Utilization of jarosite in precast concrete paver blocks

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Abstract. Sustainability has become the major concern for the construction industry in the recent era. Concrete stands as a versatile construction material, but cement being its main constituent poses a threat to the environment consuming a huge amount of energy and emanating CO₂ and other greenhouse gases in its production process. On the other hand, the extraction of natural resources for construction works has been disrupting the environmental and ecological balance due to a huge accumulation of waste or by-products. So the major concern of the hour is the formulation of a mitigation strategy to fight this uncontrolled quantum of construction and its resulting consequences. The main objective of this present study is the utilization of jarosite, a hazardous solid waste, as a replacement of cement in concrete paver blocks. Six concrete mixes were prepared to keep the water-to-cementitious material ratio fixed at 0.43. The replacement of cement with jarosite was carried out at five replacement levels (0–25%) in an increment of 5%. Mechanical properties (compressive and flexural strength) and durability properties (water absorption and abrasion resistance) of the jarosite incorporated paver blocks were determined and compared to the control specimens. Experimental results indicate that mechanical and durability properties improve with the incorporation of jarosite, which could be attributed to a much developed packing of the jarosite concrete mix.

1. Introduction
The recent era obligates the construction industry to practice sustainability as a concurrent challenge in its production activities by exploring various eco-friendly raw materials or using solid wastes in concrete [1,2]. In this context, recycling indubitably serves as the most viable alternative to ameliorate the impact that the environment can suffer from the raw material consumption and uncontrolled generation of waste [3,4]. Concrete stands as a versatile construction material. Its characteristic to assess different waste materials by incorporating them in its production process has provided it with immense importance in the construction sector [3,5]. Being provided with a second life in concrete necessitates performance evaluation of these alternative materials since their properties may differ from the material they are used as a substitute for [6]. This will help in addressing the sustainability and durability issues both at the same time.

Jarosite is a solid residue universally produced in huge quantities during the zinc extraction process. Due to the existence of heavy metals like cadmium, lead, zinc, copper, chromium, and other oxides of metals and non-metals, it has been categorized as hazardous waste [7–9]. Moreover, the concentration of the toxic element in jarosite stands out much higher than the recommended
permissible values of the United States Environmental Protection Agency (USEPA). About 0.25 million tonnes of jarosite waste is released from the industrial sector per annum in India [9]. Limited literature is available regarding the jarosite recycling and its utilization. The use of processed jarosite waste with small additions of lime and Portland cement has found applications in civil engineering. They may be used as construction materials in road bases and subbases, dams and airfields, as a replacement of conventional materials and even finds its place in the production of tiles, bricks, and other similar products [10]. Development of models simulating the coupling effect of diffusion and precipitation at the interface of chemically contrasting wastes advocates the potential use of the jarosite waste to form a self-sealing layer at combined jarosite/fly ash disposal sites [11]. Past studies have affirmed the possible use of sand and coal combustion residues (CCRs) as admixtures immobilizing the transport of heavy metals and toxic elements present in jarosite wastes [5,9,12,13].

The influence of jarosite replacing cement in precast concrete paver blocks is not studied yet. Paver blocks have recently emerged out to be an attractive economic and engineering alternative compared to asphalt and rigid pavements. Besides this, its improved mechanical and durability properties, easy maintenance, and aesthetically appealing surfaces have made it fit for application in parking lots, pedestrian crosswalks, traffic intersections, container depots, and low volume roads [3]. Therefore, our present research objective was to assess the feasibility of using jarosite waste as a partial replacement of cement in manufacturing precast concrete paver blocks.

1.1. Research significance

The production process of Portland cement involves a massive amount of energy consumption and the generation of unwanted CO₂ emissions. The cement plants account for 5 – 7% of global CO₂ emissions, while one ton of cement production generates 900 kg of CO₂ to the atmosphere [14]. This uncontrolled CO₂ emission, which falls among greenhouse gases, can be catastrophic, leading to global warming [15,16]. As a mitigation strategy, much attention has been given to the development of a new generation of blended cement with the same engineering properties and resulting in energy saving [17]. Utilization of jarosite as a replacement of cement can abate CO₂ emissions and, at the same time, counter the disposal and contamination problems because of its hazardous nature. Further, the incorporation of jarosite in the manufacture of paver blocks will be first of its kind.

2. Experimental investigation

2.1. Materials

Ordinary Portland cement (OPC) of 43 grade, complying IS:8112 [18] requirements, procured from the local market, was used throughout the investigation. The cement used had a specific surface area of 3329 cm²/gm determined as per IS:4031-Part-2 [19]. The jarosite used was availed from the Debari Zinc Smelter plant of Hindustan Zinc Limited located at Udaipur, Rajasthan, India. The jarosite samples collected were present as lumps, and it needed an amount of processing. The samples were first oven-dried at 50±5°C for 24 hours, milled into a fine powder and stored in air-tight containers for further use. The specific surface area of processed jarosite determined by the Brunauer-Emmett-Teller (BET) method was observed to be 102296 cm²/gm, and it had a pH value of 4.19, showing its acidic nature. Specific gravity values of cement and jarosite reported in Table 1 have been investigated as per IS:4031-Part-11 [20].

The chemical composition of cement and jarosite samples were determined by X-ray fluorescence (XRF) technique. The elements present in oxide form in jarosite sample were as follows: Fe₂O₃ (37.23%), SO₃ (27.36%), SiO₂ (8.16%), Na₂O (3.76%), ZnO (2.90%), PbO (2.84%), Al₂O₃ (2.40%), CaO (1.04%), K₂O (0.55%), CuO (0.14%), TiO₂ (0.10%), MgO (0.09%), P₂O₅ (0.08%), MnO (0.07%), SrO (0.05%), CdO (0.04%), Cr₂O₃ (0.03%) and BaO (0.03%). The cement sample on the other hand chemically composed of the oxides of the following elements: CaO (63.56%), SiO₂ (19.65%), Al₂O₃ (4.58%), Fe₂O₃ (4.20%), MgO (3.21%), SO₃ (2.21%), K₂O (0.79%), Na₂O (0.65%), P₂O₅ (0.16%) and
MnO (0.07%). As observed from the XRF study, the oxides of sulphur (SO₃) and iron (Fe₂O₃) were present in substantial quantities in jarosite.

Table 1. Properties of raw materials used.

| Property | Cement | Coarse aggregate (16 mm) | Coarse aggregate (20 mm) | Fine aggregate | Jarosite | SP* |
|----------|--------|--------------------------|--------------------------|----------------|----------|-----|
| Specifications | OPC Grade 43 | Crushed sandstone | Crushed sandstone | River sand (Zone III) | – | – |
| Specific gravity | 3.15 | 2.60 | 2.63 | 2.56 | 2.90 | 1.18 |
| Water absorption (%) | – | 0.63 | 0.55 | 1.42 | – | – |

* Superplasticizer

Two sizes of coarse aggregates, 16 mm graded, and 20 mm single size was used in this study. These two aggregates were blended (95% of 16 mm and 5% of 20 mm) to obtain graded aggregates of nominal size 20 mm conforming to IS:383 [21]. The fine aggregate used was procured from the Ganga riverbed located near Uttarakhand, India and affirmed to grading zone III as per IS:383 [21] specifications. The particle size distribution of natural coarse and fine aggregates can be visualized through figure 1. Specific gravity and water absorption of the different aggregates determined as per IS:2386 [22] have been presented in table 1. Potable water complying with IS:456 [23] requirements was used to prepare the considered mixes and curing the test specimens. A varying dose of sulfonated naphthalene-based super plasticizing admixture was used for all the concrete mixes. The dosage of the admixture needs to be determined through trial mixes.

Figure 1. Grain size distribution of coarse and fine aggregates used in the study.

2.2. Mix proportioning
The mix design has been done following the provisions in IRC:SP:63 [24] and IRC:44 [25] adopting the water-to-cementitious material ratio (w/cm) as 0.43 throughout the study. Replacement of cement with jarosite (0 – 25%) in an increment of 5% has been carried out. A total of 6 mixes, including the control mix, was prepared for which the dosage of superplasticizer was adjusted accordingly to achieve the desired workability in terms of slump value. The concrete mix proportions have been summarized in table 2. A mix designation (MD) in the form “PBXJ” has been used to represent the
various mixes. In “PBXJ”, “PB” stands for paver block, “J” stands for jarosite, and “X” represents the different levels of replacement of cement with jarosite (0%, 5%, 10%, 15%, 20%, and 25%).

**Table 2.** Proportions of fresh concrete mixes.

| MD   | Water (Kg) | Cement (Kg) | Jarosite (Kg) | Fine aggregate (Kg) | Coarse aggregate 16 mm (Kg) | Coarse aggregate 20 mm (Kg) | SP (%) | Slump (mm) |
|------|------------|-------------|---------------|---------------------|-----------------------------|-----------------------------|--------|------------|
| PB0J | 158.1      | 367.7       | 0.00          | 640.40              | 1167.91                     | 62.18                       | 0.7    | 17         |
| PB5J | 158.1      | 349.3       | 18.38         | 639.68              | 1166.60                     | 62.11                       | 0.8    | 16         |
| PB10J| 158.1      | 330.9       | 36.77         | 638.68              | 1164.78                     | 62.01                       | 1.0    | 19         |
| PB15J| 158.1      | 312.5       | 55.15         | 637.68              | 1162.96                     | 61.91                       | 1.2    | 17         |
| PB20J| 158.1      | 294.1       | 73.53         | 636.69              | 1161.14                     | 61.82                       | 1.4    | 17         |
| PB25J| 158.1      | 275.8       | 91.92         | 635.69              | 1159.32                     | 61.72                       | 1.6    | 19         |

2.3. Fabrication of paver blocks
The paver blocks were fabricated in steel molds having internal dimensions of 300 mm in length, 150 mm in width, and 150 mm in height using a wet-mixed method. A mixing procedure similar to that adopted for making concrete with lightweight aggregates was adopted. At first, the aggregates and half of the mix water were mixed in the drum mixer for 30 s. After this, the cement and jarosite were added to the wetted aggregates and mixed for another 30 s resulting in surface-coated aggregates. Finally, the superplasticizer mixed half of the remaining water was added and mixed continuously for 2 min to prepare the fresh concrete mix. The fresh concrete was placed into the molds in three layers of equal thickness, with each layer being tamped 25 times. Then the assembly was placed over a vibrating table and vibrated for 5 seconds. While the specimens were vibrated, a trowel was used to remove the excess material and provide a good surface finish. The paver block specimens were demolded 24 h after the casting and cured in water until the testing date.

2.4. Experimental methods
The initial slump of fresh concrete mixes using a slump cone test was carried out as per ASTM C143 [26] specification. The density of the freshly mixed concrete was calculated according to the guidelines presented in ASTM C138 [27]. Compressive and flexural strength tests of the 300 x 150 x 150 mm paver block specimens at 7 and 28 days of age were conducted according to the procedure laid down in IS:15658 [28]. For the determination of water absorption of the paver blocks IS:15658 [28] specification was followed. The abrasion resistance was determined on concrete specimens of size 300 x 300 mm in plan and depth 100 mm according to the guidelines prescribed in ASTM C779 [29], where Procedure A involving the revolving-disk type abrasion machine was followed. The water absorption and abrasion resistance test was performed on concrete specimens moist cured for 7 and 28 days. Finally, the microstructure study of powdered jarosite sample and jarosite inclusive concrete specimens were carried out using scanning electron microscopy (SEM).

3. Results and discussion
3.1. Effect of jarosite on fresh properties
The effect of the incorporation of jarosite on the initial slump value of the fresh concrete mixes is shown in table 2. It may be noted that the slump value of the mixes could be kept within a range of 16 – 20 mm by varying the dosage of superplasticizer from 0.7 – 1.6%. The decreased workability of mixes with an increase in the replacement level of jarosite could be attributed to the much higher specific surface area of jarosite particles in comparison to cement. As depicted in table 3, the reductions in fresh density values were noted to be 0.8%, 1.6%, 2.2%, 2.6% and 3.3% in comparison to control mix (PB0J) for the mixes containing 5%, 10%, 15%, 20% and 25% of jarosite respectively.
The lower specific gravity of jarosite as compared to cement possibly accounts for this reduction in the density of the fresh concrete mixes.

| MD    | PB0J | PB5J | PB10J | PB15J | PB20J | PB25J |
|-------|------|------|-------|-------|-------|-------|
| Fresh Density (kg/m³) | 2479 | 2459 | 2439  | 2426  | 2415  | 2396  |

### 3.2. Effect of jarosite on mechanical properties

#### 3.2.1. Compressive strength

Figure 2 illustrates the effect of jarosite content on the compressive strength of the paver blocks. As depicted in this figure, with increasing of jarosite content up to 15%, the paver compressive strength increases at both 7 and 28 days curing age. At the initial days of moist curing (7 days), a higher increment in compressive strength values was observed for different mixes than the latter days (28 days). Compared with the control mix, the addition of jarosite at 5%, 10% and 15% resulted in a compressive strength gain of 3.6%, 13.9% and 24.4% at 7 days, while the increment values were noted to be 3.4%, 11.7% and 19.1% at 28 days; respectively. However, the addition of jarosite of more than 15% resulted in a reduction in concrete compressive strength. For instance, using jarosite at 20% and 25% reduced the concrete strength by 4.9% and 4.4% (with respect to control) at 28 days. The increase in compressive strength could be attributed to the development in the microstructure of concrete mix with subsequent incorporation of jarosite particles. The fine jarosite particles favor the occurrence of pozzolanic activity and fill the micropores within the concrete matrix. On the other hand, the potential reduction in the cementing materials and dilution effect occurring due to the increasing replacement of cement with jarosite results in a decrease in compressive strength.

Comparing to specifications of paver blocks, according to IS:15658 [28], all the hardened jarosite concrete mixes fulfill the strength criterion for applicability in medium-traffic areas like low volume roads, city streets, small and medium market roads. It may be noted that the concrete mix with 15% jarosite replacement level even fulfilled the strength criterion of heavy traffic applications.

#### 3.2.2. Flexural strength

The flexural strength result of the jarosite concrete paver blocks follow a similar trend as the compressive strength and is presented in figure 3. The flexural strength increases by the addition of jarosite up to 15% and then decreases with further addition. As compared with the control mix, the addition of jarosite at 5%, 10% and 15% resulted in a strength gain of 1.4%, 4.7% and 9.4%, respectively, at 28 days. However, unlike compressive strength results, though there is a reduction in flexural strength at 20% jarosite replacement level, the strength is 2% higher than control
concrete. Moreover, the 28-day flexural strength value of 20% and 25% jarosite concrete mix are comparable to that of the control concrete. These results may be explained with the arising heterogeneity in concrete mixes at higher jarosite incorporation levels [5].

Figure 4. Effect of jarosite replacement on water absorption.

3.3. Effect of jarosite on durability properties

3.3.1. Water absorption. The test results for water absorption of jarosite inclusive paver block samples is presented in figure 4. The figure depicts a decrease in water absorption percentage with an increase in jarosite content and is in line with previous findings [5]. Comparing with control mix, addition of jarosite at 5%, 10%, 15%, 20% and 25% resulted in a reduction in water absorption by 1.5%, 5.3%, 6.2%, 7.6% and 8.5% respectively after 7 days of moist curing age. At 28 days of moist curing, a higher reduction in water absorption value was found. This decrease in water absorption value may be possibly due to the higher surface area of jarosite particles filling the pores and results in a densely packed concrete matrix. Moreover, the water absorption values fall within the permissible limits stipulated for paver blocks as per IS:15658 [28] specifications.

Figure 6. SEM microstructure of jarosite particles.

3.3.2. Abrasion resistance. The effect of jarosite inclusion on the abrasion resistance of paver blocks is illustrated in figure 5. The abrasion test results are presented in terms of weight loss of specimens on abrasion resistance.

Figure 5. Effect of jarosite replacement on abrasion resistance.
exposure to abrasive grit. As compared to control specimen, the reduction in weight loss of 7 days cured specimens were found to be 2%, 15.1%, 28.1%, 36.2% and 40.9% for jarosite replacement levels of 5%, 10%, 15%, 20% and 25% respectively. Similarly, the abrasion resistance increased for the 28 days cured samples with subsequent jarosite inclusion levels compared to the control specimen. The abrasion resistance of the hardened paver block mixes can be correlated to the water absorption results. The pore filling effect due to the higher specific surface area (102296 cm²/gm) of jarosite particles helps improve the abrasion resistance of the mixes.

3.4. Microanalysis using SEM
The microstructure characteristics of jarosite particles, as illustrated in figure 6, show them to be irregularly shaped, non-uniform, and with multiple humps. This is in line with the past literature studies of jarosite particles [9,12,13,30]. SEM images of the jarosite concrete mix specimens designated PB0J and PB15J have been presented in figures 7 and 8, respectively. PB0J mix containing no jarosite (control) was spotted to have a greater void (V) and portlandite (CH) compared to the PB15J mix containing 15% jarosite replacement level. PB15J mix was observed to have a denser microstructure with lesser voids (V), dense clouds of calcium silicate hydrate (CSH) gel, and fibrous hydration products, which confirms that increasing the percentage of jarosite has a pore filling effect and offers a denser concrete matrix.

Figure 7. SEM micrograph of PB0J concrete specimen.

Figure 8. SEM micrograph of PB15J concrete specimen.

4. Conclusions
Based on the present laboratory investigation, it can be concluded that the manufacture of paver blocks using jarosite stands a feasible option. Further, the following inferences can be drawn from the present study.

- The inclusion of jarosite decreased the workability of concrete mixes. Further, a reduction in fresh density value due to the replacement of cement with jarosite was found.
- Enhancement in compressive and flexural strength (mechanical properties) was observed with a subsequent increase in jarosite replacement level up to 15%. However, though there is a reduction in mechanical properties, cement can be replaced with jarosite up to 25% in paver blocks as the compressive and flexural strength values fall within a similar range to that of the control mix.
- As far as the effect of jarosite on durability properties of concrete are concerned, an improvement was observed with subsequent jarosite replacement levels.
- The study of the microstructure of hardened concrete confirms the formation of a denser matrix with jarosite incorporation.
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