

## Hazardous jarosite use in developing non-hazardous product for engineering application

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### Abstract

Jarosite released from zinc metal extraction process is hazardous in nature and its world wide disposal has become a major environmental concern. In this study, an attempt has been made to immobilise and recycle the jarosite released from Hindustan Zinc Limited, India, using CCRs, so called fly ash, and clay soil. Results revealed that the particle size of jarosite was finer than that of CCRs and had higher porosity and water holding capacity due to fine textured materials resulting in high surface area ( $10,496.18 \pm 30.90 \text{ cm}^2/\text{g}$ ). Jarosite contain higher concentration of toxic elements (lead, zinc, sulphur, cadmium, chromium and copper) than that of CCRs. Concentrations of radionuclides such as  $^{226}\text{Ra}$ ,  $^{40}\text{K}$  and  $^{228}\text{Ac}$  in jarosite found less than in CCRs are similar to that of soil. Statistically designed experiments on solidified/stabilised (s/s) sintered jarosite–CCRs products confirmed that the compressive strength of jarosite bricks reached as high as  $140 \text{ kg/cm}^2$  with 14.5% water absorption capacity at the combination of 3:1 ratio of jarosite and clay, respectively, but, concentrations of all the toxic elements recommended by United States Environmental Protection Agency (USEPA)–Toxicity Leachate Characteristics Procedure (TCLP) standard are not within the permissible limits. However, it is confirmed that the toxic elements leaching potentials of s/s-sintered products developed using 2:1 jarosite clay ratio with 15% CCRs comply with the USEPA–TCLP limits and also meet the quality for engineering applications.

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**Keywords:** Jarosite; CCRs/fly ash; Clay; Recycling; Immobilisation; Sintering; Jarosite product; Toxic elements

### 1. Introduction

Advances in hazardous waste recycling and long-term acuity are deemed imperative and now it is necessary to involve a new paradigm for optimum environmental, economic and social benefits. World wide huge quantities of hazardous wastes are generated during different industrial processes. With effect from 1992 the Treaty of the Basel Convention governs the transboundary movement of hazardous waste and more than 148 countries and the European Community have ratified the recommendation to minimize unfavourable environmental consequences of improper management of hazardous wastes [1]. Universally, zinc industries are releasing huge quantity of jarosite during zinc metal extraction process as solid residues and due to the presence of toxic substances like zinc, lead, cadmium and other

metallic and non-metallic oxides, which may cause adverse or chronic effects on environment or on human health when not properly controlled and is universally categorised as hazardous waste [2–4].

World wide, jarosite process is one of the most widely used techniques for metallic zinc extraction in which Fe(III) compound of the type  $Z[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]$  (where Z represents  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ , etc.) is precipitated [5–7] and large quantity of jarosite is released as products. The pH of jarosite waste is highly acidic in nature (pH 2.7), because in electrolytic zinc extraction process, sulphuric acid is used as a catalyst in which jarosite precipitates at very low pH (1–1.5). Further the present study confirmed from the X-ray diffractogram of jarosite that the major mineral phase is jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) and iron sulphate hydrate ( $2\text{Fe}_2\text{O}_3\cdot\text{SO}_3\cdot 5\text{H}_2\text{O}$ ). This indicates that predominance of  $\text{OH}^-$  propels the compounds to set faster/expels water from the molecules/free Gibbs energy available in excess results in heat release. The mineral phase in jarosite, iron sulphate hydroxide, is hydrophobic in nature and insoluble. However, the other phase, namely iron sulphate hydrate, is hydrophilic

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in nature, which solubilizes easily. Due to such characteristic nature, jarosite itself is a hazardous material and also it does not comply with the regulatory guideline. The concentration of toxic elements in jarosite is higher than that of recommended permissible limits of USEPA and all other countries.

In Indian industries about 0.25 million tonnes per annum (mtpa) of jarosite waste is being released. The European Union produces 0.60 million tonnes of such zinc residues every year [8,9]. The major quantity of jarosite is generated mainly from Spain, Holland, Canada, France, Australia, Yugoslavia, Korea, Mexico, Norway, Finland, Germany, Argentina, Belgium and Japan [10,11].

## 2. Potentials of fly ash for immobilisation of jarosite

Mostly, fly ash physico-chemical characteristics are similar to those of sand and clay and it contains primarily silica, alumina and iron oxide [12]. Presently, ~112 million tonnes of fly ash generated in India is being considered as one of the major resources, has great potentials for bulk utilisation, in developing building materials, road and embankment, mine filling, land development and agriculture for socio-techno economic augmentation [13]. Solidification/stabilisation (s/s) is a waste treatment/management technique now widely used world wide for immobilisation/remediation of hazardous wastes containing priority toxic elements. This process inhibits the transport of pollutant elements into the surrounding environment and improves the physical characteristics, thus reducing the transport and leaching of contaminants/toxic metals [14,15]. However, no work is reported yet for treatment of jarosite for safe disposal.

Studies indicate that fly ash can be used as partial replacement for Portland cement to immobilise the lead and other toxic elements from solidified cement fly ash matrix [16,17]. Very little work has been cited on utilisation of jarosite in tiles, ceramic products [5,6]. But, Romero and Rincon [9] explored the possibility to recover valuable elements/value added harmless material. Work carried out by Gupta [18] and Acharya et al. [19] showed that the ground water was contaminated due to the disposal of jarosite. Mostly, jarosite is being stored in the premises of the smelter plant. Nevertheless, no work has been reported on utilisation of fly ash for recycling of hazardous jarosite in developing non-hazardous products for safe utilisation in engineering applications. Jarosite seems to be a potential resource, which has to be recycled in a technically feasible and environment-friendly manner. This paper deals with the recycling potentials of hazardous jarosite in developing non-hazardous products using fly ash and clay for construction application.

## 3. Materials and method

### 3.1. Sample collection and processing for property characterisation

Jarosite was obtained from Hindustan Zinc limited (HZL), Debari, Rajasthan, India. Clay soil from local area of Rajasthan,

and fly ash from Electro Static Precipitator of Satpura Thermal Power Station, Sarni, Central India, were collected. The work was carried out at Regional Research Laboratory (CSIR) Bhopal, India. All these samples were air dried separately, well ground, sieved through 2 mm size sieve and stored in glass container. For the physico-chemical and leachability studies, sampling was done from the air-dried sample adopting coning and quartering method.

### 3.2. Physico-chemical characterisation

The particle size distribution analysis was done using Laser Diffraction Particle size analyser Model HELOS Laser diffraction system, Sympatec GMBH, Germany. Bulk density and particle density were measured following the method of Veihe-meyer and Hendrickson [20]. Porosity was calculated in relation to particle density and bulk density [21]. Water holding capacity was measured in saturated soil paste international pipette technique as well as Keen Box Method. Conductivity and pH were measured using Orion analyser (Model 1260, Orion Research Inc., USA) in 1:2 solid:water ratio of soil suspension using conductivity and pH electrode, respectively. Standard methods of analysis were employed to analyse total heavy metals and trace elements in jarosite, fly ash and clay soil [22]. Samples were digested using microwave digester (QLAB 6000 Microwave Digestion System, Canada) and heavy metals such as Cu, Zn, Mn, As, Se, Cr, Ni, Co, Ag, Cd, Pb, etc., were analysed from the digested extract by Atomic Absorption Spectrophotometer (AAS), Z-5000, Hitachi, Japan, with flame and graphite system. In all cases, high purity water of Elga (Prima 1-3 and Elgastat Maxima) system, England, was used.

### 3.3. Mineralogical and morphological characterisation

The mineralogical studies of jarosite, fly ash and clay were carried out by X-Ray Diffractometer—PW-1710, Philips, Netherlands, with Quasar software packages. The samples were scanned in the range of 5–70° 2 $\theta$ . The microstructure characteristics of jarosite were analysed by scanning electron microscope—Model JOEL JSM-5600, Japan, with energy dispersive X-ray spectroscopy (EDS) analysis facilities. The quantitative estimation of chemical composition was done by computational method using the software of Oxford Model link Pendafet—IC 300.

### 3.4. Experimental protocol

Jarosite along with clay was mixed together in different ratios. To attain good workability fly ash was used as an additive and then water was added on jarosite matrix. The details of different matrixes ratios/concentration and water consumption for making solidified/stabilised products are shown in Table 1. The composite matrix was kneaded well till it became a homogeneous workable state. Then tempered matrix was placed in rectangular cast iron mould and pressed in hand press. The mould dimension was 7.5 cm  $\times$  3.5 cm  $\times$  3.5 cm. The casted solidified

Table 1  
Experimental details and quantity/ratio of different matrixes used in developing jarosite bricks

Trials/treatment	Jarosite:clay ratio	Jarosite (g)	Clay (g)	Jarosite–clay weight (g)	Fly ash (g)	Fly ash (%)	Total weight (g)	Water binder ratio
Experiment 1								
1E	1:1	500	500	1000	Nil	Nil	1000	0.242
2E	1:1	425	425	850	150	15	1000	0.227
3E	1:1	350	350	700	300	30	1000	0.210
4E	1:1	275	275	550	450	45	1000	0.195
Experiment 2								
5E	2:1	666.66	333.33	1000	Nil	Nil	1000	0.253
6E	2:1	566.666	283.333	850	150	15	1000	0.236
7E	2:1	466.67	233.33	700	300	30	1000	0.218
8E	2:1	366.66	183.33	550	450	45	1000	0.200
Experiment 3								
9E	3:1	750	250	1000	Nil	Nil	1000	0.270
10E	3:1	637.5	212.5	850	150	15	1000	0.250
11E	3:1	525	175	700	300	30	1000	0.228
12E	3:1	412.5	137.5	550	450	45	1000	0.210
Experiment 4								
13E	4:1	800	200	1000	Nil	Nil	1000	0.290
14E	4:1	680	170	850	150	15	1000	0.265
15E	4:1	560	140	700	300	30	1000	0.242
16E	4:1	440	110	550	450	45	1000	0.225

products were then removed from the moulds and allowed to air dry. Air-dried products were sintered in Muffle furnace at  $960 \pm 2^\circ\text{C}$  for 90 min, and were thereafter removed from furnace.

### 3.5. Evaluation of engineering properties

In order to confirm the prospect of solidified jarosite-sintered products, the engineering properties such as density, shrinkage, water absorption capacity (ASTM C67-60) and compressive strength (ASTM C67-99a), which are equivalent to IS 3495(3): 1992, were examined. In each case triplicate samples were tested and average values were reported. The compressive strength was tested using Shimadzu SERVOPULSER Material Testing Machine (Compressive Testing Machine) Model EHF-EG 200 KN-40L, Japan. The rate of pressure applied was  $27.27\text{ kg/cm}^2/\text{min}$  till the brick break and the break point was measured for compressive strength.

### 3.6. Toxicity leaching potentials of solidified jarosite-sintered products

Leaching potentials of heavy metals and toxic element in jarosite wastes and CCRs were studied following United States Environmental Protection Agency (USEPA) developed and approved Toxicity Leachate Characteristics Procedure (TCLP) using Zero Head Space Extractor, Millipore, USA. This method was applied to assess and understand the degree of hazardous nature in jarosite, CCRs and s/s-sintered jarosite products. This technique is a specific laboratory extraction test for regulating hazardous materials, in which extraction was done under acidic condition using specific extraction fluid (1N NaOH<sup>+</sup> glacial

acidic acid) at a pressure of 10–50 psi with an increment of 10 psi.

### 3.7. Extraction of primary leachate

For toxic elements leaching studies, 25 g of well grained powder sample was loaded into the barrel of Zero Head Space Extractor, then the barrel was closed without any air leakage and maintained at  $\text{pH } 4.93 \pm 0.05$  using NaOH and glycerol. The amount of extraction fluid used was 20 times the weight of samples. After complete assembling the ZHE was slowly pressurised by Pressure Pump (Millipore), beginning at the pressure of 0 psi (1 psi =  $3.5\text{ kg/cm}^2$ ). Then the pressure was gradually increased by 10 psi and the fluid collected up to 50 ml expelled out of the ZHE by holding the pressure for 2 min. Similarly the extraction fluid was collected by pressurizing the ZHE at 20 psi, 30 psi, 40 psi and 50 psi. The primary leachate was stored at  $5^\circ\text{C}$ .

### 3.8. Extraction of secondary leachate

Following USEPA procedure, the extraction fluid was dispensed into the ZHE, then the ZHE barrel was removed from the pressure vessel and attached to rotary agitator and the ZHE barrel/sample container agitated end-over-end at 30 rpm for 18 h. The ZHE barrel was removed from agitator and the pressure source attached to the ZHE. The same procedure was repeated as followed in the primary extraction and the expelled fluid collected from the ZHE under different pressures. The primary and secondary leachates mixed together were analysed. Toxic elements such as Ag, As, Cd, Cr, Ni, Pb, Se and Zn were analysed by Flame and Graphite furnace units and Hydride genera-

tor system of Atomic Absorption Spectrophotometer (Z-5000, Hitachi).

4. Results and discussion

4.1. Physico-chemical properties

Jarosite wastes and fly ash constitute an assemblage of particles of wide variety ranging from clay to fine sand. Particle size curves are drawn on the basis of the data obtained from the above analysis. Fig. 1(a and b) shows the particle size distribution curve of fly ash and jarosite, respectively. Results revealed that jarosite had 63.48 ± 0.19% silt sized and 32.35 ± 0.19% clay sized particles. However, fly ash had 74.69 ± 0.16% silt sized particles. Particle size of jarosite ( $D_{50} = 3.91 \pm 0.03 \mu\text{m}$ ) was finer than that of fly ash ( $D_{50} = 6.48 \pm 0.01 \mu\text{m}$ ). Also it was observed from the size distribution analysis that ~10% of jarosite particles were below 0.91  $\mu\text{m}$ . But in fly ash of ~10% 6.48 ± 0.01  $\mu\text{m}$  sized particles could be recorded. Table 2 shows various physico-chemical properties of jarosite, fly ash and clay. As per the International Soil Classification System, the texture of jarosite waste was silty clay loam and fly ash was silt loam. Though bulk density of jarosite is less than the fly ash, specific gravity is 38.6% higher as compared to fly ash.

Romero and Rincon [9] reported that the density of jarosite was 3.77 g/cm<sup>3</sup>, but the present study showed that the mean specific gravity of jarosite is 2.92 and fly ash was of relatively higher bulk density and lower specific gravity. In the present

Table 2

Physical and electrochemical properties of jarosite, fly ash and soil

S. no.	Characteristics (replication)	Jarosite	Fly ash	Soil
1	BD (g/cm <sup>3</sup> )			
	R1	0.982	1.050	1.392
	R2	0.992	1.170	1.586
	R3	0.971	1.160	1.487
	Mean	0.984	1.127	1.488
2	Specific gravity			
	R1	2.88	2.12	2.33
	R2	2.88	2.09	2.39
	R3	3.00	2.16	2.4
	Mean	2.92	2.12	2.37
3	Porosity (%)			
	R1	66.47	38.01	35.35
	R2	66.87	37.04	37.05
	R3	67.66	37.45	36.55
	Mean	67.00	37.50	36.32
4	Specific surface area (cm <sup>2</sup> /g)			
	R1	10524.96	7117.67	NA
	R2	10463.52	7109.00	NA
	R3	10500.06	7127.38	NA
	Mean	10496.18	7118.02	–
5	Sand (%)	4.18	8.44	8.44
	Silt (%)	63.47	74.69	46.55
	Clay (%)	32.35	16.87	45.01
	Texture	Silty clay loam	Silt loam	Silty clay
6	pH			
	R1	6.70	7.08	7.61
	R2	6.80	6.98	7.73
	R3	6.85	7.03	7.59
	Mean	6.78	7.03	7.64
7	Electrical conductivity (dS/m)			
	R1	14.090	0.498	0.6940
	R2	13.440	0.504	0.6130
	R3	13.260	0.491	0.6450
	Mean	13.597	0.498	0.6506

NA: not analysed.

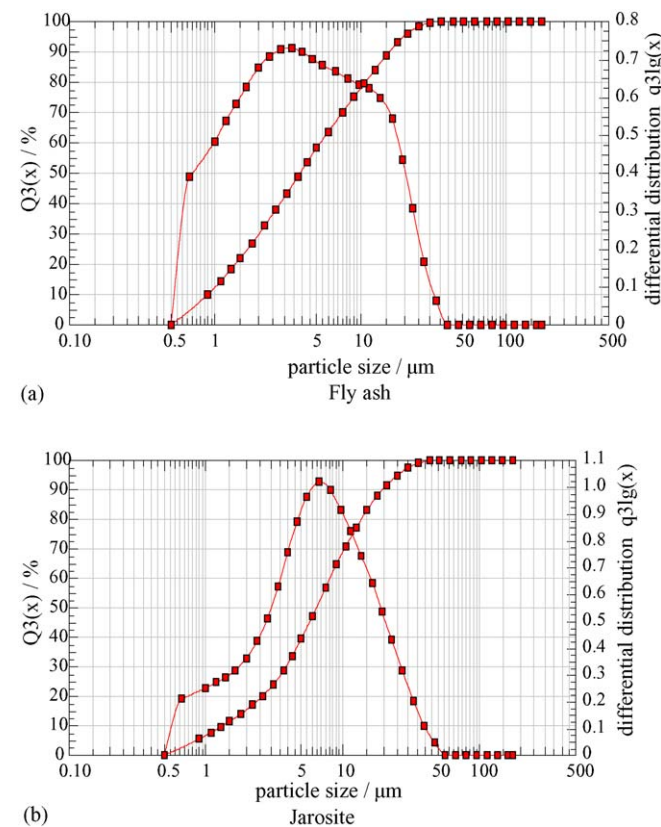


Fig. 1. Particle size distribution curve of fly ash (a) and jarosite (b).

study, due to addition of lime to neutralise the highly acidic pH of jarosite in the industry, the density was found lower than the reported value. As compared to fly ash, the jarosite has higher porosity and water holding capacity due to fine textured materials resulting in high surface area. The bulk density of soil was 1.50 g/cm<sup>3</sup> and specific gravity was 2.67 and the porosity of soil was 41%. The presence of sand, silt and clay content in soil was 8.44%, 46.55% and 45.01%, respectively. The plasticity index of soil was 12.84%. The texture of the soil was silty clay in nature and rich in kaolinite mineral. As per the Indian Standard (IS 2117-1991) the plasticity index of the soil is 15–25%. However, fly ashes and jarosite do not deserve Atterberg limits properties. The high electrical conductivity in jarosite (13.26 ± 0.437 dS/m) indicates that the presence of cations and anions is higher than fly ash (0.498 ± 0.007 dS/m). As reported by earlier researchers jarosite pH is in the range of 2.6–4.0, but

Table 3  
Chemical analysis of jarosite, fly ash and soil

S. no	Parameters	Concentration (%), mean of triplicate samples		
		Jarosite	Fly ash	Soil
1	SiO <sub>2</sub>	6.75 ± 0.412	56.53 ± 0.958	60.65 ± 0.840
2	Al <sub>2</sub> O <sub>3</sub>	6.75 ± 0.152	25.52 ± 0.57	16.22 ± 0.387
3	Fe <sub>2</sub> O <sub>3</sub>	32.12 ± 0.436	5.95 ± 0.505	12.43 ± 0.584
4	MgO	1.86 ± 0.068	1.19 ± 0.107	2.28 ± 0.312
5	K <sub>2</sub> O	0.74 ± 0.023	1.90 ± 0.258	3.22 ± 0.264
6	CaO	6.87 ± 0.151	1.62 ± 0.415	2.15 ± 0.061
7	Na <sub>2</sub> O	0.61 ± 0.424	2.19 ± 0.226	3.21 ± 0.201
8	ZnO	9.18 ± 0.175	0.00724 ± 0.0004	0.0035 ± 0.0002
9	PbO	1.95 ± 0.131	0.0058 ± 0.0003	0.0028 ± 0.00026

usually it is neutralised using lime before discharge into dump site. Virtually, pH of jarosite waste used to be highly acidic in nature and play an important role in the mobility of ions. However, pH of jarosite used in the present study is almost neutral because lime was added in the production units before its disposal. More details on physico-chemical properties of jarosite and fly ash are reported elsewhere [6,8,23,24].

#### 4.2. Chemical, mineralogical and microstructure characterisation

The major portion of jarosite consists of oxides of iron (32.12 ± 0.436%), sulphur (27.84 ± 0.41%) and zinc (9.18 ± 0.175%). The other constituents are calcium, aluminium, silicon, lead and magnesium and each constituent is present below 7% (Table 3). But fly ash's main constituents are silica (56.53 ± 0.96%), alumina (25.52 ± 0.57%) and iron oxide (5.95 ± 0.51%). Heavy metals such as copper, chromium and cadmium were also found higher in jarosite as compared to the fly ash (Table 4a). The EDX analysis further confirmed the presence of these elements. This is also supported by the earlier work that the fine particles of zinc residues contain various elements such as Fe, Zn, Pb, Si, Ca, Cu, K, Ti, Sn and Al [5,9].

The major mineral phases of jarosite are potassium iron sulphate hydroxide {KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>} and iron sulphate hydrate {2Fe<sub>2</sub>O<sub>3</sub>·SO<sub>3</sub>·5H<sub>2</sub>O}. In fly ash the dominant phases are quartz {SiO<sub>2</sub>}, mullite {3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>} and hematite [25]. Major minerals present in soil are quartz, mullite, hematite and magnetite. Fig. 2 shows the scanning electron microscope (SEM) microstructure and corresponding EDS spectra of jarosite and fly ash, respectively. It is evident from the results that the jarosite is non-uniform in structure and shape as compared to most of

Table 4a  
Heavy metals/trace elements in jarosite and CCRs (mean triplicate samples)

Parameters	Jarosite (ppm)	CCRs (ppm)
Manganese	1970 ± 20.0	500 ± 3.9
Copper	1043 ± 25.7	87 ± 1.3
Nickel	87 ± 11.0	102 ± 2.4
Chromium	178 ± 24.7	90 ± 1.7
Cadmium	317 ± 23.8	38 ± 1.0
Cobalt	38 ± 7.4	59 ± 0.7

Table 4b  
Radioactivity level of jarosite and CCRs (mean triplicate samples)

Radionuclides (Bq/kg)	Activity level of radionuclides (Bq/kg)		
	Jarosite	CCRs	Upper limit
<sup>40</sup> K (β emitters)	294.66 ± 17.68	314.00 ± 2.84	925
<sup>226</sup> Ra (α emitters)	55.40 ± 0.86	67.20 ± 0.60	370
<sup>228</sup> Ac (α emitters)	72.00 ± 3.47	77.27 ± 3.06	259

fly ashes having spherical, hollow shapes and jarosite is rich in Fe, S, Pb and Zn.

#### 4.3. Radioactivity level of jarosite and fly ash

Fly ashes released from coal burning process are enriched with radionuclides such as <sup>226</sup>Ra, <sup>40</sup>K, <sup>228</sup>Ac, etc. [26]. The concentrations of these radionuclides are usually low in the coal, when it is burnt in the boiler, the fly ash that is emitted through the stack to atmosphere gets enriched with some of the radionuclides and hence combustion of coal on a large scale for electricity generation becomes important from environmental point of view [27]. Earlier studies indicate that the radioactivity level of Indian fly ash is almost similar to that of normal soil and the radioactive level in lignite fly ash was found less than that of bituminous and sub-bituminous coal [13,28]. The radioactivity levels of hazardous jarosite and fly ash are compared with the upper limits commonly present in normal building materials. The present study confirms that the radioactivity levels in jarosite are less than that of fly ash and are below the limits specified from environmental point of view (Table 4b). The upper limits of naturally occurring radionuclides such as <sup>232</sup>Th (parent radionuclide of <sup>228</sup>Ac) (259 Bq/kg), <sup>226</sup>Ra (370 Bq/kg) and <sup>40</sup>K (925 Bq/kg) in jarosite and fly ash are below the concentration in normal building materials [29,30]. Jarosite seems to be a potential resource, which has to be recycled in a technically feasible and environment friendly manner [6,31,32].

#### 4.4. Effect of jarosite clay ratio and fly ash on density of s/s-sintered products

Firing of clay products produces a series of mineralogical, textural and physical changes that depend on many factors and

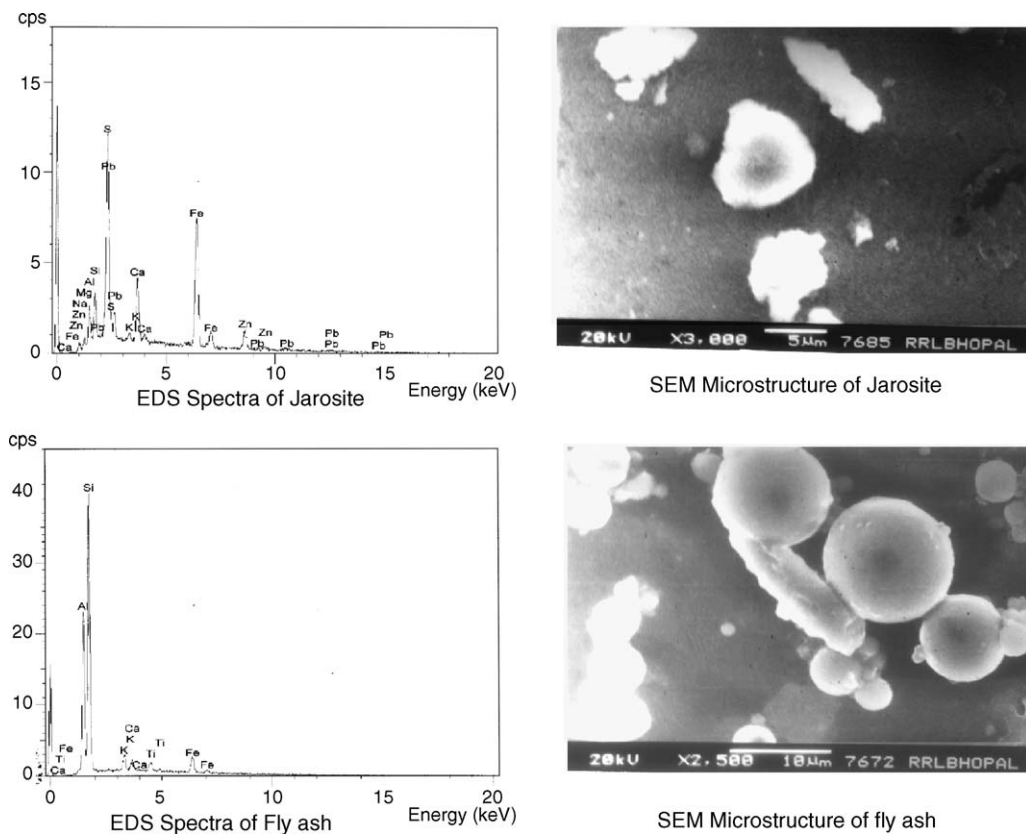


Fig. 2. SEM microstructure and corresponding EDS spectra of jarosite and fly ash.

influence the quality of bricks. A correlation between the density, water absorption capacity, shrinkage and compressive strength of the *s/s*-sintered products developed from jarosite is observed (Fig. 4). Results revealed that the density of fired bricks developed from different ratios of jarosite and clay ratio along with 0–45% fly ash resulted 1.4–1.93 g/cm<sup>3</sup>. Different experimental trials showed that the density of fired bricks had increased when the jarosite clay ratio increased (Fig. 4(a)). However, when fly ash was applied more than 15%, the density of jarosite bricks decreased with increasing jarosite. The minimum density was recorded with maximum fly ash addition wherein jarosite clay ratio was 4:1.

As per sintering kinetics theory, the sintering force is inversely proportional to the particle size and finer fly ash particles might have influenced the sintering of bricks. Work carried

out by several researchers in China, Germany, England, Denmark, etc., showed quite encouraging results on use of fly ash in developing bricks [33–36]. The density of bricks using different ratios of jarosite waste is shown in Fig. 4(a). It is apparent from the results that by increasing fly ash concentration as a partial substitute for clay the density further decreased as compared to the jarosite and clay alone, which is obvious because the density of fly ash was very low. Fig. 3 shows the *s/s* jarosite products before and after firing. Always, bricks properties are mostly influenced by the characteristics of the raw materials and the manufacturing processes. The properties of bricks comprise of: (i) colour, (ii) texture, (iii) shape and size, (iv) compressive strength, (v) water absorption and (vi) durability. The characteristics that influence the quality of the bricks are particle size, Atterberg limits (liquid limits and plastic limits) and plasticity

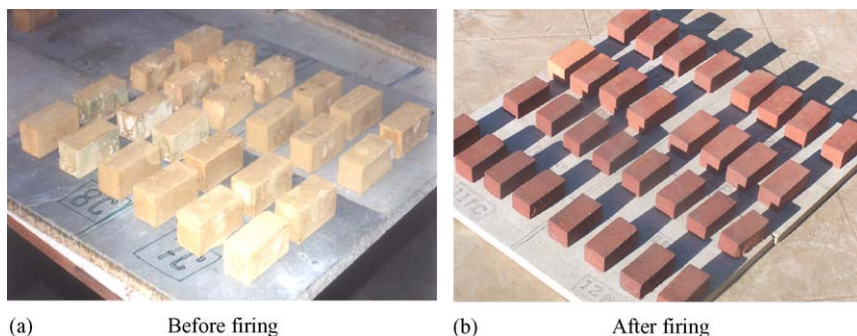


Fig. 3. Solidified/stabilised products developed from jarosite–clay and fly ash (before (a) and after (b) firing).

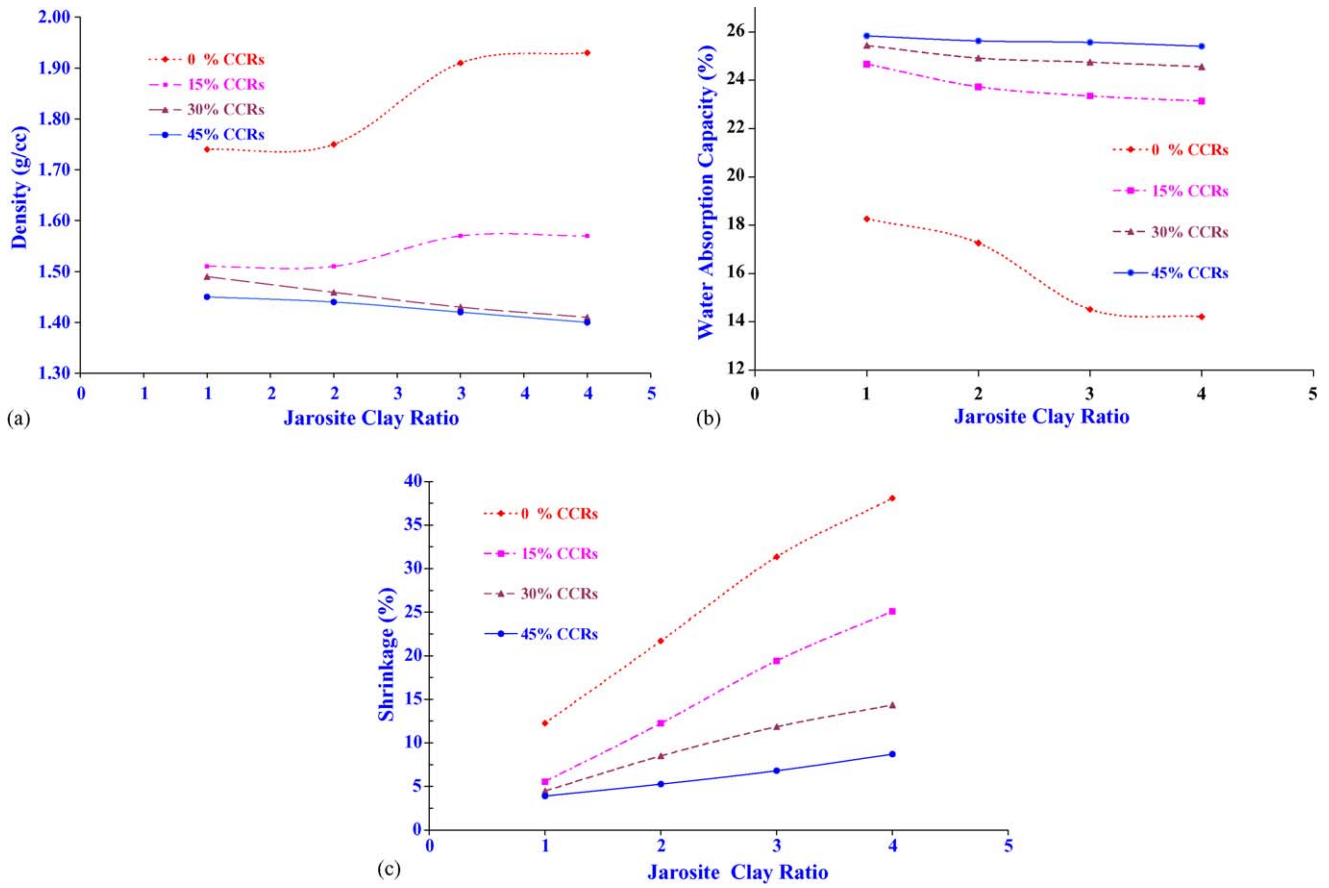


Fig. 4. Effect of fly ash (CCRs) on: (a) density of s/s-sintered jarosite–clay product, (b) water absorption capacity of s/s-sintered jarosite–clay product and (c) shrinkage of s/s-sintered jarosite–clay product.

index. Significant improvement in the quality of jarosite products is achieved using clay as replacement of sand [8], because fine texture of clay soil deserves all these requisite properties while sand does not exhibit these properties. Further material like clay can easily be moulded into any shape and changed into a glasslike material when firing at temperatures  $\sim 900^\circ\text{C}$ . Chemical composition such as silica, alumina, iron oxide and alkali elements present in clay soil plays an important role in densification of bricks structure in sintering process and converting it into alumino-silicate matrixes. The common clay minerals are illite, muscovite, kaolinite, montmorillonite, saponite, etc. However, the main constituent and mineral phase of sand is quartz (silica) which does not help in improving the brick's property.

#### 4.5. Effect of fly ash on shrinkage and water absorption capacity of s/s-sintered jarosite clay products

Fig. 4(a–c) shows the effect of fly ash (in figure referred to CCRs) on density, shrinkage and water absorption capacity of s/s-sintered jarosite products. Results revealed that with increase in quantity of jarosite the shrinkage increased and maximum shrinkage ( $38.08 \pm 0.57\%$ ) could be seen where jarosite clay ratio was 4:1. The increase in shrinkage is expected because the jarosite has highly shrinking and swelling properties in the presence of moisture.

However, addition of fly ash decreased the shrinkage and minimum shrinkage ( $4.93 \pm 0.94\%$ ) could be recorded with 45% addition of fly ash with 1:1 ratio of jarosite and clay. This may probably due to the physical, morphological and thermal characteristic of the fly ash, where it is already burned at high temperature and moreover these fly ashes were spherical, hollow shaped and some of them were cenospheric in nature. But with marble dust application shrinkage was found to be minimum as compared to other additives and even in some of the treatment when 45% marble dust was added on jarosite clay matrix the shrinkage was found only  $\sim 1.5$  [8,10]. Water absorption capacity of jarosite bricks varies from 14% to 26%. With application of fly ash the water absorption capacity increased. Water absorption capacity of bricks developed from jarosite–clay–fly ash matrixes showed that maximum water absorption ( $25.84 \pm 2.24\%$ ) was obtained when 45% fly ash was used along with jarosite–clay matrix. Increase in ratio of jarosite and clay decreased water absorption capacity and minimum ( $14.21 \pm 1.59\%$ ) was recorded where no fly ash was applied with 4:1 ratio. The changes in density, water absorption and shrinkage were due to the sintering mechanism which significantly contributes to increase in the formation of liquid phase by clay minerals fusion and partial dissociation of quartz phase (silica to glassy phase). This reduces the porosity of bricks and might have increased the shrinkage. Also due to firing, the mech-

anisms of reaction might have led to nucleation and growth of new mineral resulting in high density, low water absorption and improvement in mechanical and thermal properties. However, the particle size variation and microstructure of jarosites over fly ash and clay might have also played an important role in changes of bricks properties in terms of density, water absorption, shrinkage and compressive strength followed by sintering reaction. The effects of jarosite, fly ash and clay on compressive strength of s/s sintering products are discussed in the following sub-section.

#### 4.6. Effect of jarosite clay ratio and fly ash on compressive strength of bricks

The effect of jarosite waste on the compressive strength of s/s-sintered products is shown in Table 5. It is revealed from the results that the compressive strength of the bricks made out of 3:1 ratio of jarosite clay is found as high as 140.8 kg/cm<sup>2</sup>. The compressive strength of sintered products made from jarosite and clay ratio 1–4 showed higher strength as compared to the other products developed with incorporation of fly ash with the same ratio of jarosite and clay. But the s/s-sintered products developed from jarosite and clay alone exhibited maximum shrinkage and density. Though increase in concentration of fly ash decreased the compressive strength, minimum shrinkage and density could be recorded with fly ash application. However, minimum compressive strength is with 45% fly ash addition. It is observed that incorporation of clay about ~25% significantly contributed to improving the quality of bricks as compared to the bricks developed from jarosite sand matrixes [25]. It is observed that jarosite sintering behavior is strongly dependent on the composition, quantity and constituent impurities, leading to the formation of

transitory liquid phases which assist the densification of the main crystalline phases, hematite and magnetite or zinc ferrite.

#### 4.7. Effect of sintering on mineralogy and microstructure of jarosite products

The relationship between the firing of pottery and the natural processes leading to the petrogenesis of metamorphic rocks has already been reported elsewhere [36]. During high temperature firing, the reaction behavior of temper grains and jarosite clay matrix is dominated by dis-equilibrium conditions and characterised by the presence of different reacting substances. According to the earlier work of Lingling et al. [33], during heating of clay fly ash bricks, the interlayer or absorbed water of illite is completed at ~250 °C followed by de-hydroxylation starting at 300 °C and further continuing up to 600 °C. However, new crystallite phases were formed when firing above 900 °C, which are Al–Si spinel and mullite.

Earlier studies conducted by other researchers on high temperature firing showed that firing above 950–1200 °C can only achieve the most desired densification or to obtain a solid material which could resist load for engineering application [37–40]. In the present study, initially temperature was maintained at 950 ± 2 °C to fire jarosite clay matrix bricks for random samples but it was recorded that the firing was not sufficient. The temperature was further increased and fired at 1000 ± 2 °C during which excess firing was recorded on the samples. Hence, in all these experiments, s/s jarosite clay matrixes were fired at 960 ± 2 °C and found most desirable product for use in construction applications.

During firing at high temperature, there is considerable increase in the formation of liquid phase due to the fusion of clay

Table 5  
Effect of jarosite clay ratio and fly ash on compressive strength of bricks

S. no	Experiments	Jarosite:clay	Fly ash (%)	Compressive strength (kg/cm <sup>2</sup> )				
				R1	R2	R3	Mean	S.D.
Experiment 1								
1	T1	1:1	0	53.369	57.307	53.525	54.73	2.230
2	T2	1:1	15	49.613	48.067	49.113	48.93	0.789
3	T3	1:1	30	45.577	51.822	49.038	48.81	3.129
4	T4	1:1	45	46.440	44.886	42.418	44.58	2.028
Experiment 2								
5	T1	2:1	0	79.791	81.920	77.052	79.59	2.440
6	T2	2:1	15	46.293	44.619	45.971	45.63	0.888
7	T3	2:1	30	37.267	37.652	37.440	37.45	0.193
8	T4	2:1	45	31.649	32.227	36.433	33.44	2.612
Experiment 3								
9	T1	3:1	0	142.212	141.480	138.705	140.80	1.850
10	T2	3:1	15	44.554	44.691	45.990	45.08	0.793
11	T3	3:1	30	34.181	36.115	34.360	34.89	1.069
12	T4	3:1	45	32.490	32.704	29.385	31.53	1.857
Experiment 4								
13	T1	4:1	0	118.944	122.836	123.687	121.82	2.529
14	T2	4:1	15	38.302	34.049	33.154	35.15	2.750
15	T3	4:1	30	25.882	25.784	25.329	25.67	0.295
16	T4	4:1	45	19.526	19.278	18.559	19.12	0.502

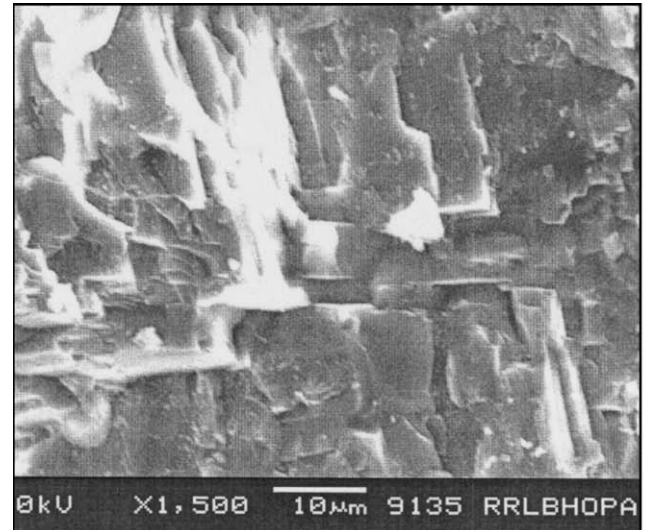


minerals and partial dissociation of quartz phase (silica to glassy phase). This reduces the porosity in the fine porous of the solid bricks and specific surface area under capillary tension force and might have increased the shrinkage [41–43]. As reported by Riccardi et al. [38], due to firing, the mechanism of reaction is leading to nucleation and growth of new mineral is further confirmed from XRD analysis results [25] and SEM microstructure as shown in Fig. 5(a–c). SEM microstructure of the internal surface of bricks showed that there is an increase in aggregation with increase in concentration of jarosite. The aggregation/binding of different matrixes was found least in 2:1 ratio of jarosite clay with 15% fly ash (Fig. 5(a)). However, increase in ratio of jarosite increased the binding of different matrixes and particle aggregation (Fig. 5(b)). The aggregation could be recorded maximum in 3:1 ratio of jarosite clay where no fly ash was applied in which the formation of micropore space and inter-granular bridges could be recorded (Fig. 5(c)) due to sintering. Particle size of jarosite ( $D_{50}$ ) is  $3.91 \pm 0.03 \mu\text{m}$ , which is finer than that of fly ash and has higher porosity and water holding capacity. Due to such fine texture jarosite yielded high surface area ( $10,496.18 \pm 30.90 \text{ cm}^2/\text{g}$ ), which significantly contributed to increasing the aggregation of s/s-sintered products. Though optimum accumulation of different waste substances was recorded with s/s-sintered products developed with 3:1 ratio of jarosite clay combination, it exhibits highest shrinkage and leaching toxic elements are not in safe limits. However, s/s-sintered products developed with the mix design 2:1 as well as 3:1 with 15% fly ash incorporation meet the standard quality and also showed good binding.

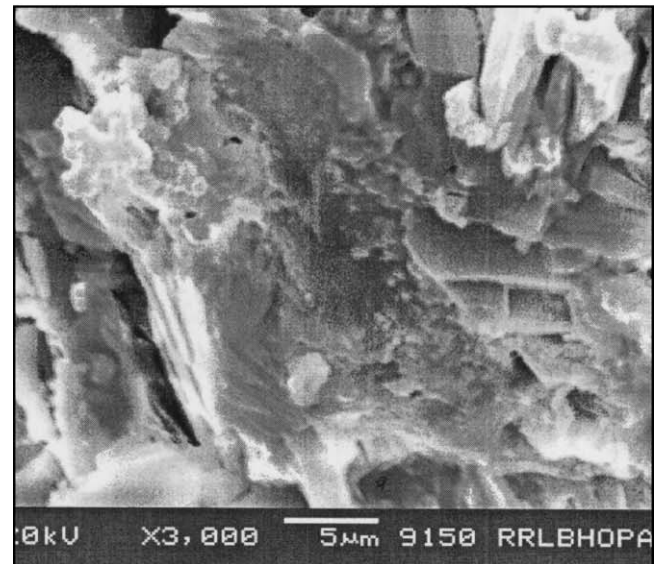
#### 4.8. Toxicity leachate characteristic study

Table 6 shows the effect of jarosite and other additives on toxicity leachate characteristics of s/s-sintered products and sample details are shown in Table 1. The sample identity 1E and 9E shows the mix design of 1:1 and 3:1 ratios of jarosite and clay, respectively, but, fly ash was not applied. The other samples 6E, 10E and 14E are the mix design of 2:1, 3:1 and 4:1, respectively, in which 15% fly ash was incorporated. Though leaching studies were done for the entire experimental samples, selection of reported random samples was done on the basis of: (i) optimum use of jarosite, (ii) optimum mix design in which desired brick quality was achieved to meet the standard for use in engineering applications and (iii) to check the effect of increasing concentration of jarosite.

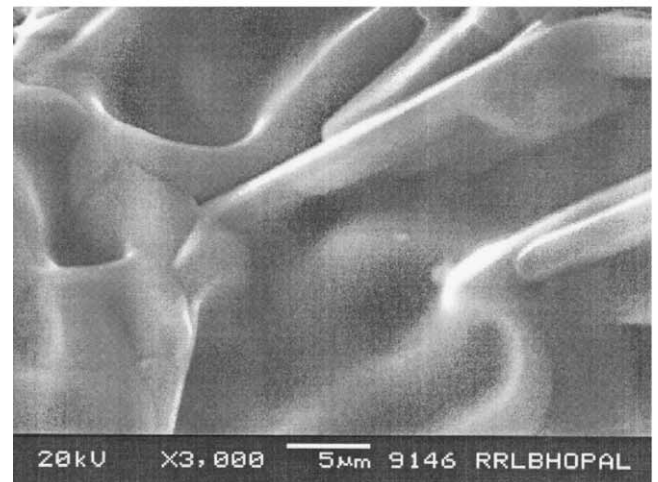
USEPA–TCLP studies confirm that the toxic elements leaching concentrations of silver, lead, cadmium and selenium in raw jarosite are 78.54 ppm, 35.87 ppm, 27.33 ppm and 2.53 ppm, respectively. These concentrations are higher than the USEPA toxicity limits confirming their hazardous nature. Results revealed that increase in concentration of jarosite clay, from 1:1 to 3:1, there was an increase in the leaching of most of the toxic elements in s/s-sintered products. Further studies are in progress to confirm the effect on leaching concentration of toxic elements beyond 4:1 ratio of jarosite clay. Nevertheless, s/s-sintered products developed with jarosite clay alone exhibit higher concentration of leaching than that of jarosite clay with



(a) 2:1 ratio of jarosite and clay alongwith 15% fly ash



(b) 3:1 ratio of jarosite and clay alongwith 15% fly ash



(c) 3:1 ratio of jarosite and clay

Fig. 5. SEM microstructure of s/s-sintered products developed from 3:1 ratio of jarosite and clay along with and without 15% fly ash. (a) 2:1 ratio of jarosite and clay along with 15% fly ash, (b) 3:1 ratio of jarosite and clay along with 15% fly ash and (c) 3:1 ratio of jarosite and clay.

Table 6  
Toxicity leachate characteristics of raw jarosite and s/s-sintered jarosite clay CCRs products (ppm)

S. no.	Toxic elements	Raw jarosite	s/s-sintered jarosite products					USEPA limits
			1E	6E	9E	10E	14E	
1	Ag	78.54	25.1	0.248	0.271	0.265	0.262	5.00
	S.D.	1.43	0.002	0.001	0.005	0.012	0.015	
2	As	3.3	3.345	1.465	11.233	2.498	1.287	5.00
	S.D.	0.43	0.292	0.122	0.144	0.063	0.046	
3	Cd	27.33	3.16	0.314	0.710	0.677	0.596	1.00
	S.D.	1.04	0.010	0.011	0.016	0.010	0.007	
4	Cr	64.02 ± 0.5	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	5.00
5	Ni	3.44	6.257	6.317	7.862	7.042	6.569	70.00
	S.D.	0.28	0.132	0.184	0.049	0.017	0.283	
6	Pb	35.87	10.45	0.694	3.465	0.456	0.591	5.00
	S.D.	0.83	0.040	0.026	0.163	0.005	0.024	
7	Se	2.53	2.46	0.169	0.193	0.174	0.149	1.00
	S.D.	0.65	0.021	0.006	0.013	0.013	0.008	

S.D.: standard deviation. The details of toxic elements leaching potentials of jarosite products developed using different additives, namely 1E, 6E, 9E, 10E and 14E, are shown in Table 1.

15% fly ash mix designs. Fly ash incorporation significantly reduced the leaching of toxic elements in s/s-sintered products in jarosite. Further, jarosite pH was just below neutral (pH 6.78) and hence the concentration of toxic elements such as Zn, Cd, Pb, Cr, etc., might probably stabilise with jarosite clay fly ash matrix.

Effect of jarosite on s/s-sintered jarosite clay products on toxicity leachate characteristics revealed that the concentration of almost all the toxic elements in the sintered products developed from jarosite clay ratio of 1:1, 2:1 and 3:1 with 15–30% CCRs is found within the permissible limits and more details were discussed elsewhere [10]. Sintering influenced transformations of texture and structure resulting in significant changes in the mechanical, thermal and chemical characteristics of the jarosite product. Most of the heavy metal oxides are part of low-soluble crystalline phases or of the glassy phase yielded at the higher temperatures and this behavior could contribute to reduce the toxic elements leaching potentials [41]. The sintering efficiency depends on the presence of contaminates such as SiO<sub>2</sub>, PbO, CaO and alkaline oxides, contributed from fly ash and jarosite for the formation of a transitory liquid phase which helped the densification of the main crystalline phases, hematite, magnetite and zinc ferrite. During sintering process, under solid-state reaction, the toxic substance/elements were detoxified/immobilised through complexing in silicate matrix. But in the present study efforts have not only been made to immobilise the vulnerable pollutants in jarosite for safe disposal but also to develop a process in developing non-hazardous value added products.

## 5. Conclusion

Jarosite poses serious problem for disposal due to release of toxic elements, which ultimately contaminate the soil, ground water, aquatic life and human health. Results revealed from the present study that the compressive strength of jarosite

products attained as high as  $140.8 \pm 1.85 \text{ kg/cm}^2$  and the water absorption capacity is  $14.51 \pm 0.50\%$  at the combination of 3:1 ratio of jarosite and clay, respectively, but, shrinkage was higher ( $31.36 \pm 1.00\%$ ) and toxic elements were not under safe limit. Results revealed that during sintering process under solid-state reaction, toxic substances/elements in jarosite were detoxified/immobilised through complexing in the silicate matrix. During firing of jarosite bricks, a considerable amount of liquid phase formed might have reduced the porosity and specific surface area under the capillary tension forces in the fine pores of the s/s jarosite-sintered products resulting in less water absorption and higher compressive strength. This could be attained by the mineralogical changes/phase transformation due to firing the s/s products at  $960 \pm 2^\circ \text{C}$  and further this was confirmed from the SEM microstructure of the fracture surface. It was confirmed that the leaching potentials of toxic elements such as Pb, Cd, Cr, As, Se, Ag and Ni in s/s-sintered products developed using 1:1, 2:1 and 3:1 jarosite clay ratios with 15–30% fly ash were below the concentration of USEPA–TCLP standard. However, the optimum mix design of 2:1 with 15% fly ash was found to be the intermediate condition to have both satisfactory compressive strength of  $45.63 \pm 0.88 \text{ kg/cm}^2$  with shrinkage of  $12.24 \pm 0.59\%$  in which toxic elements concentration was below safe limits and has the potential to use in construction applications as walling materials. The outcome of the study is expected to result in as one of the major solutions for safely recycling the hazardous jarosite released from zinc industries in developing non-hazardous products which can ultimately be used in building applications.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2006.04.054.

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