effect on plasticity and setting time of cement paste by sulfates of zinc, iron, potassium, and sodium were also investigated and a decrease in setting time of cement and plasticity in the presence of these types of sulfates.

A similar study was reported by Katsioti et al. [38]. They indicated that the jarosite-alunite precipitate was an effective supplement of natural gypsum in cement production. A total of nine different mixes from 0-100% of jarosite/alunite precipitate with the replacement of gypsum were produced and tested for various properties such as grindability, setting time, compressive strength, and water-soluble chromium content. Furthermore, the mineralogical study was also made for the hydration products formed at 2, 7, 28 and 90 curing days, using XRD analysis. Finally, they concluded that, by cost analysis, jarosite/alunite precipitate was cheaper than natural gypsum because the quarrying, grinding, and transporting cost of natural gypsum would be higher than jarosite/alunite precipitate.

1.3.2.6 *Jarosite used as a substitute of fine aggregate in the concrete mix*

A series of a laboratory test for finding the potential of jarosite as a sand substitute in concrete production was reported by Vyas et al. [39]. Samples were prepared by replacing different percentages of sand (0, 20, 40, 60, 80, and 100%) with jarosite waste and tested for leaching characteristics (TCLP) and compressive strength after 28 days curing period.

In cement concrete mixes, ordinary Portland cement (OPC), sulfate resistant Portland cement (SRPC) and combinations of both were used as a binder. Finally, they observed that the concrete mix with the replacement of 60% of sand by jarosite waste with 40% OPC and 60% SRPC resulted in the optimum combination. TCLP leaching results indicated that S/S technique was potential in blocking leaching of heavy metals Zinc (Zn), Cadmium (Cd), and Lead (Pb) with an efficiency of 93, 90 and 87% respectively.

Similarly, Mehra et al. [40-41] advocated the potential for partial replacement of fine aggregates with jarosite waste in the favorable performance of concrete. The durability study and mechanical characteristics of concrete were checked considering the environmental appropriateness of concrete. For trial phases, different concrete mixes were prepared with three water to cement ratios, and five jarosite replacement levels. Furthermore, 25% of cement content were replaced by fly ash in concrete production. The durability and strength properties showed that the produced concrete was quite satisfactory in comparison to the ideal concrete mix. It was concluded that the jarosite based concrete, along with fly ash, might be a new alternative practical solution to its disposal concern. Also, 15% jarosite waste as a fine aggregate replacement might be the best match for road and building construction.

1.3.2.7 *Jarosite used as a cement replacement in concrete production*

Arora et al. [42] reported the potential of jarosite-fly ash mix for use as cement substitute in concrete. Chemically, jarosite contains silica, alumina, ferric oxide and lime, which are also a part of Portland cement. The workability and early strength of M40 grade concrete produced through replacement of cement with jarosite-fly ash mixes, in replacement ratio of 10% jarosite (constant) and 0, 10, 20 and 30% of fly ash (varied by weight of cement), were evaluated. The results showed that the compressive strength at 7 and 28 days after curing increased by 31.55 and 5% respectively.

1.3.2.8 *Jarosite used as a proxy in remote sensing*

Swayze et al. [43] reported that the compound family of jarosite is associated with sulfide minerals, which is highly acidic and toxic in nature. Its acidic nature with heavy metal concentration would be potential to use as a proxy in remote sensing studies in surveying the area of highly acidic and toxic element leachability. With the help of these survey data found in mine areas, the potential sources of acidic drainage could be established rapidly and in a proficient way (Figure 1.4).

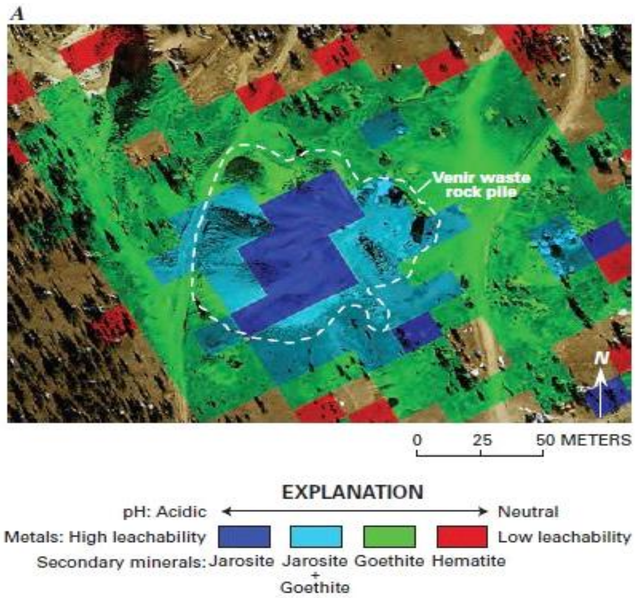

Figure 1.4 Remote sensing study used for the identification of sources of acidic drainage [43]

The jarosite waste in the form of a hydrated mineral was discovered on Mars surface by Mossbauer spectrometer in 2004. An extension of work done on jarosite revealed that the reflectance spectroscopy method could be used in remote sensing studies to recognize H_3O bearing and iron-deficient jarosite on the surface of Earth and Mars [43].

1.3.2.9 *Jarosite used in metals recovery*

Numerous researchers have focused on the recovery of valuable metals from the hydrometallurgical jarosite treatment process. Kunda and Veltman [44] reported the recovery of hematite and magnetite with two types of decomposition treatment namely thermal decomposition and decomposition in an aqueous slurry formation. With the help of thermal decomposition, jarosite may be converted into hematite. Dutrizac [95] reported the two-stage reactions, involving in the conversion of jarosite to hematite. Firstly, it was the formation of ferric sulfate by reaction with sulfuric acid, followed by hydrolytically decomposition of ferric sulfate to ferric oxide (Hematite):

$$2Na[Fe_3(SO_4)_2OH_6] + 6H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Na_2SO_4 + 12H_2O$$

$$3Fe_2(SO_4)_2(OH)_6 \longrightarrow \underset{\text{(Hematite)}}{3Fe_2O_3} + 9H_2SO_4$$

Bohacek et al. [45] obtained the black magnetite pigments (Fe_3O_4) by the neutralization of the hydronium jarosite, which remains as a suspension in aqueous solutions of $FeSO_4$ with NH_3 at controlled pH and temperature. Hage et al. [33] were successful in the production of magnetite from synthetic sodium jarosite by pure acid-washed cellulose as a reducing agent and MgO as a neutralizing agent. The conversion mechanism for producing magnetite from jarosite was not fully explained, and the resulted products did not potentially match with commercial pigments for further utilization. A laboratory study described by Jandova et al. [46] shows the conversion/recovery of pigment quality magnetite from sodium jarosite by alkali decomposition of sodium jarosite blended with sodium or ammonia hydroxide solutions at 60 °C and subsequent reaction with $FeSO_4$ at 95°C. The following reaction occurs:

$$2Na[Fe_3(SO_4)_2(OH)_6] + 3FeSO_4 + 12NaOH \longrightarrow \underset{\text{(Magnetite)}}{3Fe_3O_4} + 7\,Na_2SO_4 + 12H_2O$$

Ju et al. [47] reported the clean hydrometallurgical route for recovering iron, zinc, silver, lead, copper, and cadmium from hazardous jarosite waste. It was found that after the sintering of jarosite at 650 °C for 1h and subsequent leaching with aqueous NH_4Cl solution at 105°C, more than 95% metals such as Zinc (Zn), Lead (Pb), Cobalt (Cu), Cadmium (Cd) and Silver (Ag) were extracted, and with simultaneous reduction in Zn powder, more than 93% of Pb, Cu, Ag, and Cd could be recovered. Further, leaching of NH_4Cl residue in 30% aqueous NaOH solution at 160 °C resulted in the recovery of about 94% of As and 73% of Si. Also, the resulting residue, which was almost non-hazardous and decontaminated, contained about 55% Fe by weight, which could be used as an iron concentration.

The anglesite ($PbSO_4$) and silver recovery from jarosite waste with the help of roasting and sulfidization-flotation process in zinc hydrometallurgy were presented by Haisheng et al. [48]. They reported that after roasting, subsequent with flotation, the recovery of lead and silver were 66.86 and 81.60% respectively. Sintering of jarosite at 600–700 °C resulted in decomposing to recover valuable minerals such as anglesite and silver mineral. It was concluded that the combination of roasting and sulfidization-flotation afford an auspicious process for the recovery of zinc, lead, and silver from jarosite waste.

1.3.2.10 *Jarosite as a soil fertilizer*

Numerous works have been done for exploring the potential use of jarosite as a fertilizer for crops due to the high sulfur and iron contents. Ryan and Stroehlein [49] reported the utilization of jarosite as an iron source of crop soils. Jarosite itself behaves as a useless and impractical source of iron because the rate of release into the soil is very low. With the addition of sulfuric acid to the jarosite mixture, there was an increase in iron in the solution, and as such, the jarosite became a potential fertilizer. For the optimization of jarosite-sulfuric acid percentage, various concentrations were prepared, and a ratio of 2:1 (jarosite to sulfuric acid) was found to be the optimum ratio for fertilizing.

Kanabo et al. [50] examined some synthetic jarosite with "low contaminant," primarily as plumbojarosite and ammoniojarosite. The synthetic jarosite result was compared with standard results of fertilizers coming from glasshouse experiments on wheat, clover, and rice.

Williams et al. [51] reported the use of jarosite as potassium and sulfur fertilizer in a sandy, coastal plain soil, which was typically ineffective in agricultural activities and it was having very low inherent organic matter.

1.3.2.11 *Jarosite used in ceramic and glass products*

The estimated European market for ceramics and glass products is 15 to 20 million tons per year [52]. On the other hand, large quantities of waste materials are required to be disposed of in a leach-proof condition. The conversion of jarosite and granite wastes into numerous ceramic and glass products are potentially used now. Various properties of jarosite waste regarding glass and ceramic products were examined, and the quality of a product is mainly measured through thermal conductivity, chemical durability, specific heat, hardness, impact strength, thermal expansion and abrasion resistance. It was concluded that the process for glass and ceramic production was successful and it could be used to minimize the quantities of jarosite in land storage facilities. Karamanov et al. [53] reported that the conversion of industrial jarosite waste to building ceramics had been successfully applied in the former Soviet Union. The products have excellent properties, but the deficiency in the aesthetics was associated with clear or dense ceramics. For improving these deficiencies in the appearance of the finished product, they recommended doing sintering crystallization. This crystallization involved a two-stage heating treatment of the jarosite waste. In the first stage, the crystallizing bulk of the waste was done, and the waste which did not crystallize was separated and removed. In the second stage, the crystals formed were melted, and re-crystallisation begins from the surface and gradually going deeper. The resulting product showed a texture similar to marble.

From the aforesaid literature review, it is perceived that there is a lack in the studies to utilize stabilized jarosite in various areas of civil engineering such as in brick manufacturing, design of embankment or as a subgrade material for pavement design. As such, the current study will make a bridge to utilize stabilized jarosite, by studying the various parameters namely Strength, Durability and Toxicity Characteristic Leachate Procedure (TCLP) of GGBS-lime stabilized jarosite. Table 1.2 presents the summary the aforesaid studies as per their application/utilization areas.

Table 1.2 Summary of various application/utilization of jarosite

Applications	**Authors**	**Material used**	**Summary**
Brick Manufacturing	Kalwa et al. [22]	Jarosite-local clay-fly ash	Effectiveness of sintered bricks produced from different ratios of jarosite-clay mix along with 0–45% fly ash was measured.
	Pappu et al. [2,8, 24]	Jarosite-sand/clay-coal combustion residual/marble residual	Reported the potential to reduce and recycle raw waste materials for producing value added products, and concluded that the sintering and solidification (S/S) product exhibits the utilization potential in building materials like bricks, blocks, cement, tiles, and composites.

	Makhatha et al [26]	Jarosite-clay-fly ash	Reported the possibility to use sintered product of jarosite along with clay and fly ash in construction applications.
Construction work/Industry	Robinson-Todd [27]	Jarosite-fly ash-cement	Reported that, After blending of 9 parts of jarosite with 2 parts of fly ash and 1 part of cement by weight were sufficient to produce solidify product such as an inert rock-like substance.
	Levens et al. [29]	Jarosite-lime - Portland cement	The stability of jarofix and Jarochaux product has been studied and concluded that, treated jarosite reduces the exposure of sulphides, thus the movement of toxic elements decreased.
	Mymrin et al. [5,32]	Jarosite-ferrous slag-surface cleaning waste-lime/cement.	Jarosite blended with ferrous slag and surface cleaning waste resulting in a new constructional material which possesses an excellent strength and water resistance and to be used in various civil engineering applications.
Sub-grade and Geotechnical material	Sinha et al. [19,35]	Jarofix-clay-bottom ash	The potential of jarofix, blended with local soil and bottom ash used in design of embankment and sub grade layers of road pavement, were analysed and concluded that treated material exhibits very low compressibility, thus efficiently used in embankment design.
	Sinha et al. [36]	Jarosite	Reported the various geotechnical properties of jarosite and concluded that jarosite can be used as a constructional material in embankment and sub grade design of road pavement.

Liner in the landfill	Ding et al. [20]	Jarosite-fly ash	Jarosite mixed with fly ash may be possible to utilize as a liner in landfills which has self-sealing and self-healing properties.
Gypsum substitute in Cement production	Bombled [37]	Jarosite	Reported the potential of jarosite as a substitute of natural gypsum in cement production along with the rheological properties of cements pastes affected by non-calcium cations.
	Katsioti et al. [38]	Jarosite	Reported that the jarosite precipitate was an effective supplement of natural gypsum in cement production and concluded that the jarosite precipitate was cheaper than natural gypsum.
Substitute of fine aggregate (sand) in concrete mix	Vyas [39]	Jarosite based concrete	The concrete mix made up with 60% jarosite (as a fine aggregates) and 40% ordinary Portland cement verified to be optimum combination and potentially used in constructional purpose.
	Mehra et al. [40,41]	Jarosite-fly ash based concrete	Reported that, jarosite- fly ash based concrete can be a good alternative to disposal concern of jarosite and concluded that, 15% jarosite replacement as a fine aggregate was optimal mix for road and building construction.
Cement replacement in concrete production	Arora et al. [42]	Jarosite-fly ash	The effectiveness of jarosite-fly ash blends was reported and concluded that jarosite can be successfully used as a cement substitute in concrete construction.
Proxy in Remote Sensing	Swayze et al. [43]	Jarosite	Suggested that, jarosite is associated with sulphide minerals, which is highly acidic and toxic in nature, thus this nature were helped

			as a proxy in remote-sensing studies to survey the highly acidic and toxic area.
Metals Recovery from jarosite	Jandova et al. [46]	Jarosite-Ammonia hydroxide-$FeSO_4$	Reported the recovery of pigment quality magnetite from sodium jarosite by alkali decomposition procedure.
	Bohacek et al. [45]	Jarosite (Neutralization)	Obtained the black magnetite pigments (Fe_3O_4) by the neutralization of the hydronium jarosite.
	Ju et al. [47]	Jarosite (sintering & leaching)	Reported the process for recovering iron, zinc, silver, lead, copper and cadmium from jarosite and concluded that after the sintering of jarosite at 650 ˚C for 1h and subsequent leaching with aqueous NH_4Cl solution at 105 ˚C, more than 95% metals such as Zn, Pb, Cu, Cd and Ag could be extracted.
	Han et al. [48]	Jarosite (Roasting & sulfidization-flotation)	The Anglesite and silver recovery from jarosite waste with the help of roasting and sulfidization-flotation process in zinc hydrometallurgy were reported and concluded that the combination of roasting and sulfidization-flotation can be a promising process for the recovery of zinc, lead, and silver.
Soil fertilizer	Ryan et al. [49]	Jarosite-sulphuric acid	Reported that blending of sulphuric acid in jarosite, increased the iron in solution, thus makes jarosite became a potential fertiliser.
	Kanabo et al. [50]	Jarosite	Examined the potential of jarosite as fertilisers by performing glasshouse experiments on wheat, clover and rice and compared the results from standard fertiliser.

	Williams et al. [51]	Jarosite	The jarosite tested as potassium and sulphur fertiliser in sandy and coastal plain soil and concluded that jarosite exhibits the good properties of fertiliser.
Ceramic and glass products	Pelino [52]	Jarosite	After examination of various properties of jarosite as a glass/ceramic product such as thermal conductivity, durability, impact strength etc. concluded that, production was successful.
	Karamanov et al. [53]	Jarosite	The resulting ceramic product made up from jarosite showed a texture similar to marble and successfully applied in the former Soviet Union.

1.4 Scope and Objectives

To study the potential of utilizing jarosite in civil engineering, the author attempts to evaluate the potential of jarosite waste stabilized with blast furnace slag (GGBS) and hydrated lime considering strength, deformation, durability and leaching characteristics. The main objectives of the study are:

1. **Strength study:** Evaluation of Unconfined compressive strength (UCS) test and Split tensile strength test of stabilizing jarosite at 7, 28, 60 and 90 days curing periods.
2. **Durability study:** For evaluation of durability and degree of adequate hardness to resist field weathering of stabilized jarosite-GGBS-lime matrix, freezing, Freezing-Thawing (F-T) analysis will be performed in the laboratory.
3. **Toxicity characteristic leachate procedure (TCLP) study:** For determination of heavy metals and toxic elements in raw and stabilized product, the inductively

coupled plasma (ICP) test will be conducted on untreated and treated samples of jarosite using TCLP procedure.

4. **Economic Viability:** The economic viability of treated jarosite will be studied by comparing production cost of GGBS-lime stabilized jarosite and jarofix (cement stabilized jarosite).
5. **Practical usefulness:** An attempt will be made to develop a relationship among unconfined compressive strength (q_u) and split tensile strength (q_t) with various lime content (L), GGBS content (G) and curing period (t).
   - These relationships will help an engineer/user to choose the optimum amount of lime/GGBS to attain the target compressive or tensile strength of jarosite-GGBS-lime blends.
   - Also, enhancing the possibility to concentrate either on tensile strength or on compressive strength for getting the desired results, an attempt will be made to formulate a unique scalar q_t / q_u ratio.