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Recycling Marble Wastes and Jarosite Wastes into Sustainable Hybrid Composite Materials and Validation through Response Surface Methodology

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Abstract

During marble processing such as cutting, polishing and grinding, a considerable amount of fine residues refereed as marble processing rejects (MPRs) are produced and have become a serious environmental issue. So the current study deals with the conversion of MPRs into hybrid ceramic composite bricks (CCB) with Jarosite waste in a clay matrix system. Mix design and optimization of CCB was performed to illustrate the potentials of MPRs and Jarosite wastes as low-cost high-value composites materials. Response Surface Methodology (RSM) model was also used in this work for simulation and to optimize the process for improving CCB quality employing classic mixture approach. Detoxification through mineralogical changes was achieved during firing composite bricks at 960^0 C ± 2^0 C and was confirmed using the XRD analysis. Compressive strength of CCB using 15% MPRs with 1:1 Jarosite waste - clay matrix ratio met the standard quality (>35kg/cm^2) for its use in construction purpose. It is evident from the RSM model results and statistical analysis for the response compressive strength, shrinkage, water absorption capacity, density and leachate concentration of Cd as well as Pb in the CCB is in laudable agreement with actual experimental performance.

Key Words: Marble processing residues; Hazardous Jarosite waste; Hybrid Composite; Response surface methodology; Optimization; Toxic substances; Mechanical properties; Sintering mechanism

1. Introduction

Marble stone has been used as a versatile material for cement (Nezerka et al., 2018), wall tiles, floor tiles (Lu et al., 2018), furniture, panels for modular kitchen (Munir et al., 2018), architectural interiors and exteriors to name a few (Seghir et al., 2018). The major producers of marble products are India (~10%), Spain (~6%), Italy (~20%), China (~16%), Portugal (5%) followed by France and Brazil (Thakur et al., 2018). It is roughly estimated that there are about 500 million tons (MT) of marble products worldwide (Alyamac et al., 2017; Khodabakhshian et al., 2018). During marble cutting and processing operations to attain finished products of required dimension from the raw marble stone, about 20% losses occur which form a fine grain. As a consequence of revenues generated from marble industries, annually it is expected about 200 MT of marble processing residue or marble processing rejects (MPRs) as a waste powder/sludge have been produced universally (Thakur et al., 2018). In India, about 16 MT of marble waste has been produced during 2018-2019. The Rajasthan state in India holds one of the world's largest marble deposits in a cluster and accounts for about 90% marble production in the country (Thakur et al., 2018). MPRs being dumped on the river beds or on roadsides and on undulated open land is a major environmental concern and has become a major threat to surrounding ecosystem (Arel, 2016). In dry conditions, the marble waste particulate dangle in the air around us and have the tendency to be deposited on vegetation, crops and significantly affects the ecology. Also, it results in decrease in porosity/ permeability of the topsoil contributing to the water-logging followed by decreasing the soil fertility, crop yield as a result of increase in soil alkalinity. Attempts have been made by several researchers to effectively use the marble wastes in a number of applications including road(Aruntaş et al., 2010), aggregates (Mashaly et al., 2016), cements, pigment, tiles (Sardinha et al., 2016), ceramics and building materials etc., (Topçu et al., 2009). No work is reported on the impact of marble wastes on the mechanical properties of bricks and their long term durability (Mothé Filho et al., 2002)(Okagbue and Onyeobi, 1999). Scanty information is available in the existing literature on the usage of different treatment techniques for the proper disposal of these wastes materials (Polikreti and Maniatis, 2004)and their use in civil engineering applications (Thakur et al., 2018). Study performed on use of MPRs in making polymer composites with jute textile or with glass fiber mat or MPRs alone yielded an improved mechanical strength in terms of flexural strength and stiffness of polyester/ epoxy-based composites (Borsellino et al., 2009; Icduygu et al., 2012; Saxena et al., 2008), but the complete details and their durability performance is missing. Yet, there is very limited work carried out in this direction and further research is essential in the area of marble waste characterization, recycling and understanding their environmental significance.

Jarosite is a mineral, generally formed by the oxidation of sulfate in an acidic sulfate-rich environment from sulfide sediment, acid mine drainage along with weathering of sulfate ore deposits of pyrite (FeS_2) mineral (Asokan et al., 2006; 2010). The prime constituents of the Jarosite waste include oxides of iron, zinc and Sulphur, various other elements such as Al, As, Cr, Co, Cu, K, Mg, Mn, Na, Ni, Pb, S, Si, etc., are also present in Jarosite waste (Asokan et al., 2010; Pappu et al., 2006) (Mehra et al., 2016a)(Mehra et al., 2016b). As per the Ministry of Environment and Forest (MOEF), Government of India's regulatory guidelines, the primary and secondary production of Zn comprising Jarosite waste is categorized as the hazardous waste (Asokan et al., 2006). So the prime aim of this research has been to effectively use the marble wastes and jarosite wastes into high-value sustainable hybrid composite materials

2. Materials and Methods

Samples of marble processing residues (MPRs) from marble processing industry; Jarosite waste from Hindustan Zinc Limited and clay soil nearby marble industry were collected from Udaipur, Rajasthan, India. All these samples prior to use were oven-dried at 105± 2 ^{o}C, crushed using the contact pressure and then sieved using 2mm size sieve. For characterization and experimental work, ceramic composite bricks (CCB) specimens were prepared from the processed samples employing conning and quartering method.

2.1 Experiment Design

Ceramic-composite bricks (CCB) consists of MPRs, Jarosite waste, and clay, which is considered as 'q' component materials. To optimize CCB quality, the classic mixture approach was used. In this approach, the sum of the proportions of raw materials must be one (1) and the variables are not independent. The advantage of this approach is that the required experimental region has been defined more naturally.

2.1.1 Modeling: Classic Mixture Approach

In the classic mixture approach, the total weight of CCB is fixed and quantity of each of the *q* component variables is decided accordingly to have a fixed mass as the total amount is constrained to sum to one. In the present study, CCB was a mixture of three raw materials namely Jarosite waste (x_1), clay (x_2), and MPRs (x_3), in this each x_i represents the weight fraction of each raw materials. The weigh fractions in which the components sum to one, and the region demarcated by this constraint results in triangle (or simplex) as revealed in **Fig.1** (a) of section 2.1.1.

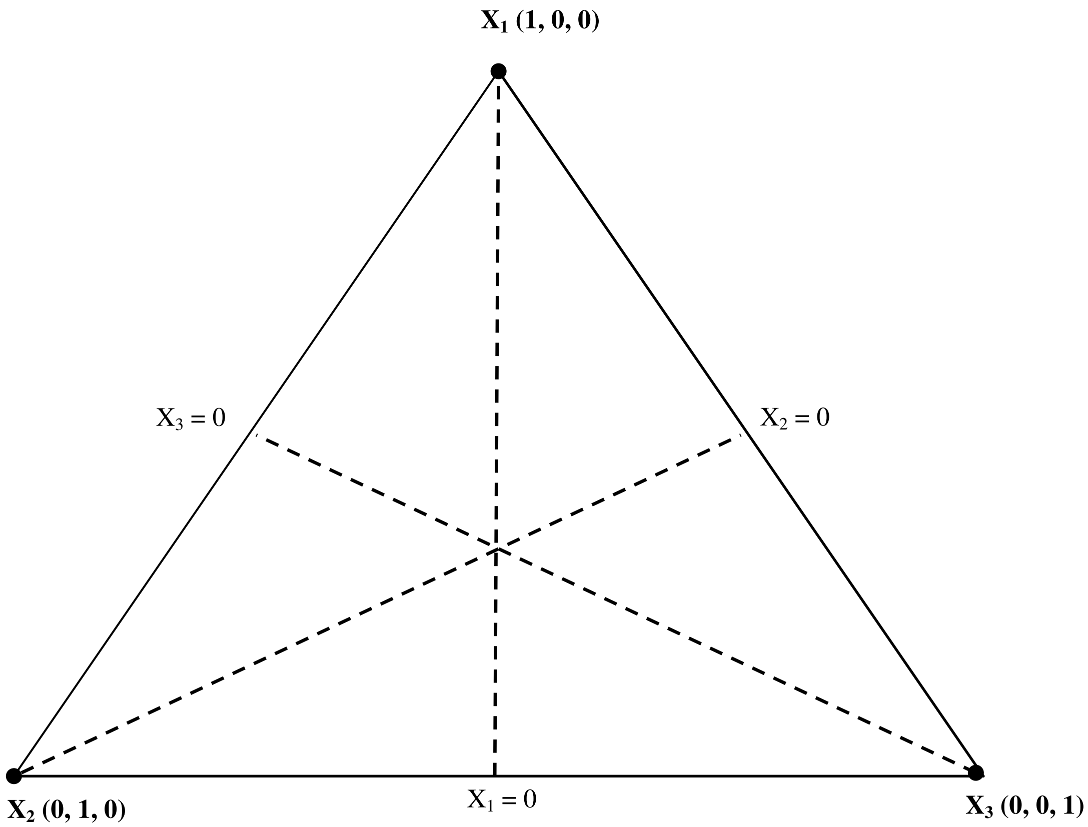


Fig. 1(a).The triangular simplex region from three-component mixture experiment

As per the classic mixture model, all defined properties were quantified for each mixture and were modeled as a function of each raw material. The polynomial functions were adopted for modeling. For three raw materials (Jarosite waste, clay, MPRs), the linear polynomial model for a response '*y'* was represented as:

$$\mathbf{y = b^*_0 + b^*_1\, x_1 + b^*_2\, x_2 + b^*_3\, x_3 +} \qquad \textbf{(1)}$$

Where,

bi^*stands for the constants

'e' is the error term*,* showin*g* combined effects of each variable.

In case of experiment with mixture, $x_1 + x_2 + x_3 = 1$ -, the model can be re-written as:

$$\mathbf{y = b_1\, x_1 + b_2\, x_2 + b_3\, x_3 + e} \qquad \textbf{(2)}$$

Where,

$$\mathbf{b^*_0 = b^*_0 .\ (x_1 + x_2 + x_3)}$$

This form is known as the Scheffé linear mixture polynomial(Ziegel, 1992)

Correspondingly, the quadratic polynomial can be written as:

$$\mathbf{y = b_0 + b^*_1\, x_1 + b^*_2\, x_2 + b^*_3\, x_3 + b^*_{12}\, x_1x_2 + b^*_{13}\, x_1\, x_3 + b^*_{23}\, x_2\, x_3 + b^*_{11}\, x_1^2 + b^*_{22}\, x_2^{2+}\, b_{33}\, x_3^2 + e}$$

(3)

This can be further represented as:

$$\mathbf{y = b_1\, x_1 + b_2\, x_2 + b_3\, x_3 + b_{12}\, x_1x_2 + b_{13}\, x_1\, x_3 + b_{23}\, x_2\, x_3 + e} \qquad \textbf{(4)}$$

Where,

$$\mathbf{x_1^2 = x_1 .(1 - x_2 - x_3).}$$

$$\mathbf{x_2^2 = x_2 .(1 - x_1 - x_3).}$$

$$\mathbf{x_3^2 = x_3 .(1 - x_1 - x_2).}$$

Since the CCB mixtures did not exist above the entire region as revealed in **Fig.1** (a), a -sub-region of the simplex that contains the ranges of different feasible mixtures should be defined by limiting the raw materials proportions. The representation sub-region for the three raw materials is shown in **Fig.1** (b) of section 2.1.1 and is well-defined by the subsequent weight fractions (where x_1= Jarosite waste, x_2= clay, x_3 = MPRs);

$0.15 \leq x_1 \leq 0.25$

$0.10 \leq x_2 \leq 0.20$

$0.60 \leq x_3 \leq 0.70$

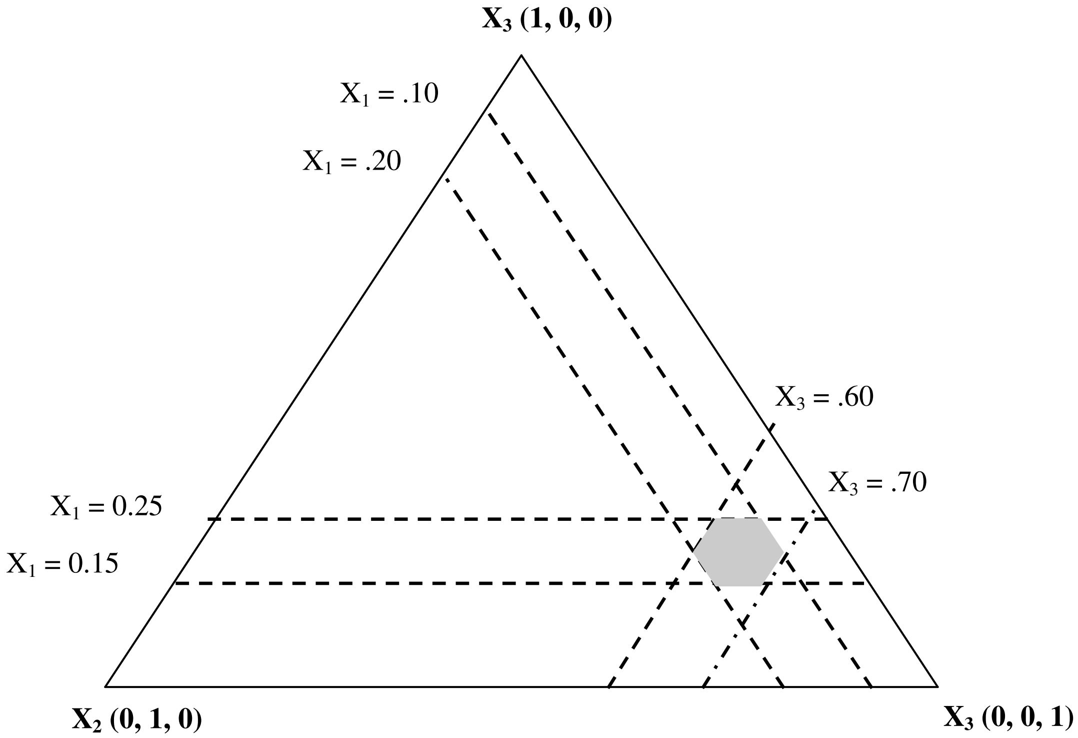


Fig. 1 (b). Example of sub-region of full simplex containing a range of feasible mixtures

2.1.2 Model Fitting and Validation

To authenticate the satisfactory conditions of the selected model quantitatively as well as graphically, the polynomial models reported in the classic mixture approach was used to fit data by means of least squares techniques and analysis of variance (ANOVA). From the ANOVA significance of the treatment effect can be obtained. The different steps that are involved in model selection along with the fitting are almost the same for polynomials models and the classic mixtures approach.

2.1.3. Optimization

The performance of CCB and detoxification of toxic species may depend on the raw materials used, their quantity, concentration, process technique under which CCB was prepared. Optimization can be accomplished employing the mathematical (numerical) / graphical (contour plot) approaches. The graphical optimization approach is limited where there are only a few responses considered to ascertain the quality of CCB. Numerical optimization needs defining an objective function known as score function/desirability. This would reflect the levels of each response in terms of minimum (zero) to maximum (one) desirability. The geometric representation of the desirability functions for each individual response is one of the approaches, where *n* is the number of responses to be optimized (Derringer and Suich, 1980):

$$D = (d_1 \times d_2 \times \ldots \times d_n)^{1/n} \quad \textbf{(5)}$$

Another approach to represent desirability functions is to use a weighted average

$$D = \frac{(w_1 \times d_1 + w_2 \times d_2 + \ldots + w_n \times d_n)}{n} \quad \textbf{(6)}$$

Here '*n' represents* the number of responses while w_1 represents weighting functions varying from 0 to 1.

The Desirability functions can also be expressed mathematically.

On defining the desirability functions for each response, the optimization was done. Also, statistical analysis for the responses compressive strength, water absorption capacity, shrinkage, density and toxic elements leachability (Pb, Cd) in CCB was done. To validate the results, the model was fit to data using analysis of variance (ANOVA) and least-squares technique, validated and interpreted graphically using contour plot, trace plots, and 3D graph.

2.2 Physico-chemical Characterisation

Standard methods were followed for the analysis of bulk density/ particle density (Veihmeyer and Hendrickson, 1946)and Porosity (Bodman, 1942). Saturated soil pastes international pipette technique was used to measure the water absorption capacity. Electrical conductivity and pH were measured employing the Orion analyzer (Model 1260, Orion Research Inc., USA) in 1:2 soil suspensions. Laser Diffraction Particle size analyzer Model HELOS Laser diffraction system, Sympatec GMBH, Germany was used to analyze the particle size distribution. For chemical analysis, ground samples were subjected to digestion by microwave digester (QLAB 6000 Microwave Digestion System, Canada) and subsequently the digested samples were filtered employing Whatman filter paper 50. These samples were then analyzed using the Atomic Absorption Spectrophotometer (AAS), Z-5000, Hitachi, Japan with flame and graphite system and hydride generator facilities. In each experiment, high purity water of Elga (Prima 1-3 and Elgastat Maxima, England) system was used.

2.2.1 Mineralogical and Morphological Characterization

The mineralogical investigation was performed by an X-ray diffraction analysis system using an automated powder diffractometer (Model: Philips PW 1710), with Quasar software packages, using a Cu tube (Wavelength of X-Ray (λ) =1.5418 A) and generator settings of 40 kV and 30 mA. Different samples were homogenized by grinding in a mortar and pestle for about 10 minutes and were then loaded into an aluminum sample holder for analysis. Data was collected at a scanning speed of 0.01 degree 2θ/sec. PC-APD software was used for data smoothing. The samples were scanned in the range of 5^{0} - 70^{0} 2θ. The microstructure characteristics were studied using Scanning Electron Microscope (SEM) Model JOEL JSM-5600, Japan with Energy Dispersive X-ray Spectroscopy (EDS) analysis facilities. Test samples were dispersed in inorganic solvent and spread over on the aluminum stud with silver paint and sputtered with gold before examination in SEM. The Energy Dispersive Spectroscopy spectrum of samples was also recorded, which showed the peak of chemical elements present in the samples. The software of Oxford Model link Pendafet- IC 300 was used for the quantitative estimation by computational method.

2.2.2 Toxicity Leachate Characteristics

The toxicity leachate characteristics of different heavy metals and toxic elements present in the MPRs, Jarosite waste, clay, and CCB were studied following USEPA developed Toxicity Leachate Characteristics Procedure (TCLP) using Zero Head Space Extractor (ZHE), Millipore, USA. Extraction fluid was prepared using acetic acid and 0.1 N NaOH to maintain a pH of 4.93 ± 0.05. The quantity of extraction fluid used was equal to 20 times the weight of the dry solid sample of 25 gm. Primary extraction fluids were extracted from the ZHE at the pressure of 0, 10, 20, 30, 40 and 50 psi (1 PSI = 3.5 kg/cm^2) and leachate was stored at 5° C. Following USEPA procedure, secondary extraction fluids were extracted after agitating the sample pressure barrel from rotary agitators at 30 rpm for 18 h under different pressure. The primary and secondary extraction fluids (leachate) were mixed together and analyzed the content of Ag, As, Cd, Cr, Hg, Ni, Pb, Se, and Zn.

2.3 Development of Ceramic Composite Bricks (CCB)

The casting of ceramic composite bricks (CCB) using MPRs with Jarosite waste experimented in clay system. The well-prepared MPRs with Jarosite waste and clay were solidified/ stabilized (S/S) in rectangular cast-iron mold 97.5 cm x 3.5 cm x 3.5 cm). The casting of products (s/s) was done in a hydraulic based hand press under contact pressure. Casted products were subsequently allowed to air dry after the removal from the molds. Thermal stability and strength of s/s of the developed products were achieved through sintering process. Sintering was done after air-drying all these s/s products for 15 days (d) and then firing in muffle furnace at 960 ± 2 ^{0} C for ninety minutes. CCB samples were removed from the furnace when it was reached at room temperature (32 ± 2 ^{0}C) for further studies. The experimental details, raw materials used and experiment identification is shown in **Table S1** of section 2.3 .

2.3.1 Testing mechanical and physical properties of CCB

Standard test methods have been followed to evaluate the mechanical and physical properties (water absorption, shrinkage, and density) of CCB. ASTM standard method was followed to study the bulk density (ASTM C830-00), shrinkage (ASTM C356-10), water absorption capacity (ASTM C67-60) and compressive strength (ASTM C67-99a) of CCB, which are equivalent to IS 3495(3): 1992. In each case triplicate samples were tested. 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 kg/cm2/min till the ccb failure and the breakpoint was measured for compressive strength. The compression strength was estimated with regards to maximum load applied to correspond to its area and expressed in kg/ cm^2.

2.4 Data Analysis

CCB was developed applying a statistically designed experimental approach using Surface Response Methodology (SRM). The Mixture design parameters and their concentration ranges for the CCB Matrix (Jarosite waste-Clay-MPRs) and the details of raw materials component quantity for making s/s and achieving CCB are shown in **Table S2** and **Table S3** of section 2.4. The proportions for the 3-component mixture (Jarosite waste, clay and MPRs) experiment initially were selected in terms of weights. The total weight of the raw materials was kept constant at 1 kg as required by the model. Since the weight fractions should sum to unity, the raw materials in a mixture experiment are not independent. The parameter levels of the 3 mixture components are shown in **Table S2** of section 2.4.

2.5 Model Fitting and Validation

The polynomial models described in the classic mixture approach were fit to data using analysis of variance (ANOVA) and least-squares technique. The optimized experimental results (using Jarosite waste and clay soil ratio of one with 15% CCRs) showed that it is possible to make a composite having desirable mechanical properties such as compressive strength (50–81kg/cm^2); water absorption (13–17%); shrinkage (11–32%); and density (1.6–1.8gmcm^{-3}) to use as a construction material. From the ANOVA, significance of the treatment effect was obtained. Sequential F-tests were then performed using linear model and adding terms. The degree of freedom for each input was denoted as DF and the F-statistic was calculated for each type of model and the highest order model with significant terms. Significance was judged by determining the probability that the F-statistic calculated from the data exceeded the theoretical value. When the probability was less than 0.05 (99.9% confidence level) or 0.01 (99.98% confidence level) represent significant results. For the comparison of the actual error from replication to the residual error to a lack-of-fit test was performed using ANOVA. When residual error is significantly higher than the actual error, the model implies significant lack of fit for which another model was found to be more suitable. The anticipated result during a lack-of-fit test was achieved, when the model designated in step 1 not showed significant lack of fit (F test was irrelevant). This showed that the probability was greater (Prob>F) and F value was lesser than the required significance levels at 99.5% confidence level (0.05). To verify the model suitability, statistical analysis was performed and it included root mean square error (RMSE), predicted r^2, adjusted r^2, and predicted error sum of squares (PRESS). The RMSE in this work was the standard deviation linked with experimental error. The adjusted r^2 was a degree of the variation on the mean explained in the model that was adjusted for various characteristics in the model. The predicted r^2 measured the variation in new data that was elucidated by the model. A simple linear regression technique (least squares) was employed to fit the model to the data exhibiting rough linear relationship. ANOVA was done and F-test along with the lack-of-fit test confirmed the suitability of the used model. After the model adequacy was performed, the assumptions were validated in the ANOVA residual analysis. 'Design Expert' software was subsequently employed to design and investigate the experimental data. In the present study, the program used particular 14 points from a gradient of candidate points. It includes the preeminent points to be fitted in a quadratic polynomial (**Table S3**). The goal was to optimize the raw materials inputs quantity to produce best quality of bricks, which should meet the following criteria:(i) Compressive strength ≥ 25 kg/cm^2; (ii) Water absorption ≤ 20%; (iii) Shrinkage < 15% (iv) Brick density below 1.75 $g/cm^{3;}$ (v) Leachate Concentration of Lead < 5.0 ppm and (VI) Leachate concentration of Cadmium <1.0 ppm. In this paper, due to page limitation, the statistical analysis is described in detail for response brick compressive strength only. The CCB was tested for their chemical toxicity leachability following USEPA norm and mechanical properties according to the Bureau of Indian Standard (BIS 1077:1992) and assessed their suitability to be used as an engineering brick in construction materials. The impact of application of different waste matrixes on the mineralogical and microstructure characteristics variations was also studied and corroborated to the results in relation tothe mechanical strength. In each experiment, minimum four replicate experiments were performed and all data were analyzed statistically.

3. Results and Discussions

3.1 Physico-chemical Characteristics of MPRs, Jarosite waste and Clay

MPRs, Jarosite waste (JW) and clay soil were subjected to their Physicochemical properties analysis and the properties are shown in **Table 1** of section 3.1. The results showed that MPRs exhibits a fine grain size with particles ranging from nanometers to micrometer. The bulk density of MPRs was quite higher (1.879±0.020 gm/cc) as compared to clay. The porosity of clay and MPRs showed almost in the range of 36-39%. On a contrary, porosity (67.00±0.61%) and water absorption capacity (109.96±0.148) of Jarosite waste was very high as compared to clay and MPRs where in MPRs and clay exhibits relatively lower water absorption capacity. As the pH of Jarosite waste was neutralized using lime at the zinc industry's discharge zone and –the pH was almost neutral (6.78±0.08), and the electrical conductivity was extremely high (13.597±0.437 (dS/m) indicating the presence of ions in higher concentration. MPRs showed an alkaline pH (8.360±0.102) and the electrical conductivity was very low (0.2769±1.004) while pH of clay was almost neutral, the electrical conductivity was higher (6.44±0.305 dS/m) over MPRs. The Electrical conductivity (dS/m) is low as compared to normal clay soil and fly ash and generally it is compared with soil as the soil fertility and water quality contamination depends on the presence of EC and other heavy metals. The electrical conductivity is important for bricks because at the end of the service life is over, we have to dispose safely which should not affect the soil quality as well as it should not leads to leachate of any toxic substance/element to the groundwater and contaminate the soil. It is important parameters to be considered as Jarosite waste used in the present study is a hazardous waste.

Table 1. Physico-chemical properties of marble waste and Jarosite waste

Parameter	**MPRs**	**JW**	**Clay**
Bulk Density (g/cc)	1.879±0.020	0.984±0.014	1.49±0.079
Specific Gravity	2.516±0.009	2.92±0.07	2.379±0.031
Porosity (%)	39.657±0.388	67.00±0.61	36.317±0.713
Water absorption Capacity (%)	24.15±0.60	109.96±0.148	43.69±0.52
pH	8.360±0.102	6.78±0.08	7.643±0.062
Electrical Conductivity (dS/m)	0.2769±1.004	13.597±0.437	6.44±0.305

Mean of triplicate test results

Table 2 of section 3.2 illustrates the chemical properties of MPRs, Jarosite waste and clay. The major chemical constituents present in Jarosite waste are oxides of iron, sulfur and zinc (Table 2). The other constituents are calcium, aluminum, silicon, lead, and magnesium, and each constituent is present below 7 %. Jarosite waste contain toxic elements like zinc (8.24+0.0755), lead (1.9±0.023%), sulphur (12.23±0.2%), cadmium (317±23.8ppm), chromium (178±24.7 ppm), copper (1043±25.7 ppm), which are far higher than that of MPRs and clay, where more details about the presence of chemical constituents in Jarosite waste, clay and MPRs have been reported and discussed elsewhere (Asokan et al. 2006a, Asokan et al, 2006b, Asokan et al, 2010). The primary chemical constituents in MPRs are oxides of calcium (about 45%) and magnesium (about 5%). There are many trace elements such as oxides of aluminum, iron, silica, potassium, carbon, sulfur are present the MPRs.

Table 2. Chemical properties (%) of MPRs, Jarosite waste, and clay

Parameters	MRPs	JW	Clay
SiO_2	1.73±0.04	6.75±0.412	60.65±0.69
Al_2O_3	1.12±0.09	6.75±0.152	16.22±0.32
Fe_2O_3	1.42±1.94	32.12±0.436	12.43±0.48
MgO	4.41±0.34	1.86±0.068	2.28±0.25
K_2O	0.01±0.00	0.74±0.023	3.22±0.22
CaO	45.40±0.61	6.87±0.151	2.15±0.05

All values are expressed in percentage

The major chemical constituents in clay are oxides of silica (60.65±0.69%) followed by alumina (**Table 2**). More details on the chemical properties of Jarosite waste are reported elsewhere(Asokan et al., 2010). All these characteristics have been further evaluated and validated from the SEM EDX analysis as reported in **Fig.2** (a & b) of of section 3.1, where the EDX peak shows the chemical element present in MPRs (**Fig.2a**) and Jarosite waste (**Fig.2b**).

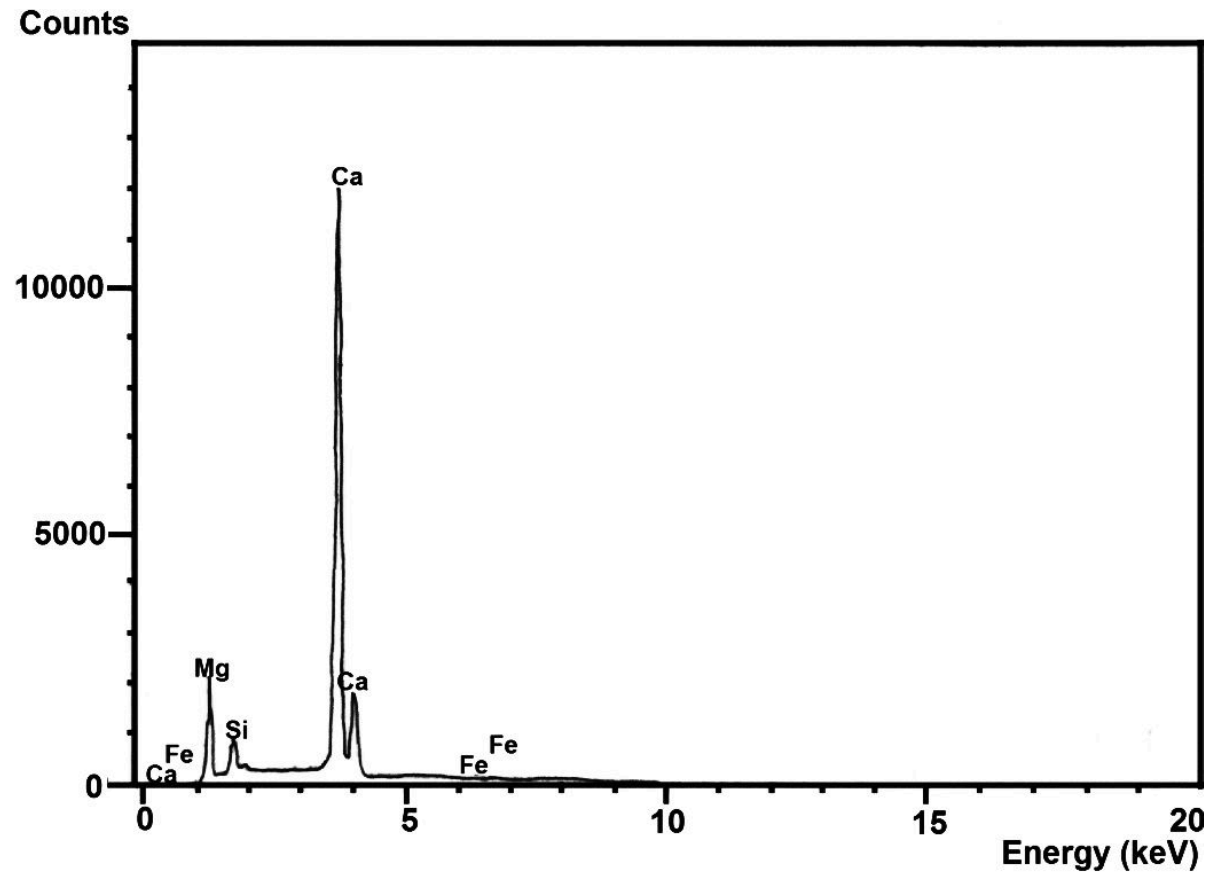


Fig. 2(a). EDX spectrum of marble waste

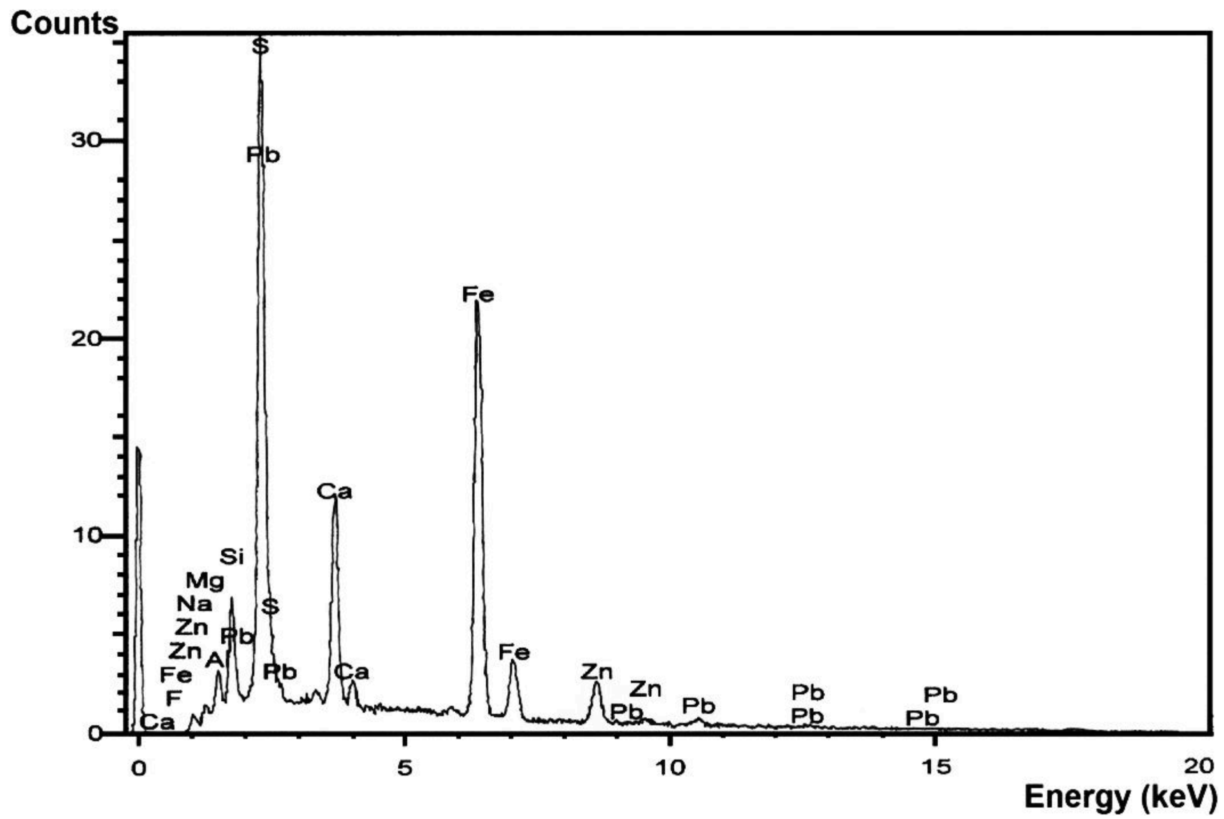


Fig. 2(b). EDX spectrum of Jarosite waste

3.2 Mineralogical Characteristics

The marble processing rejects and residues contain Dolomite (CaMg) $CO_3)_2$), Diopside (CaMg) Si_3, and Wollastonite ($CaSiO_3$). The X-ray diffraction analysis as shown in **Fig. 3(a)** of section 3.2 reveals the foremost mineral phase present in MPRs. Other minerals such as Vaterite ($CaCO_3$) and Calcium silicate ($CaSiO_3$) were also identified in MPRs. The key mineral phases in Jarosite waste were Jarosite (KFe_3 $(SO_4)_{2(}OH)_6$ and Anglesite ($PbSO_4$). Other compounds such as Iron Sulphate Hydrate ($2Fe_2O_3$ SO_3 $5H_2O$), Ammonium Iron sulfate hydroxide ($NH_4Fe_3(SO_4)(OH)_6$,Iron hydroxide ($Fe(OH)_3$) and Calcium sulfate ($CaSO_4$)were also present in Jarosite waste and are shown in **Fig. 3(b)** of section 3.2 .This shows the prevalence of OH^- that propels the different constituents to absorb/expel water from the molecules and were discussed by researchers(Asokan et al., 2010, 2006). Major mineral phases present in clay soil have been shown in **Fig.3(c)** of section 3.2 . Results showed that the dominant phases in clay were Ferroaetinolite {Calcium Iron Silicate hydroxide – Ca_2Fe_5 (Si_8O_{22}) $(OH)_{2)}$, Vertumnite ($Ca_4Al_4.Si_4O_6.$ $(OH)_{24}$. $3H_2O$), Ferroaetinolite (Ca_2Fe_5 $(Si_8O_{22}$ $(OH)_2$), Kaolinite ($Al_2O_3.2SiO_2.2H_2O$) and Cristobalite Quartz (SiO_2).

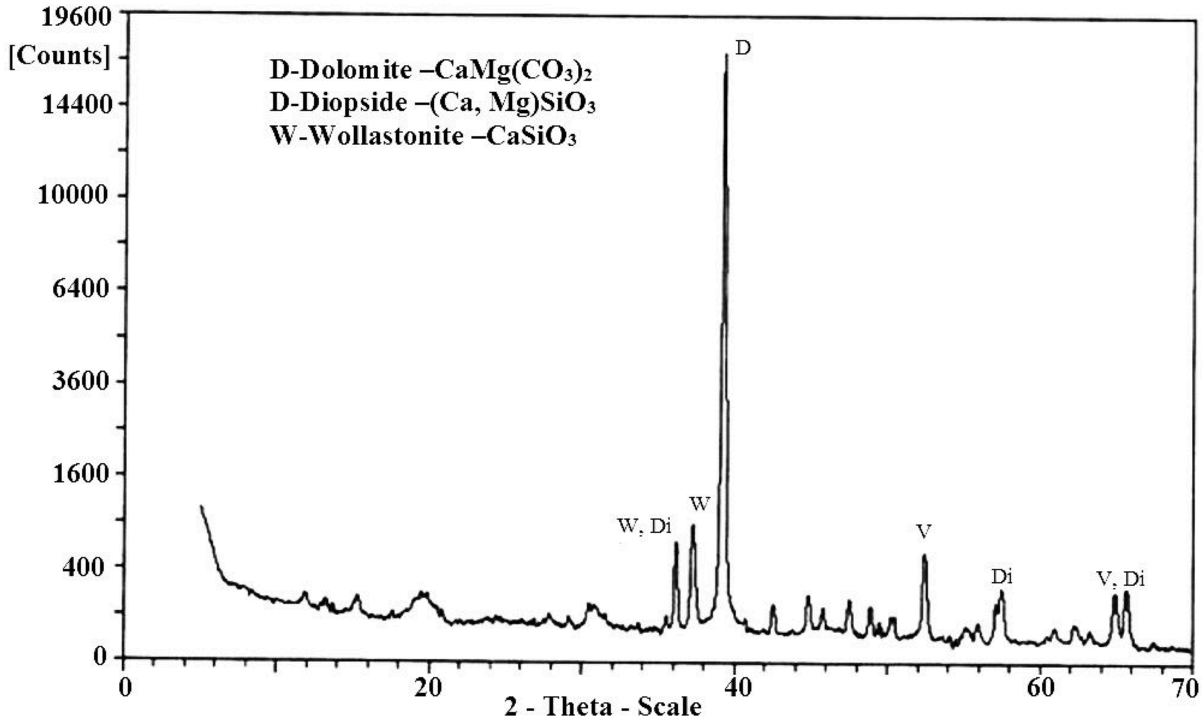


Fig. 3(a). X-ray diffractograms of MPRs

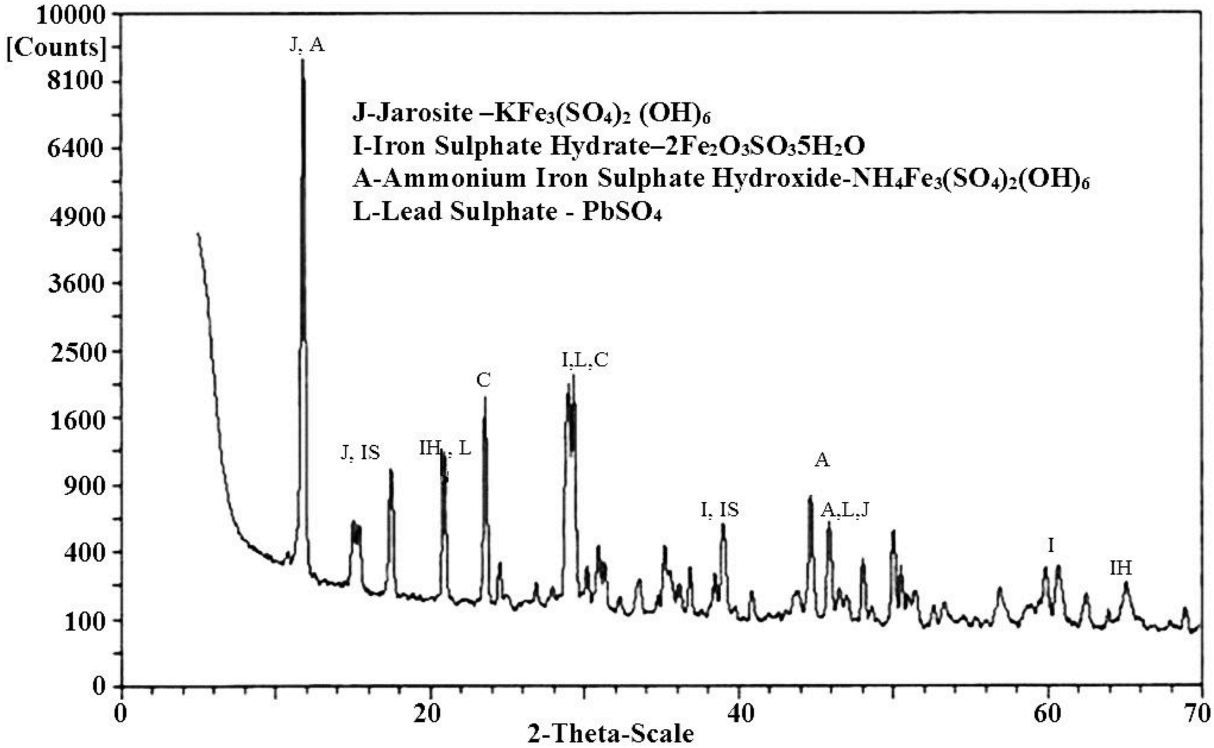


Fig.3 (b). X-ray diffractogram of Jarosite waste

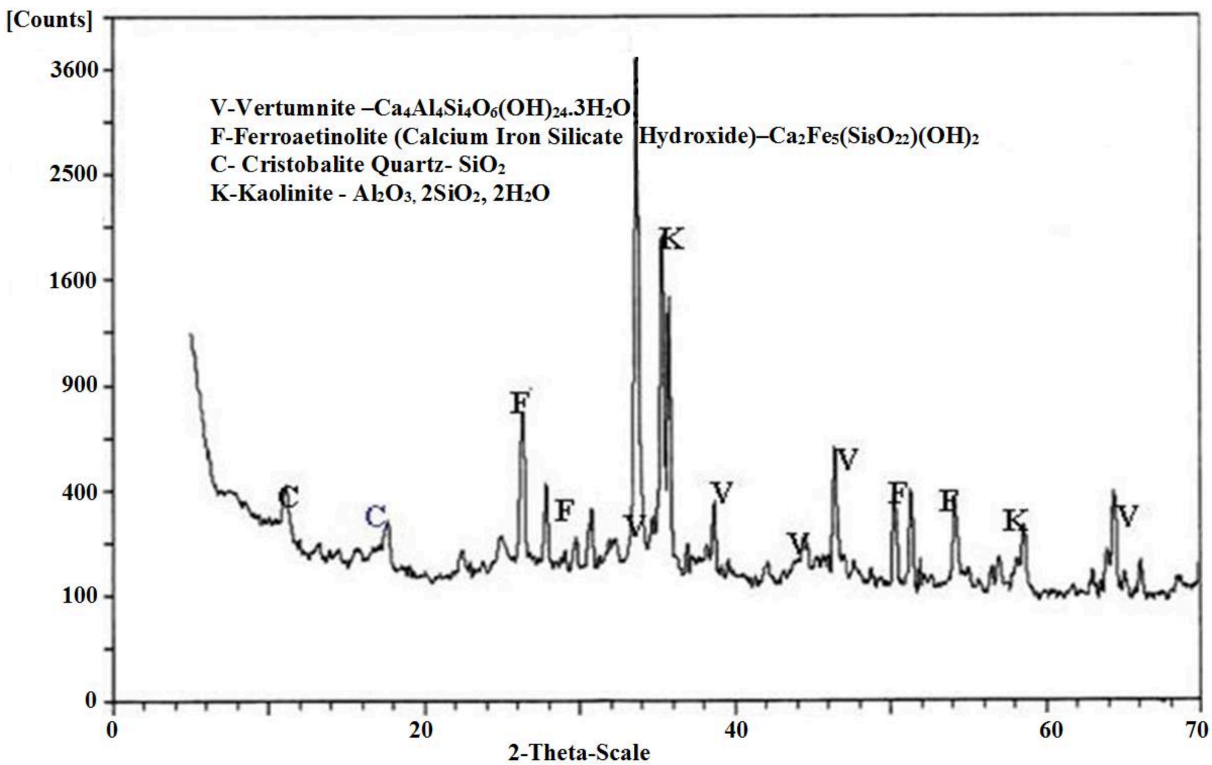
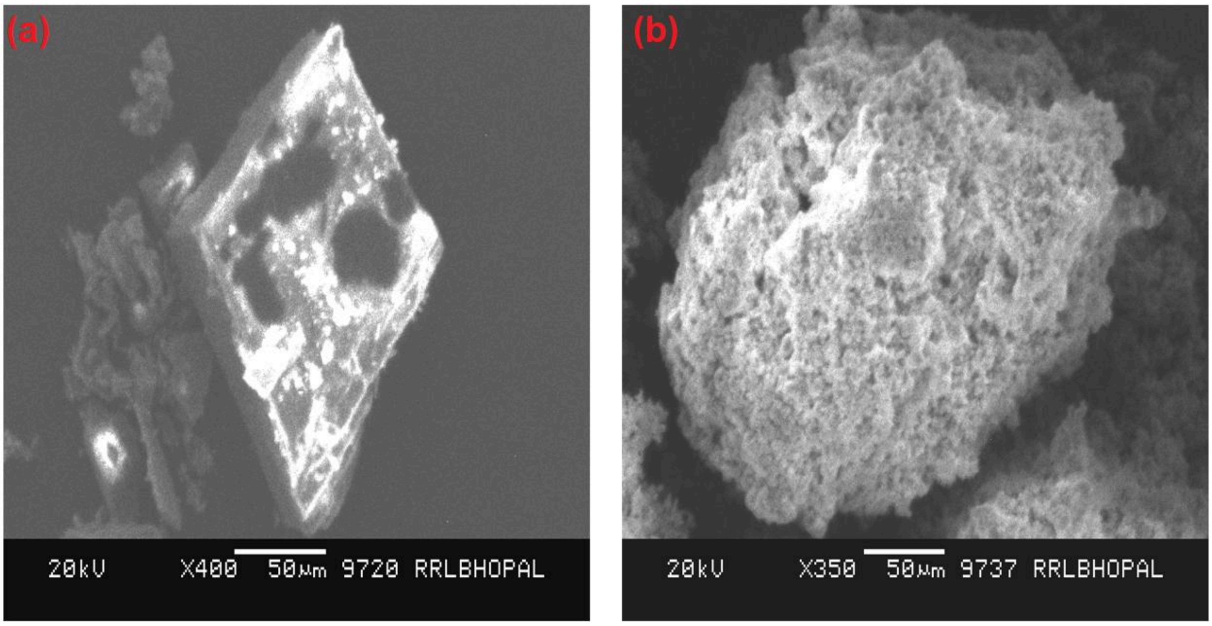


Fig.3(c). X-ray diffractograms of clay soil

3.3 Morphological Characteristics

The microstructure of marble processing residues (MPRs) is shown in **Fig. 4 (a)** of section 3.5 **.** Result reveals that MPRs particles exhibit cleavage structure having sharp edges. It was also confirmed from the microstructure that the majority of the particles have irregular shape with solid structure. The particle surface was found to be unsmooth and some of them were angular shape of with solid structure. The microstructure of Jarosite waste is shown in **Fig. 4(b)** of section 3.5 that demonstrates the irregular shape of the particles with multiple humps. Though the surface of Jarosite waste particles was found to be smooth with large lumps, it contains lots of porosity and demonstrates exceedingly swelling / shrinking properties. The particles were made of flaky units with some binder which may be oxides of zinc, sulfur, calcium /lead and the same was confirmed from the chemical analysis results.



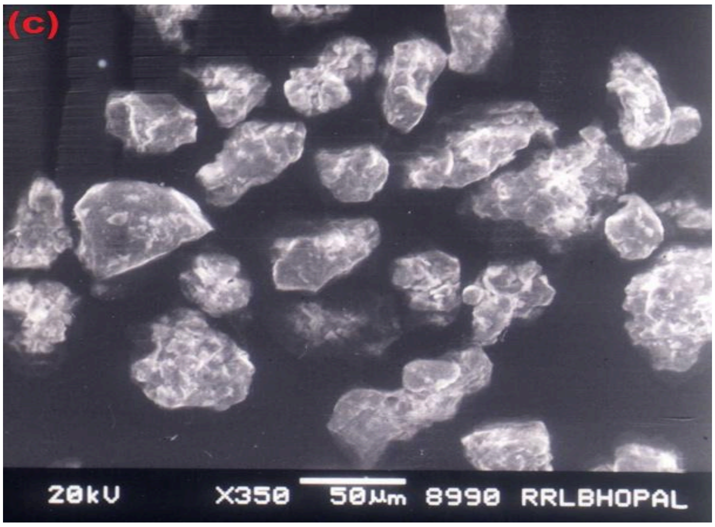


Fig. 4 (a).SEM microstructure of MPRs of different size, shape, and structure; 4(b). SEM microstructure of Jarosite waste particles; 4(c). SEM microstructure of clay soil showing different size, shape, and structure

It can be seen from the SEM microstructure that there is a huge variation in the particle size of Jarosite wastes. The particle surface irregularities indicate that these particles can exhibit good binding characteristics with other extraneous materials. **Fig. 4 (c)** of section 3.5 shows SEM microstructure of clay soil and SEM study reveals that clay particles are solid and irregular in shape having sharp edges. Particle size varied from 2-65 micrometer and surface was not smooth. Most of the particles have non-uniform shapes; expected to have good packing and bonding within the matrix system.

3.4 USEPA TCLP Toxicity Leachate Characteristics of MPRs, Jarosite waste, and Clay

Table 3 of section 3.4 shows the toxicity leachate concentration of MPRs, Jarosite waste and clay along with the permissible limits and USEPA hazardous waste numbers. It is evident from the results that the concentration of almost all the toxic elements for example Pb, Cd, Ni, Ag, As, Cr, Se, and Zn in MPRs was lower than that of Jarosite waste/clay and were below the TCLP toxic limits recommended by USEPA and falls under non-hazardous waste category.

Table 3. Toxicity characteristics leachate concentration in MPRs, Jarosite waste, and clay extracted as per the US EPA TCLP norms

Jarosite / additives	Leachate concentration of toxic elements							
	Pb	Ni	Cd	Zn	Ag	As	Cr	Se
MPRs R1	0.15	1.34	0.010	< 4	3.09	2.66	21.20	2.07
MPRs R2	0.15	1.30	0.010	< 4	3.09	2.44	22.12	1.06
MPRs R3	0.13	1.42	0.012	< 4	2.88	2.28	22.07	1.98
Mean	0.14	1.35	0.011	< 4	3.02	2.46	21.80	1.70
SD	0.01	0.06	0.001	< 4	0.12	0.19	0.52	0.56
JW R1	36.8	3.71	27.000	356.0	77.82	3.70	63.60	2.95
JW R2	35.2	3.46	26.500	360.0	78.54	2.85	64.57	1.78
JW R3	35.62	3.15	28.500	358.0	79.2	3.34	63.88	2.86
Mean	35.87	3.44	27.333	358.0	78.52	3.30	64.02	2.53
SD	0.83	0.28	1.041	2.0	0.69	0.43	0.499	0.65
Clay R1	0.16	3.95	0.030	< 4	2.69	1.63	11.30	1.22
Clay R2	0.26	3.10	0.032	< 4	2.83	1.37	13.21	0.99
Clay R3	0.22	2.94	0.028	< 4	2.94	1.46	12.88	1.02
Mean	0.21	3.33	0.030	< 4	2.82	1.49	12.46	1.08
SD	0.05	0.54	0.002	< 4	0.13	0.13	1.02	0.13
US EPA Limit ppm	5.0	70.0	1.0		5.0	5.0	5.0	1.0
US EPA HW Number	D008	D012	D006		D011	D004	D007	D010

Values for the concentration of Pb, Ni, Cd, and Zn are expressed in ppm and the rest (Ag, As, Cr, Se) are in ppb.

US EPA HW Number – United State Environmental Protection Agency Hazardous waste Identification Number.

MPRs used in this study confirmed that they were nontoxic and were in compliance with the permissible limit. Most of the elements including nickel, chromium, silver, arsenic and selenium concentrations in Jarosite waste were also below the USEPA toxic limits (**Table S4**). The concentration of lead (34.85±0.83 ppm) and cadmium (27.333±1.041ppm) was extremely higher than that of the US EPA TCLP limits. These results confirmed that the Jarosite waste falls under the hazardous waste category.

3.5 Effect of MPRs on the Mechanical Properties of CCB

The s/s composite brick specimens were developed before and after sintering, following the mix design using different proportionate of MPRs. The impact of different matrix composition on the performance of ceramic composite bricks (CCB) in terms of compressive strength, shrinkage, water absorption, and density is reported in **Table 4** of section 3.5.

Table 4. Impact of different matrix composition on the performance of CCB

Experiment Trial 5	Jarosite waste: Clay Ratio	Jarosite waste (g)	Clay (g)	MPRs (g)	Comp strength (kg/cm^2)	Water absorption (%)	Shrinkage (%)	Density (g/cc)
1	1:1	500	500	00	65.40	15.90	12.26	1.74
2	1:1	425	425	150	52.80	16.65	4.20	1.62
3	1:1	350	350	300	49.60	17.93	3.45	1.57
4	1:1	275	275	450	46.12	22.65	2.73	1.44
5	2:1	666.66	333.33	00	84.90	17.26	21.70	1.79
6	2:1	566.666	283.333	150	35.24	20.44	7.05	1.58
7	2:1	466.67	233.33	300	31.70	21.86	4.83	1.49
8	2:1	366.66	183.33	450	29.86	24.50	2.12	1.43
9	3:1	750	250	00	140.80	14.51	31.36	1.91
10	3:1	637.5	212.5	150	35.70	19.94	10.55	1.55
11	3:1	525	175	300	32.70	21.20	5.64	1.49
12	3:1	412.5	137.5	450	29.86	23.84	1.81	1.43
13	4:1	800	200	00	125.80	14.50	38.08	1.93
14	4:1	680	170	150	29.98	20.95	13.19	1.53

15	4:1	560	140	300	29.20	23.30	6.79	1.49
16	4:1	440	110	450	23.15	24.57	1.51	1.41

3.5.1 Compressive Strength

The effect of different concentrations of MPRs with Jarosite waste in the clay matrix system on the compressive strength of ceramic composite bricks (CCB) and water absorption behavior is shown in **Fig. 5 (a-b)** and **TableS5** of section 3.5.1 . Results revealed that CCB made out of 15% MPRs with equal ratios of Jarosite waste and clay resulted in compressive strength of 52.8 kg/cm^2, which is higher than that of the BIS specification (< 35 kg/cm^2) meeting the quality standard for use in construction application. With increase in quantity of MPRs with maintaining equal ratios of Jarosite waste and clay, there was decrease in the compressive strength of CCB and minimum compressive strength was 46.12 kg/cm^2 with 45% MPRs incorporation.

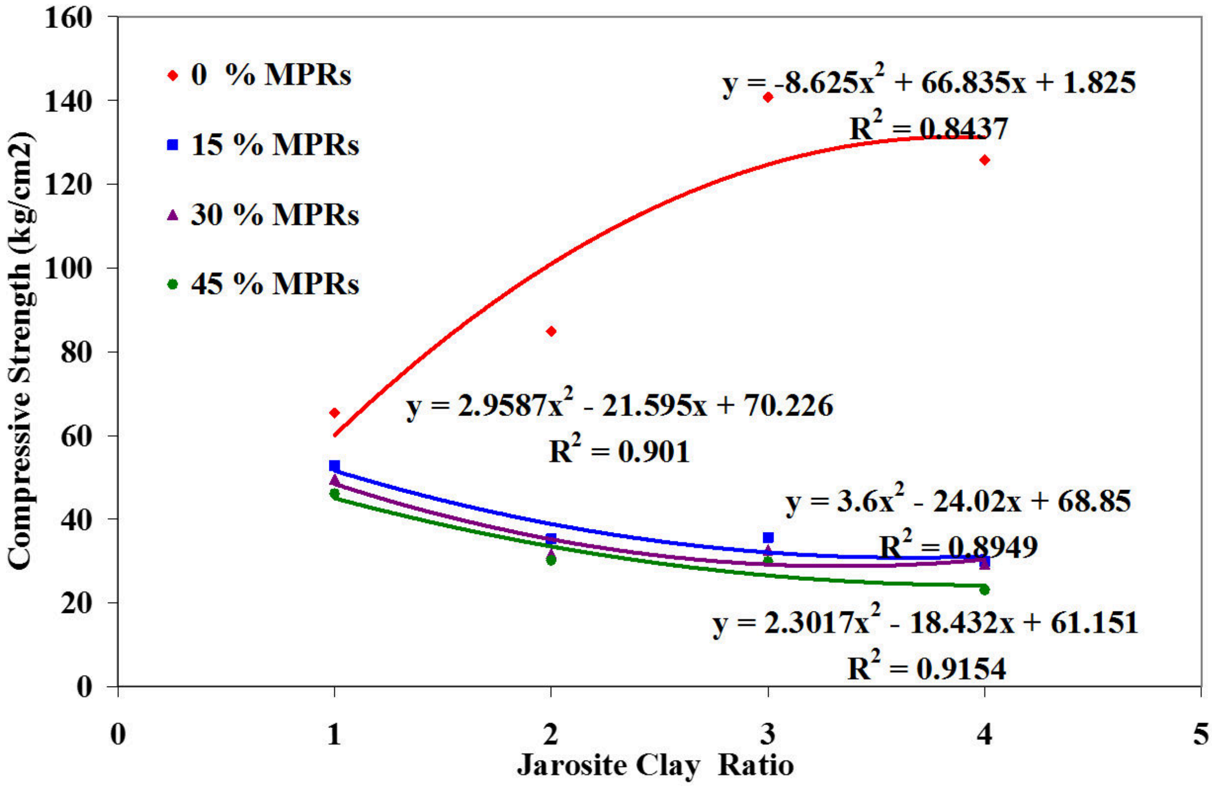


Fig. 5 (a). Effect of MPRs on compressive strength of CCB

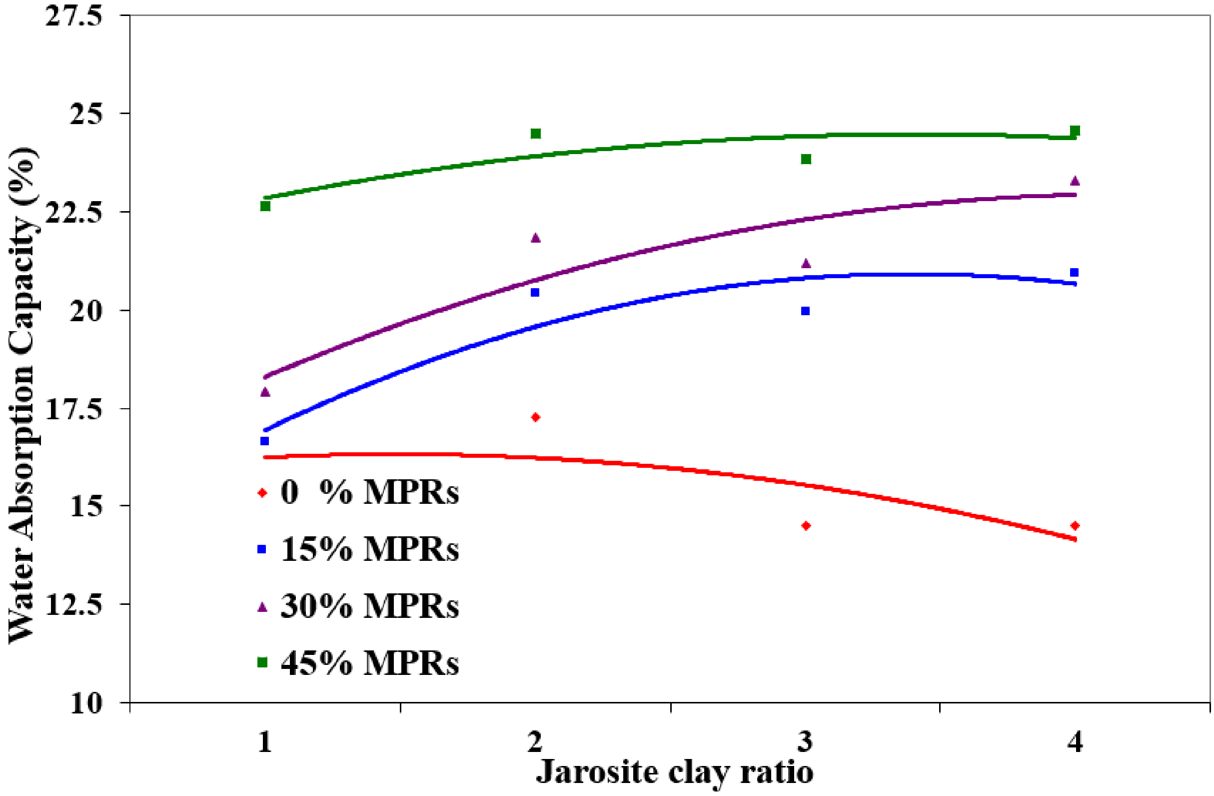


Fig. 5 (b). Effect of MPRs on water absorption of CCB

Without MPRs, the ceramic composite bricks made of Jarosite waste and clay alone resulted in higher compressive strength, very high shrinkage which might probably be due to the formation of a considerable amount of liquid phase within the fine particles. It might have possibly reduced the porosity under the capillary tension forces in the fine pores. Nevertheless, maintaining the MPRs integration (15-45%) and increasing Jarosite waste by reducing clay content decreased the compressive strength of CCB. Wherein minimum compressive strength (23.15 kg/cm^2) was recorded using a 4:1 ratio of Jarosite clay with 45% MPRs and maximum compressive strength (140.8 kg/cm^2) was recorded using 3:1 ratio of Jarosite clay without MPRs (**Table 4**). The trend on the distinction of compressive strength of CCB and the impact of application of MPRs with Jarosite waste and clay ratio can be seen from the **Fig. 5 (a)** of section 3.5 . Linear regression equitation was fitted for the response compressive strength data of CCB and this confirms statistically that the compressive strength of CCB decreases with increasing Jarosite clay ratio as well as increasing the MPRs concentration. The r^2 values were 0.915 for 45% MPRs incorporation with varying Jarosite clay ratios. The r^2 values specify a good fit of data with the equations that describe the relationship between the compressive strength of CCB and influence of different raw materials. Thermal decomposition of carbonates during the process also contributes to the development of a micro-porosity which affects the quality of bricks. During firing, the decomposition of $CaCO_3$as well as its transformation into CaO might have resulted in a notable increase in microspores space contributing to the reduced compressive strength of CCB with increase in concentration of MPRs.

3.5.2 Water Absorption and Shrinkage

The water absorption capacity of CCB and the relationship between the impact of the addition of different concentration and ratio of matrixes are shown in **Fig. 5 (a)** and **Table 4** of section 3.5.1. Results revealed that with MPRs application, the achieved minimum water absorption capacity was 16.65 % when Jarosite waste clay ratio was maintained one with 15% MPRs (**Table 4**. It is evident from the results that increase in MPRs in CCB, increased the water absorption capacity and maximum water absorption (24.57%) was recorded with 45% MPRs addition (**Fig.5 a**). It is important to note that, with increase in ratio of Jarosite to clay, water absorption capacity decreased, and the shrinkage was increased. **Fig. 5 (c)**) of section 3.5.2 shows the effect of different concentrations of MPRs on shrinkage of CCB in Jarosite waste and clay system. Maximum shrinkage was recorded (38%) in the CCB made out of 4:1 ratio of Jarosite waste and clay without MPRs (**Table 4**). When MPRs were applied, the shrinkage was found to be reduced and minimum shrinkage (1.51%) was attained with maximum (45%) MPRs application in 1:1 ratio of Jarosite waste and clay matrix (**Fig. 5 c**).

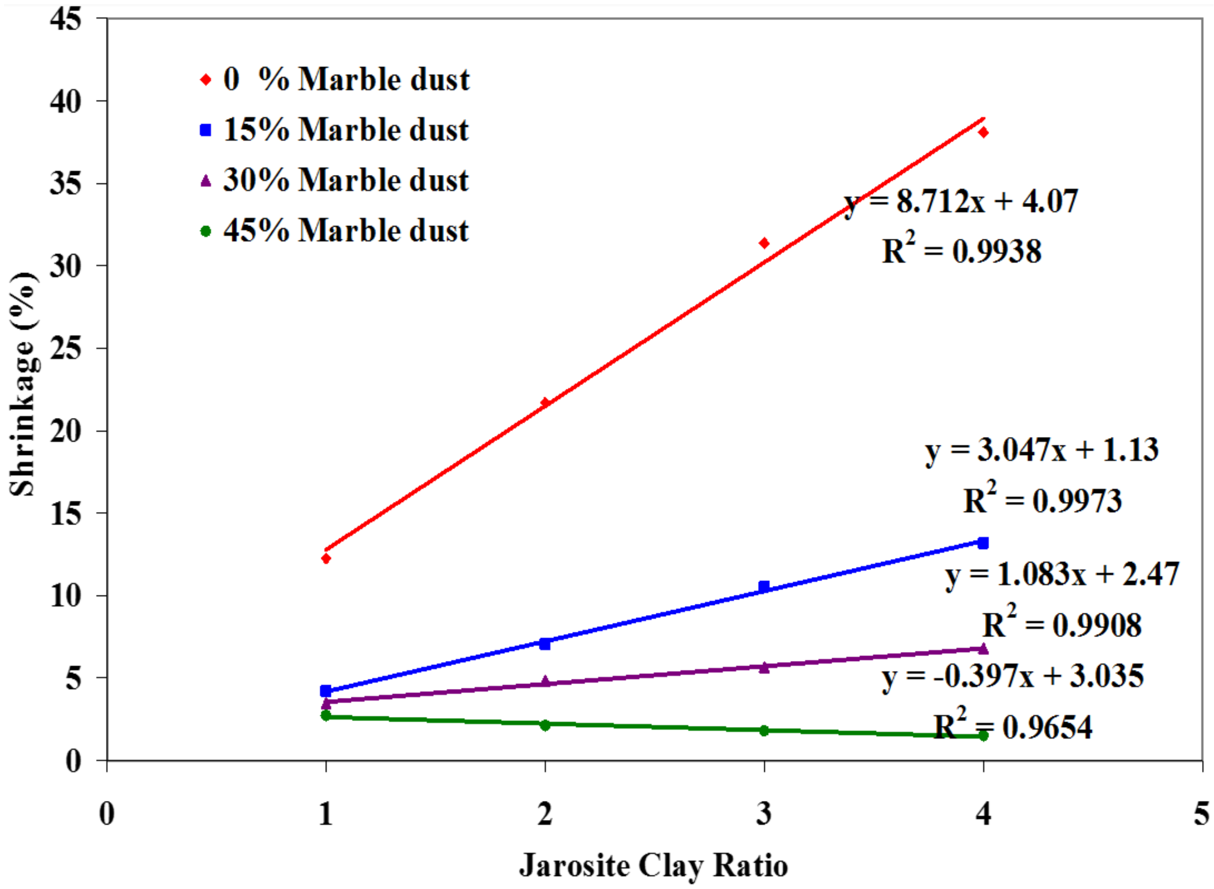


Fig. 5 (c). Effect of MPRs on shrinkage of CCB

The correlation coefficient (r^2) values from the regression equations fitted for the response water absorption (**Fig. 5a**) and shrinkage (**Fig. 5 b**) indicate a very good fit of data, which satisfactorily describe the relationship between MPRs, Jarosite waste and clay matrix system and shrinkage of CCB. As compared to all combinations, MPRs application (15%) not reduced the shrinkage of CCB and improved finished quality. Carbonates strongly influence the porosity resulting in improvement in texture and physical-mechanical properties of CCB. The morphology of MPRs might have also greatly influenced the porosity in CCB. The carbonates in MPRs and clay facilitates the formation of crevice and pores when the bricks were fired at about 960ºC. This analysis has been supported by the earlier studies that the nonappearance of carbonates contributes to the constant reduction in porosity (Cultrone et al., 2004). The major chemical constituent in MPRs is $CaCO_3$ and decomposition of such carbonates influences micro-porosity during sintering under crystallization process. The transformation of $CaCO_3$ into CaO greatly affected CCB towards increase in water absorption capacity and reduced shrinkage.

3.5.3 Density

The impact of different matrix composition on the density of CCB is shown in **Table 4** and **Fig. 5d of**) of section 3.5.3 .

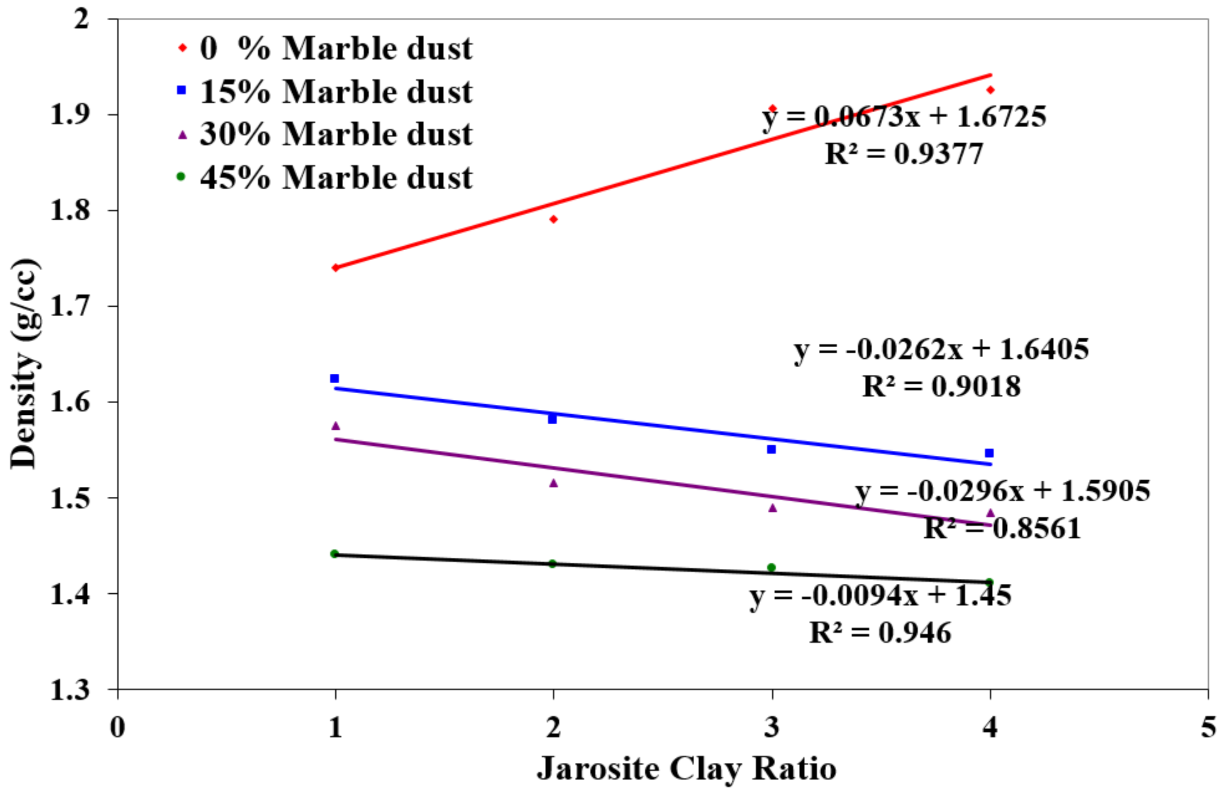


Fig. 5 (d) Effect of MPRs on the density of CCB

It is obvious from the results that MPRs application (0-45%) reduced the density of CCB and minimum density (1.41gm/cc) was with maximum MPRs (45%) application in the Jarosite waste and clay matrix system. With varying ratios of Jarosite waste and clay matrix (1:1 – 4:1) in the CCB, maximum density (1.93 gm/cc) was recorded with a maximum concentration of Jarosite waste in clay system (Jarosite waste clay ratio 4:1) without MPRs. The outcome of present experimental program and the results obtained from the design expert model corroborating density, shrinkage water absorption capacity, and compressive strength of CCB developed using MPRs, Jarosite waste and clay matrix system were summarized and analyzed

(**Table 4** and **Figs.5 a-d**). Results revealed that with increase in concentration of MPRs, compressive strength of CCB decreased and water absorption capacity increased. The shrinkage and density substantially decreased. The CCB developed using 15% - 45% of MPRs with different ratio of Jarosite and clay (1:1- 4:1) matrix system resulted in 23.13-52.8 kg/cm^2 compressive strength. The variation in the quality of CCB has been attributed to the substantial differences in the composition/concentration of mineral phases in different waste matrixes. The findings of the present study confirm that high proportion of calcite in MPRs attributes to the creation of more pore size in CCB due to its high-temperature decomposition and the release of CO_2 resulting in reduced density, shrinkage, compressive strength and increased in water absorption capacity, which is also supported by earlier performed work (Cultrone et al., 2004).

3.6 Effect of MPRs on Mineralogical Properties of CCB

To study the effect of sintering on the s/s composite made out of MPRs, Jarosite waste and clay matrix, XRD analysis was done for selective samples in which the most desired results (mechanical strength and toxicity leachate limits) were achieved. **Fig. 6(a)**) of section 3.6 shows XRD analysis results of s/s green (unfired green bricks) developed using MPRs (15%) with Jarosite waste clay matrix ratio of 1. It was observed from the results that major mineral phases in the s/s products are Dolomite {Ca Mg $(CO_3)_2$}; Lead Carbonate Hydroxide {$2PbCO_3Pb\ (OH)_2$} and Ammonium Calcium Sulphate Hydrate {$NH_4)2[(CaSO_4)_5\ (OH)_6$}.Riccardi *et al.,* (1999) reported that in "Ca-rich sample the intensity of the calcite reflections decreases as the firing temperature increases (Riccardi et al., 1999). At temperatures of 850ºC the gehlenite is present together with hematite, whereas the wollastonite is recorded" only in highest temperature fired products. In the present study, as shown in **Fig. 6(b)** of section 3.6 , there were changes in the mineral phase of s/s composites after firing at 960º C and formation of new phases could be recorded. The identified mineral phases after high temperature firing in the CCB were Dolomite {Ca Mg $(CO_3)_2$}; Alumina {Al_2O_3}; Hematite {Fe_2O_3} and Quartz {SiO_2}. The feldspar was found to show a single reflection in the samples with Ca deficient specimen having a larger peak than in Ca-rich sample due to the compositional changes, while temperature increases.

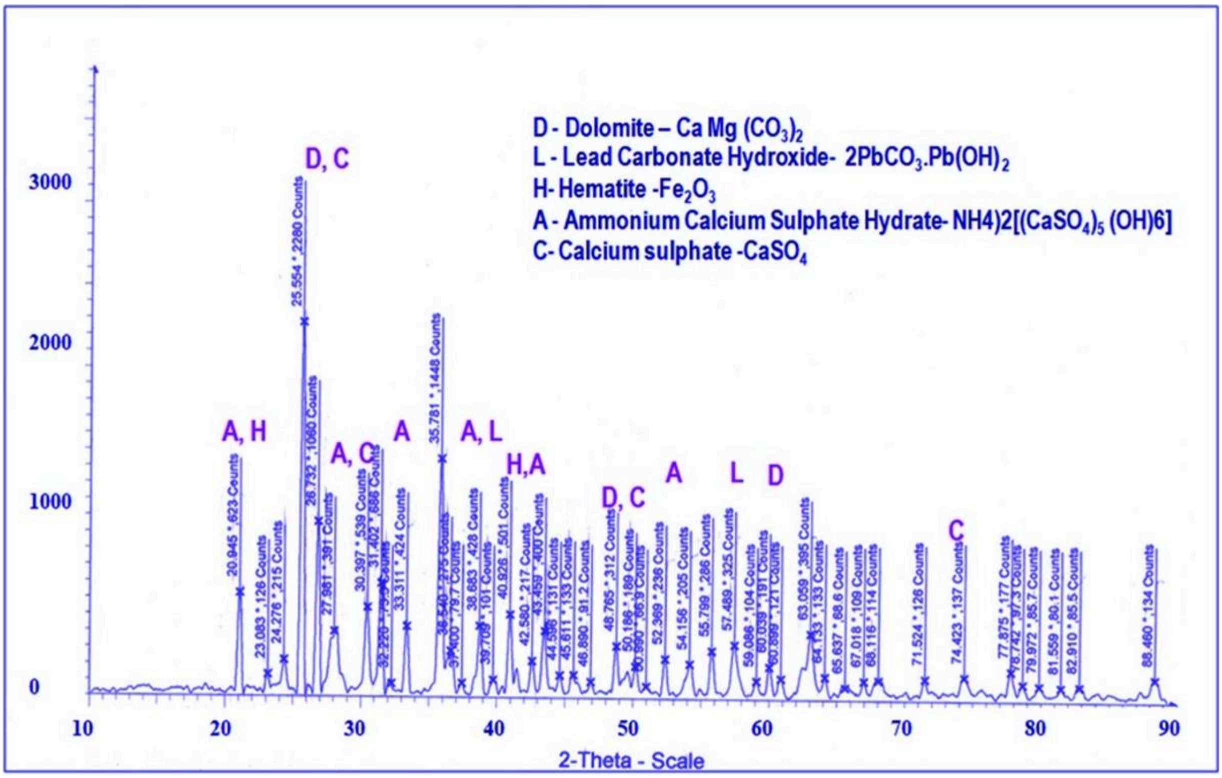


Fig. 6 (a). XRD analysis of solidified unfired green composite products developed using Jarosite waste clay ratio 1:1 with 15% marble waste

CaO is expected to migrate over wider domains resulting in an amplification of the stability field of gehlenite. The reaction kinetics, as well as the occurrence of new phases, is controlled by dehydration and decarbonation reactions. It could be concluded from the study that in CCB, sintering behavior is significantly dependent on the parameters such as quantity, composition, and grain size distribution. This leads to the foundation of transitory liquid phases that facilitates the densification of the main crystalline phases, anorthite, hematite, magnetite, dolomite, calcite and or zinc ferrite. The quality of s/s green products fabricated using MPRs, Jarosite waste and clay matrix have undergone substantial changes owing to the firing in the presence of several phase constituents in the matrices. It has resulted in the loss of K^{+} and OH^{-} groups. A similar phenomenon has been observed in the case of CCB as MPRs are rich in calcium oxide when it was mixed with Jarosite waste and clay matrices/ minerals. S/S products, in the presence of humidity, CaO rapidly reacted and were transformed into portlandite (Ca $(OH)_2$).

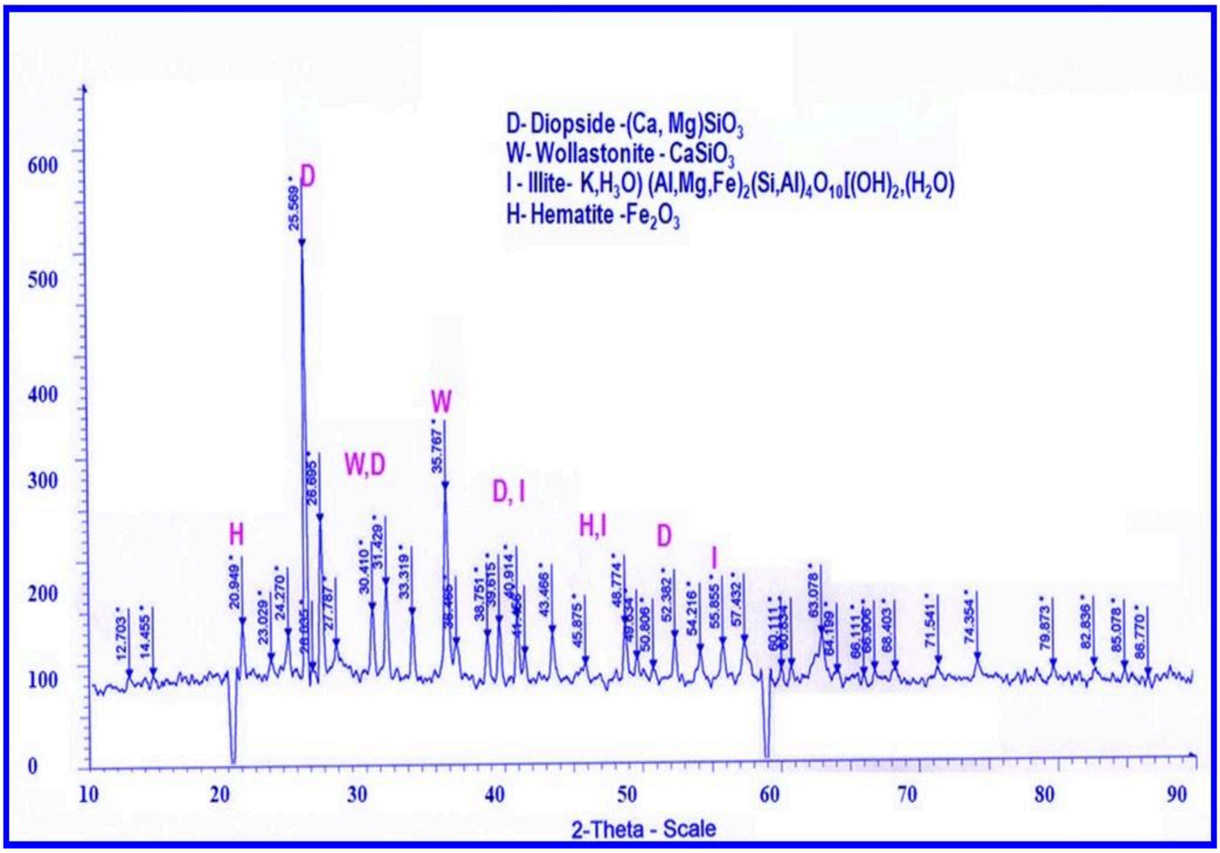


Fig. 6(b). XRD analysis of solidified sintered composite products developed using Jarosite clay ratio 1:1 with 15% marble waste

This reaction was exothermal and caused a substantial increase in volume. There was no shrinkage in CCB developed using MPRs with Jarosite waste and clay matrix. As supported by Cultrone et al., (2004), the reaction kinetics is as follows (Cultrone et al., 2004):

$$\underset{CaCO_3}{\text{Calcite}} \xrightarrow[\Delta T]{\uparrow CO_2} \underset{CaO + H_2O}{\text{lime}} \longrightarrow \underset{Ca(OH)_2}{\text{portlandite.}} \quad (6)$$

The decomposition of dolomite occurs as per the following equation:

Dolomite lime periclase (7)

$$CaMg(CO_3)_2 \xrightarrow[\Delta T]{} CaO + MgO + 2CO_2 \quad (8)$$

Prominent crystallization pressure was found to be exerted by the newly formed portlandite in the confined spaces of the CCB rich in CaO, which usually occurs in ceramics employing raw materials rich in carbonates.

3.7 Effect of MPRs on Microstructure Properties of CCB

Fig. 7(a-f) of section 3.7 displays the SEM microstructure of CCB's internal surface developed using MPRs (15% and 30%) with Jarosite waste and clay matrix ratio of 1, 2 and 3. CCB was prepared using different ratios of Jarosite waste and clay with 15% and 30% MPRs. In Fig. 7, the details are: (a) 1:1 ratio of Jarosite waste and clay with 15% MPRs; (b) 1:1 ratio of Jarosite waste and clay with 30% MPRs; (c) 2:1 ratio of Jarosite waste and clay with 15% MPRs ; (d) 2:1 ratio of Jarosite waste and clay with 30% MPRs ; (e) 3:1 ratio of Jarosite waste and clay with 15% MPRs ; (f) 3:1 ratio of Jarosite and clay with 30% MPRs. MPRs mainly consist of CaO and firing CaO at high-temperature results in better blending of Jarosite waste clay matrix. In the CCB developed using 15% MPRs with 1:1 ratio of Jarosite waste clay matrix, the texture of the surface was found to be compacted, well densified, solid, monolithic and waste matrices were found well bonded with each other. When MPRs were used at 15% along with Jarosite waste clay matrix, the internal section of the bricks showed good binding, plain surface and slightest pore space could also be seen. As a result, water absorption capacity of bricks was found to be least as compared to the products developed with 30 % and 45 % MPRs application. **Fig. 8 (a-c)** of section 3.7 displays the morphological (SEM) structure of the internal surface of s/s sintered products fabricated using Jarosite waste clay ratio of 1 and 2 in which no additives were applied.

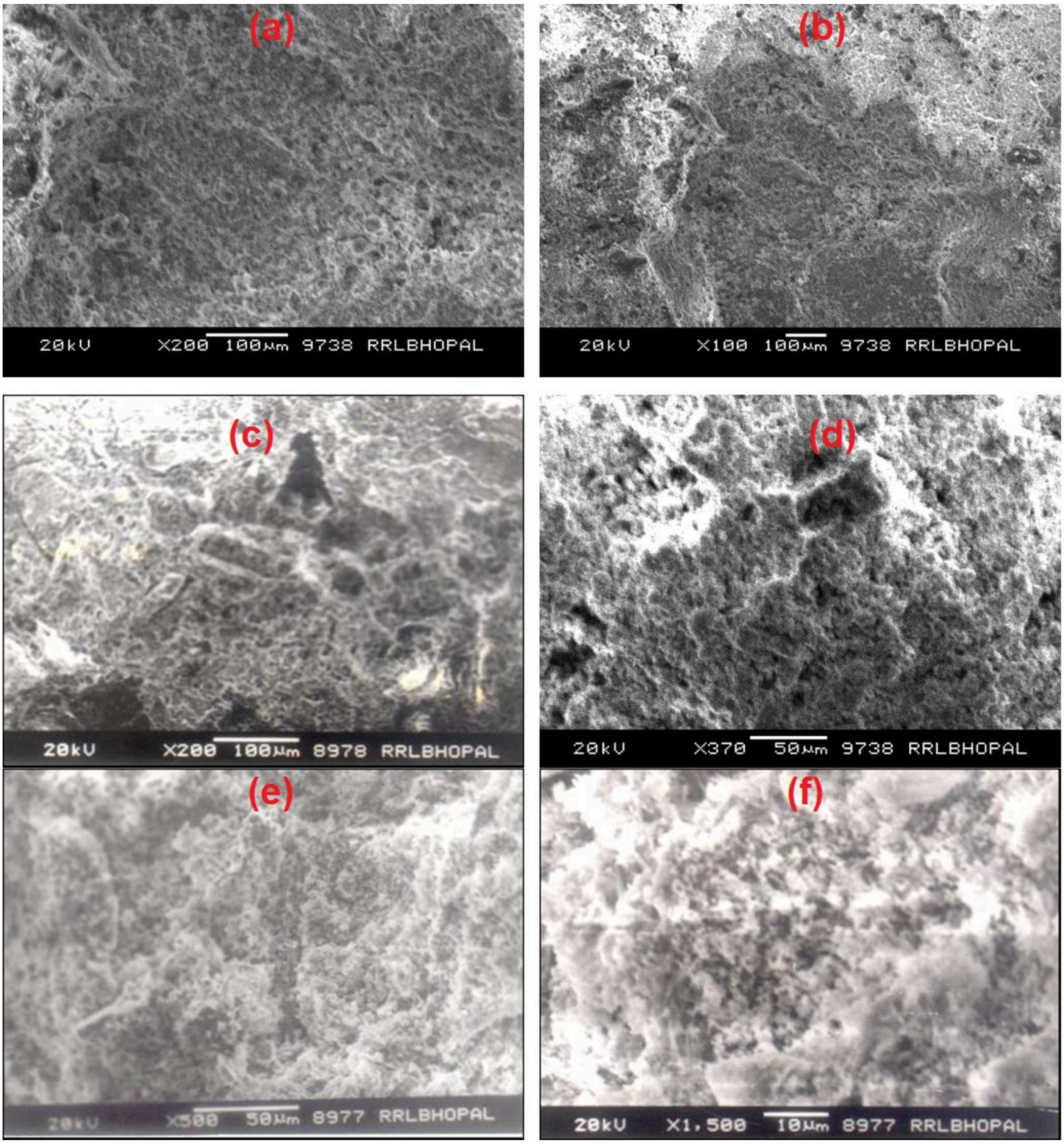


Fig. 7 SEM microstructure of fracture surface of CCB

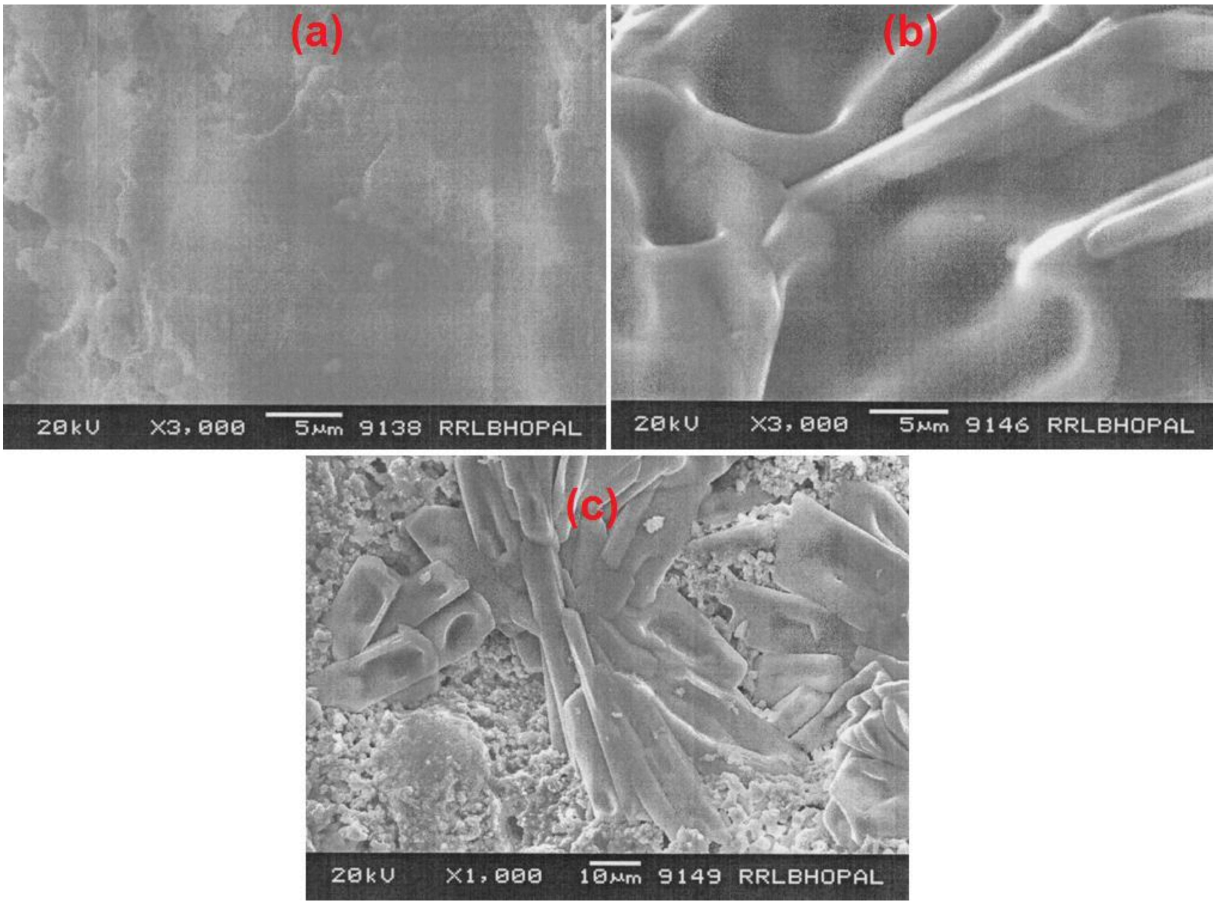


Fig. 8 SEM microstructure of fracture surface of s/s sintered products developed from different ratios of Jarosite waste and clay without additives (a) 1:1 ratio of Jarosite waste and clay (b) 2:1 ratio of Jarosite waste and clay (c) 3:1 ratio of Jarosite waste and clay.

Due to the fine texture of Jarosite waste, there is significant densification of the product and no pore space could be seen. The shrinkage was optimum and the products did not meet the requisite properties (toxicity leachate concentration) as recommended by the USEPA standard for use in engineering application.

3.8 Effect of MPRs on Toxicity Leachate Concentration in CCB

To investigate the potential of MPRs as additives in immobilizing hazardous Jarosite, the TCLP approach was followed as a tool in confirming the environmental significance of toxic substances in the wastes matrixes. **Table 5** of section 3.8 shows the comprehensive results on the effect of MPRs, Jarosite waste and clay matrix on leachate concentration of the most critical elements such as Ag, Cd, Pb and Se in CCB.

Table 5. Effect of MPRs, Jarosite waste and clay matrix on toxicity leachate concentration in CCB

Sample ID	Quantity (g) of s/s sintered matrices			TCLP leachate concentration (ppm)			
	Jarosite waste	clay	MPRs	Ag	Cd	Pb	Se
1M	500	500	0	2.51	0.316	10.45	0.246
2M	**425**	**425**	**150**	**0.061**	**0.291**	**3.84**	**0.224**
3M	**350**	**350**	**300**	**0.04**	**0.256**	**2.81**	**0.207**
4M	275	275	450	0.028	0.23	1.76	0.188
5M	666.66	333.33	0	2.6	0.378	11.8	0.27
6M	566.666	283.333	150	0.15	0.347	4.08	0.246
7M	466.67	233.33	300	0.096	0.316	3.11	0.233
8M	366.66	183.33	450	0.061	0.277	2.11	0.213
9M	750	250	0	2.71	0.71	13.465	0.293
10M	637.5	212.5	150	0.276	0.518	4.38	0.267
11M	525	175	300	0.211	0.47	3.46	0.254
12M	412.5	137.5	450	0.15	0.421	2.52	0.236
13M	800	200	0	2.82	0.741	15.3	0.317
14M	680	170	150	0.401	0.592	4.71	0.287
15M	560	140	300	0.316	0.539	3.91	0.273
16M	440	110	450	0.241	0.495	2.96	0.254
Raw Jarosite waste (ppm)				78.51	27.33	35.87	2.53

Results from the study revealed that there was a significant decrease in the leachate concentration of lead in CCB with MPRs application. It is obvious from the results that in the

Jarosite waste clay matrix composite sintered brick system, the maximum concentration of Ag leachability was 2.82 ppm where no MPRs were applied. The leachability of Ag in this CCB, sample (**Table 5)**, was lower than that of USEPA recommended limit (5 ppm) and the concentration of Lead was recorded as 15.3 ppm, which is quite higher than that of USEPA standard limits (i.e. 5ppm). In all cases, the leachate concentration of all critical toxic elements in CCB was remarkably reduced as compared to the initial concentration of lead in Jarosite waste (78.51 ppm). It is recorded from the results (**TableS6**) that with the increment in the concentration of Jarosite waste, there is considerable increase in the lead content in CCB. The CCB developed with Jarosite waste clay matrix ratio 1, 2, 3 and 4 resulted in leachate of lead 10.45 ppm, 11.8 ppm, 13.465 ppm, and 35.87 ppm, which was higher than the USEPA standard confirming it as hazardous nature. The leachate concentration of all these elements was low in the CCB developed with incorporation of MPRs, which has confirmed the non-hazardous nature of CCB. Results revealed that through the sintering process under solid-state reaction, Jarosite mineral's toxic elements were detoxified and immobilized through complexing in the calcium silicate matrix. The leachate concentration of other toxic elements such as Ag, As, Cd, Co, Cu, Cr, Ni in the CCB with incorporation of MPRs (15-30%) under optimized conditions were recorded as below the USEPA prescribed standard confirming non-hazardous materials (**Table 6**).

Table 6. Mixture design parameters with responses of CCB

	Component	Component	Component	Response	Response	Response	Response
Run order	A:Jarosite waste (g)	B:Clay (g)	C:MPRs (g)	Comp. Strength (kg/cm^2)	Water Abs. (%)	Shrinkage (%)	Density (g/cc)
10	395.00	278.75	326.25	36.4986	21.6019	1.20686	1.55419
5	275.00	500.00	225.00	56.298	17.4042	4.93337	1.69279
13	275.00	275.00	450.00	62.6037	20.3158	4.51261	1.54597
3	800.00	110.00	90.00	95.1573	16.3918	31.8146	1.9482
9	657.50	218.75	123.75	59.738	19.3763	15.6145	1.76205
4	500.00	500.00	0.00	64.2422	19.488	13.1416	1.73207
2	275.00	275.00	450.00	61.2037	22.0158	4.61261	1.49597
11	800.00	110.00	90.00	95.1573	16.3918	31.8146	1.9482
14	500.00	500.00	0.00	62.1322	17.218	12.1416	1.69921
1	440.00	110.00	450.00	18.3033	24.6452	2.10036	1.48196
6	515.00	282.50	202.50	37.7824	20.9435	4.88401	1.63995
12	275.00	500.00	225.00	58.258	15.6142	4.73337	1.64279
8	650.00	350.00	0.00	84.7985	17.4845	20.6217	1.77608
7	620.00	110.00	270.00	24.8051	20.9703	9.04665	1.67207

As reported and discussed in the previous section, the quality of CCB developed using 15-30 % MPRs with a 1:1 Jarosite waste clay ratio met the mechanical strength for use in engineering applications as burned clay building brick as recommended by Indian Standard (IS 1077:1992) specification. The toxicity leachability results confirmed that MPRs was a potential resource in immobilizing / detoxifying hazardous Jarosite waste as well as contributed towards attaining quality products for use in building construction applications.

An earlier study on MPRs applications for hydrothermal solidification of clay –quartz mixture showed that calcined marble dust could be employed as a substitute source of active CaO and hydrated phase contributed to the improvement in the strength of s/s samples suitable as new building material(Sarkar et al., 2006). Since the hydrothermal s/s process involves considerable energy for calcinations to obtain lime from $CaCO_3$, the present study showed that MPRs could be used for manufacturing sintered bricks. It greatly influenced and acted as catalyst for immobilizing hazardous Jarosite waste (Montanaro et al., 2001).

In summary, although the incorporation of MPRs decreased the compressive strength and contributed to reducing shrinkage and density significantly. Whereas the CCB developed using 15% MPRs with 1:1 Jarosite waste clay matrix ratio showed a mean compressive strength of 54.61 kg/cm^2, which is acceptable quality for use in construction purpose. This combination could be an intermediate and optimum condition in which the product met all desirable mechanical properties for use in building construction applications. The element leachate concentration was within the USEPA recommended safe limits. **Table 5** shows the summary of the optimized conditions in achieving optimal quality of MPRs, Jarosite waste, and clay matrix composite products (CCB) for safe utility in construction application.

3.9 Model Validation in Optimizing CCB Quality and Waste Matrixes Concentration

In the present paper, among several responses evaluated and analyzed, the model was fit to data for the response compressive strength using analysis of variance (ANOVA) and least-squares techniques. The validated and graphically interpreted contour plot, trace plots and 3D graph can be used to predict the effect of response variables (quality) of composite bricks with varying concentration of MPRs and Jarosite waste in clay matrix system.

3.9.1 Model Validation in Optimizing CCB

The experimental conditions for mixture model and responses compressive strength, water absorption, shrinkage, and density are shown in **Table 6** of section 3.9.1. The polynomial models described in classic mixture approach were fitted to data employing least squares techniques and analysis of variance (ANOVA). From the ANOVA results, the significance of the treatment effect was obtained. The results of ANOVA for compressive strength are displayed in **Table S4**. From this table, the row with source “Quadratic” indicates that the coefficients of the quadratic model terms are not equal to zero as indicated by a low value (< 0.05) of “Prob > F” also called as p-value. The associated p-values (Prob > F) are interpreted when the true coefficient equals zero. The row with source “Special Cubic” the special cubic coefficients contrast from zero. Since the “Prob >F” of 0.0481 is less than 0.05, the special cubic terms were also included in the model. Similarly, the cubic coefficients are required in the model. The residual coefficients are not required as “Prob > F” of 0.945 exceeds the value 0.05.The lack of fit value indicates the lack of fit with respect to pure error. The lack of fit value should be non-significant (Prob F > 0.05), to fit the data to the model. A lack of fit test was carried out using ANOVA. For compressive strength, the lack-of-fit test (**Table S5**) for the special cubic model gives “Prob > F” equal to 0.945, which is not significant indicating the experimental data fit the model. **Table S6** shows the model summary statistics for the response compressive strength. It shows that the special cubic model provides a "Predicted r^2" values of 0.9970 which is in excellent agreement with the "Adjusted r^2" of 0.9985.

3.9.2 Process Optimization

Response trace plots and contour plots are used to interpret graphically the validated model results. **Fig. 9** of section 3.9.2 shows the response trace plots for compressive strength. The response trace plot comprises of 3 overlaid plots, one for each constituent of the CCB namely

Jarosite waste, clay, and MPRs. The plot demonstrates the “effect” of variation of each component on compressive strength. Results revealed that with the increment in the amount of Jarosite waste, there is an increase in the compressive strength. The effect was higher with the higher amount yielding higher strength. MPRs application reduced compressive strength and minimum was with maximum use (45%) of MPRs. **Fig. 10** of section 3.9.2 depicts the response contour plots for compressive strength of CCB. From these figures, it is apparent that as in case of trace plots, increase in concentration of Jarosite waste increased compressive strength. The addition of clay increased the compressive strength up to a certain level with slight decrease in compressive strength at higher concentrations. This confirms that high plasticity soil alone cannot be a very good candidate in making good quality bricks and MPRs as well as Jarosite waste considerably influenced the improvement in the performance of CCB. **Fig.11** of section 3.9.2 shows the 3D graph of compressive strength. It reveals that the response of each characteristic changes with change in constituents. Sintering influenced the texture along with structure leading to the substantial changes in the mechanical properties of the CCB. The sintering efficiency was found to be dependent on the presence and content of SiO_2, CaO, and PbO, along with the alkaline oxides in MPRs. Jarosite waste and clay matrix system which contributed to the Jarosite waste phase transformation resulted in densification and transformation into main crystalline phases, hematite and magnetite, and calcium silicate compound. Desirability functions were used to discover the optimum mixture proportions by Numerical optimization.

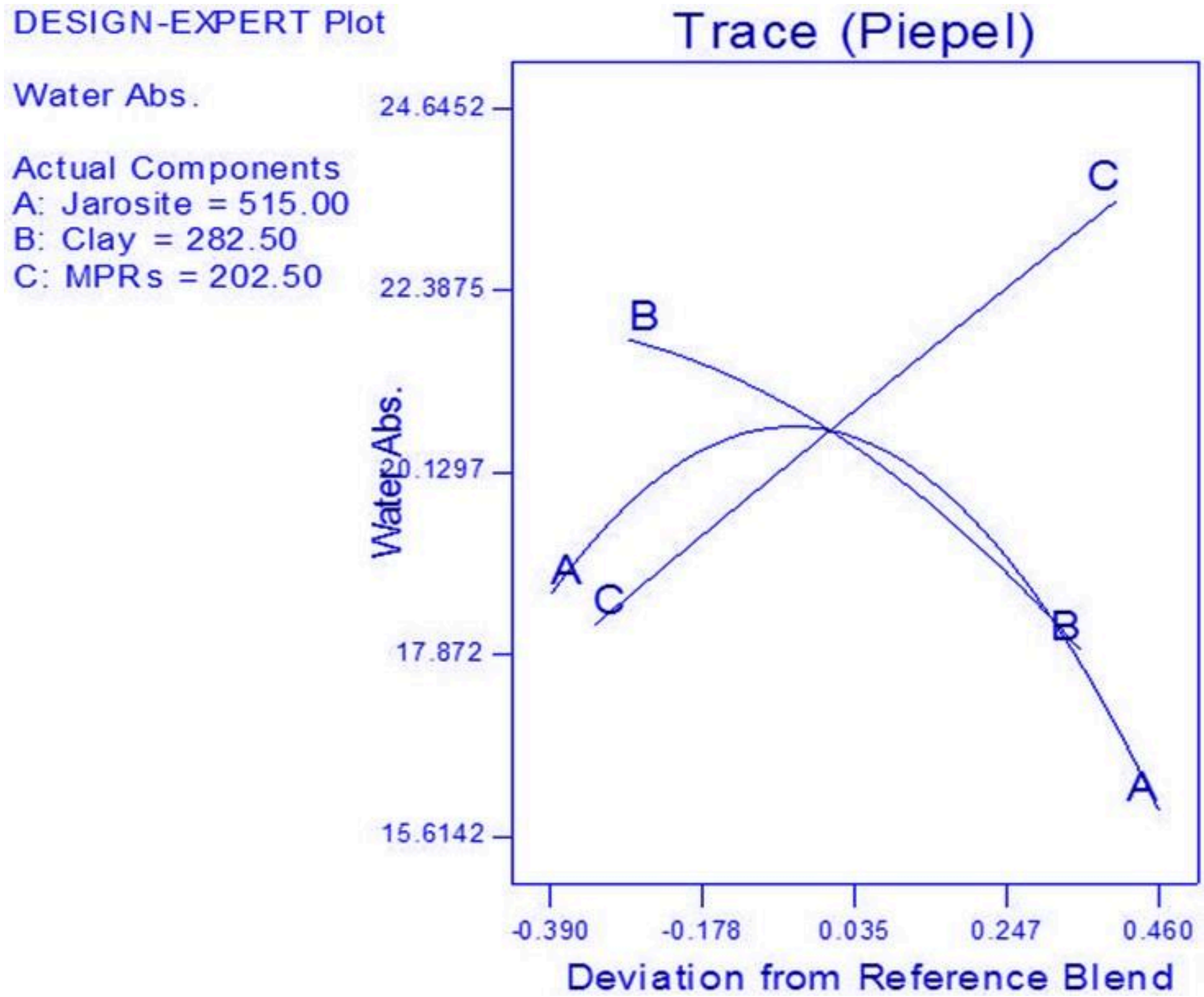


Fig. 9 Response trace plot for compressive strength of CCB

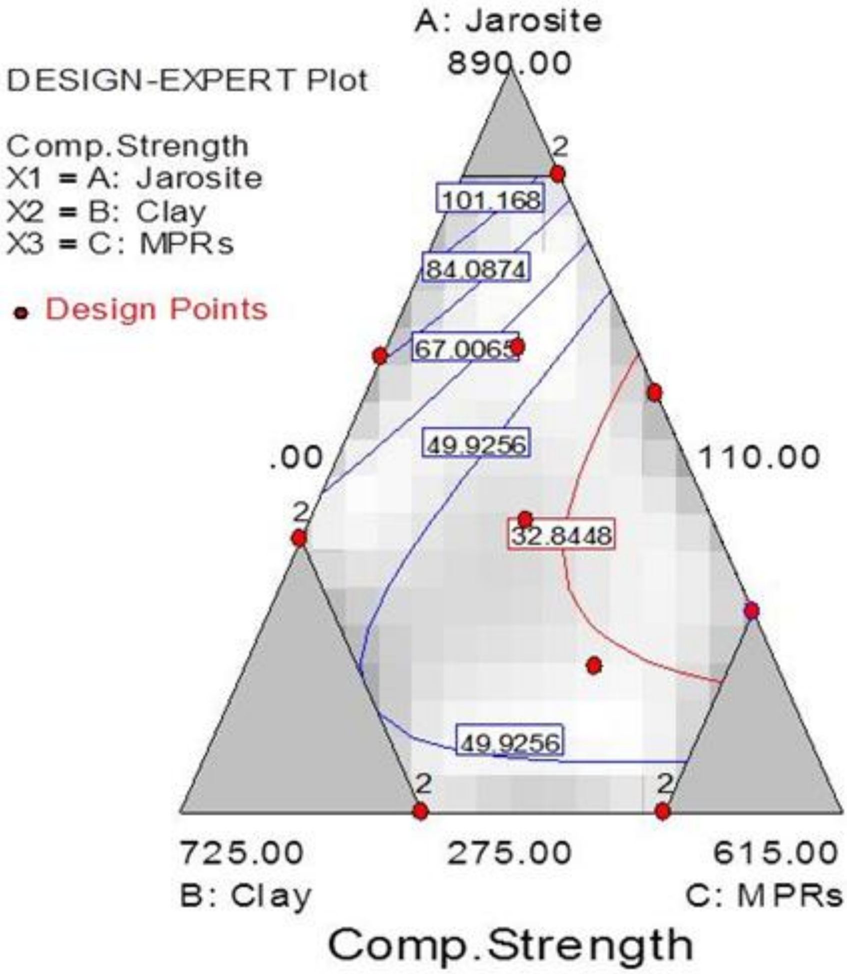


Fig. 10. Response trace plot for compressive strength of CCB

The desirability function values vary between 0 and 1. The desirability value for brick compressive strength is between 18.3 and 95.15 (kg/m^2) and 0 otherwise. **Table S7**shows the constraints and parameter range for desirability function. Based on the model prediction, the optimum mix design which maximizes the brick properties are shown in **Table 7** of section 3.9.2. The model predictions for brick properties at a given set of brick and the overall desirability value for these brick mixtures were 1, 0.52 and 0.788. The optimized mix design of the mixture approach model is 275g Jarosite waste; 321.21g Clay; 403.79g MPRs in which the response Compressivestrength resulted in 60.24 kg/cm^2; water absorption 20.13%; shrinkage 3.92 % and density 1.55 g/cm^3. These predicted results were compared with the actual experimental results and established that the response characteristics are in very good agreement with each other.

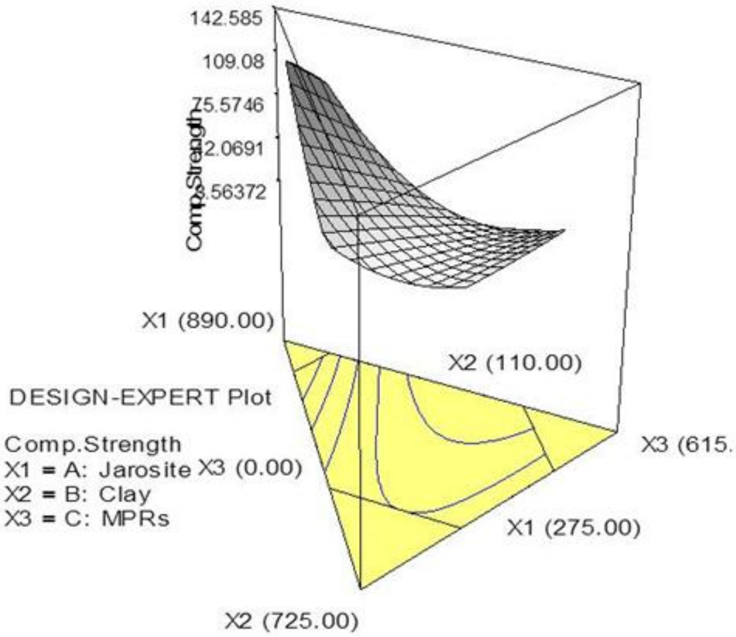


Fig. 11 Response 3D graph for compressive strength of CCB

Table 7. Optimum Mix design to maximize the brick properties

Number	**Jarosite waste (g)**	**Clay (g)**	**MPRs (g)**	**Comp. Strength** (kg/cm^2)	**Water Abs.** (%)	**Shrinkage** (%)	**Density (g/cc)**	**Desirability**	
1	275.00	321.21	403.79	60.2467	20.1301	3.92915	1.5514	0.788	Selected
2	668.44	150.15	181.41	47.2889	19.7845	14.642	1.75118	0.520	
4	276.53	273.47	450.00	61.3518	21.2195	4.4735	1.51731	1.000	

Table 8 of section 3.9.2. shows the leachate concentration of toxic elements in CCB under optimized conditions. Integration of MPRs (15% MPRs) with a 1:1 Jarosite waste clay matrix ratio showed intermediate conditions to achieve desirable quality of CCB in terms of mechanical strength and toxicity leachate point of view to use CCB as alternative materials to burned clay bricks.

Table 8. Leachate concentration of toxic elements in CCB under optimized conditions

Sr. No.	Elements	MPRs (15%) with 1:1 Jarosite waste clay ratio	USEPA Limit(ppm)
1.	Pb	3.84±0.027	5.0
2.	Cd	0.291±0.007	1.0
3.	Ni	4.14±0.16	70.0
4.	Ag	0.061±0.01	5.0
5.	Cr	< 0.0005	5.0
6.	As	0.384±0.036	5.0
7.	Se	0.224±0.046	1.0

All the values are in ppm

4. Opportunity for sustainable manufacturing of CCB

Bricks have been traditionally used as major construction materials in civil infrastructure and housing sector. To meet the demand in the society, exploitation of natural resources, especially the clay minerals leads to damaging the environment and eco-system. The available fired bricks are expensive, they involve huge energy for production while firing at high temperature and not much attracted by end-users. The builders, architects, and consumers are exploring the scope for newer and alternative materials to traditional fired bricks for construction, civil infrastructure, and other building applications. The increasing price of bricks, non-availability of natural clay, manufacturers and user agencies are looking for new materials to overcome the present issues on traditional bricks on a competitive technical and economic perspective. The developed CCB in the present program is expected to meet the end-users' requirement as well as it paves a way for effective use of waste resources as a raw material in making composite bricks equivalent and better in quality than that of traditional bricks. Presently, India produces about 550 million tons of inorganic wastes annually. This huge quantity of wastes creates major environmental danger both for living and non-living systems internationally. The major sources of such wastes are marble wastes, fly ash, red mud, metallurgical wastes including Jarosite waste. To address these alarming challenges, the CCB developed in the present study would provide innovative solutions with great commercial opportunities for effective use of inorganic wastes and organic wastes in manufacturing value-added hybrid green composite bricks in a sustainable manner.

Conclusions

Multidisciplinary research work was performed in the present study using an integrated approach to investigate and understand the characteristics of MPRs, hazardous Jarosite wastes and clay soil. Subsequently, these waste materials were converted into harmless sustainable ceramic composite bricks (CCB). The findings of the present study showed that application of MPRs reduced the plasticity, improved the quality of CCB and acted as catalyst to immobilize toxic substance in CCB made out of complex wastes. The Jarosite waste served as a raw material to partially replace clay in making CCB. The statistically design experimental results confirmed that addition of 15-30 % MPRs with 1:1 Jarosite clay matrix is an intermediate condition to have satisfactory compressive strength (49.62-52.8kg/cm^2), water absorption (16.65-17.93%), shrinkage (3.45-4.2%) and density (1.57-1.63g/cc) in which toxicity leachate concentration was within the USEPA safe limit as well as CCB meeting the desirable quality as per IS standard to be used in building construction. The toxicity leachate studies also demonstrated that the leachate concentration of toxic elements in the CCB developed using15-30 % MPRs with Jarosite waste clay matrix ratio 1 were found to be below the USEPA TCLP toxicity limits and CCB meeting all desirable quality, equivalent to that of burned clay bricks. From the RSM model, it is evident that the predicted results were compared with the experimental data and confirmed that the response characteristics are identical.

Realization of this technology will provide multiple solutions on multidisciplinary subject for multifunctional applications. Commercial exploitation of findings of this study will create new employment, contribute to enhance economy & provide holistic solutions for Jarosite waste and marble waste safe and effective utilization globally.

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Recycling Marble Wastes and Jarosite Wastes into Sustainable Hybrid Composite Materials and Validation through Response Surface Methodology

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Abstract

During marble processing such as cutting, polishing and grinding, a considerable amount of fine residues refereed as marble processing rejects (MPRs) are produced and have become a serious environmental issue. So the current study deals with the conversion of MPRs into hybrid ceramic composite bricks (CCB) with Jarosite waste in a clay matrix system. Mix design and optimization of CCB was performed to illustrate the potentials of MPRs and Jarosite wastes as ~~low~~ low-cost ~~high~~ high-value composites materials. Response Surface Methodology (RSM) model was also used in this work for simulation and to optimize the process for improving CCB quality employing classic mixture approach. Detoxification through mineralogical changes was achieved during firing composite bricks at 960^0 C ± 2^0 C and was confirmed using the XRD analysis. Compressive strength of CCB using 15% MPRs with 1:1 Jarosite waste - clay matrix ratio met the standard– quality (>35kg/cm^2) for its use in construction purpose. It is evident from the RSM model results and statistical analysis for the response compressive strength, shrinkage, water absorption capacity, density and leachate concentration of Cd as well as Pb in the CCB is in laudable agreement with actual experimental performance.

Key Words: Marble processing residues; Hazardous Jarosite waste; Hybrid Composite; Response surface methodology; Optimization; Toxic substances; Mechanical properties; Sintering mechanism

1. Introduction

Marble stone has been used as a versatile material for cement (Nezerka et al., 2018), wall tiles, floor tiles (Lu et al., 2018), furniture, panels for modular kitchen (Munir et al., 2018), architectural interiors and exteriors to name a few (Seghir et al., 2018). The major producers of marble products are India (~10%), Spain (~6%), Italy (~20%), China (~16%), Portugal (5%) followed by France and Brazil (Thakur et al., 2018). It is roughly estimated that there are about 500 million tons (MT) of marble products worldwide (Alyamac et al., 2017; Khodabakhshian et al., 2018). During marble cutting and processing operations to attain finished products of required dimension from the raw marble stone, about 20% losses occur which form a fine grain. As a consequence of revenues generated from marble industries, annually it is expected about 200 MT of marble processing residue or marble processing rejects (MPRs) as a waste powder~~ / ~~/sludge have been produced universally (Thakur et al., 2018). In India, about 16 MT of marble waste ~~have~~ has been produced during 2018-2019. The Rajasthan state in India holds one of the world's largest marble deposits in a cluster and accounts for about 90% marble production in the country (Thakur et al., 2018). MPRs being dumped on the river beds or on road-sides and on undulated open land is a major environmental concern and has become a major threat to surrounding eco-system (Arel, 2016). In dry conditions, the marble waste particulate dangle in the air around us and have the tendency to be deposited on vegetation, crops and significantly affects the ecology. Also, it results in decrease in porosity/ permeability of the topsoil contributing to the water-logging followed by decreasing the soil fertility, crop yield as a result of increase in soil alkalinity. Attempts have been made by several researchers to effectively use the marble wastes in a number of applications including road(Aruntaş et al., 2010), aggregates (Mashaly et al., 2016), cements, pigment, tiles (Sardinha et al., 2016), ceramics and building materials etc., (Topçu et al., 2009). No work is reported on the impact of marble wastes on the mechanical properties of bricks and their long term durability (Mothé Filho et al., 2002)(Okagbue and Onyeobi, 1999). Scanty information is available in the existing literature on the usage of different treatment techniques for the proper disposal of these wastes materials (Polikreti and Maniatis, 2004)and their use in civil engineering applications (Thakur et al., 2018). Study performed on use of MPRs in making polymer composites with jute textile or with glass ~~fibre~~ fiber mat or MPRs alone yielded an improved mechanical strength in terms of flexural strength and stiffness of polyester/ ~~epoxy~~ epoxy-based composites (Borsellino et al., 2009; Icduygu et al., 2012; Saxena et al., 2008), but the complete details and their durability performance is missing. Yet, there is very limited work carried out in this direction and further research is essential in the area of marble waste characterization, recycling and understanding their environmental significance.

On the other hand, Jarosite is a mineral, generally formed by the oxidation of sulphate sulfate in an acidic sulphate sulfate-rich environment- from sulphide sulfide sediment, acid mine drainage along with- weathering of sulphate sulfate ore deposits of pyrite (FeS_2) mineral (Asokan et al., 2006; 2010). The prime constituents of the Jarosite waste include oxides of iron, zinc and Sulphur, various other elements such as Al, As, Cr, Co, Cu, K, Mg, Mn, Na, Ni, Pb, S, Si, etc., are also present in Jarosite waste (Asokan et al., 2010; Pappu et al., 2006) (Mehra et al., 2016a)(Mehra et al., 2016b). As per the Ministry of Environment and Forest (MOEF), Government of India's regulatory guidelines, the primary/ and secondary production of Zn comprising Jarosite waste is categorized as the hazardous waste(Asokan et al., 2006). So the prime aim of this research has been to effectively use the marble wastes and jarosite wastes into high high-value sustainable hybrid composite materials

2. MethodologyMaterials and Methods

Samples of marble processing residues (MPRs) from marble processing industry; Jarosite waste from Hindustan Zinc Limited and clay soil nearby marble industry were collected from Udaipur, Rajasthan, India. All these samples prior to use were oven oven-dried at 105± 2 ^{o}C, crushed using the contact pressure and then sieved using 2mm size sieve. For characterization and experimental work, ceramic composite bricks (CCB) specimens were prepared from the processed samples employing conning and quartering method.

2.1 Experiment Design

Ceramic Ceramic-composite bricks (CCB) consists of MPRs, Jarosite waste, and clay, which is considered as 'q' component materials. To optimize CCB quality, the classic mixture approach was used. In this approach, the sum of the proportions of raw materials must be one

(1) and the variables are not independent. The advantage of this approach is that the required experimental region has been defined more naturally.

2.1.1 Modeling: Classic Mixture Approach

In the classic mixture approach, the total weight of CCB is fixed and quantity of each of the *q* component variables is decided accordingly to have a fixed mass as the total amount is constrained to sum to one. In the present study, CCB was a mixture of three raw materials namely Jarosite waste (x_1), clay (x_2), and MPRs (x_3), in this each x_i represents the weight fraction of each raw materials. The weigh fractions in which the components sum to one, and the region demarcated by this constraint results in– triangle (or simplex) as revealed in **Fig.1** (a) of section 2.1.1.

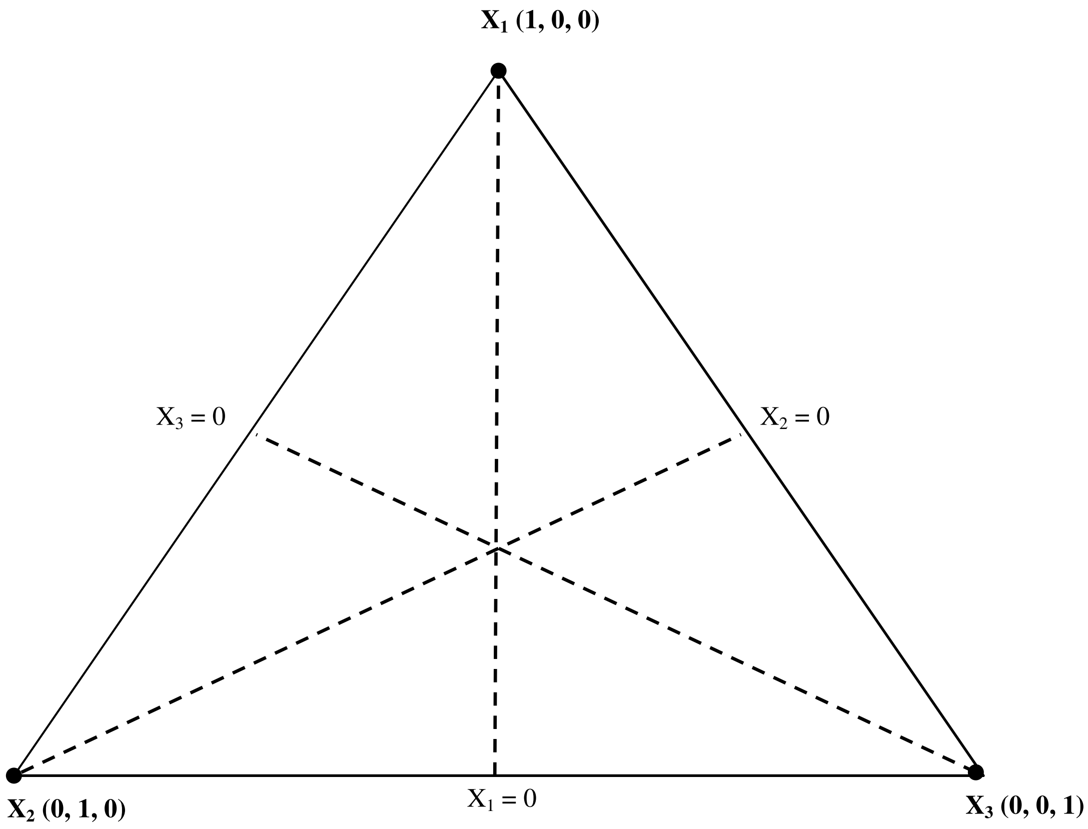

Fig. 1(a).The triangular simplex region from three-component mixture experiment

As per the classic mixture model, all defined properties were quantified for each mixture and were modeled as a function of each raw material. The polynomial functions were adopted for modeling. For three raw materials (Jarosite waste, clay, MPRs), the linear polynomial model for a response '*y*' was represented as:

$$y = b^*_0 + b^*_1 x_1 + b^*_2 x_2 + b^*_3 x_3 + e \qquad (1)$$

Where,

bi^* stands for the constants

'*e' is the* error term, showing combined effects of each variable.

In case of experiment with mixture, $x_1 + x_2 + x_3 = 1$ hence, the model can be re-written as:

$$y = b_1 x_1 + b_2 x_2 + b_3 x_3 + e \qquad (2)$$

Where,

$$b^*_0 = b^*_0 . (x_1 + x_2 + x_3)$$

This form is known as the Scheffé linear mixture polynomial(Ziegel, 1992)

Correspondingly, the quadratic polynomial can be written as:

$$y = b_0 + b^*_1 x_1 + b^*_2 x_2 + b^*_3 x_3 + b^*_{12} x_1 x_2 + b^*_{13} x_1 x_3 + b^*_{23} x_2 x_3 + b^*_{11} x_1^2 + b^*_{22} x_2^2 + b_{33} x_3^2 + e \qquad (3)$$

This can be further represented as:

$$y = b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 + e \qquad (4)$$

Where,

$$x_1^2 = x_1 .(1 - x_2 - x_3).$$

$$x_2^2 = x_2 .(1 - x_1 - x_3).$$

$$x_3^2 = x_3 .(1 - x_1 - x_2).$$

Since the CCB mixtures did not exist above the entire region as revealed in **Fig.1** (a), a sub- sub-region of the simplex that contains the ranges of different feasible mixtures should be defined by limiting the raw materials proportions. The representation sub-region for the three raw materials is shown in **Fig.1** (b) of section 2.1.1 and is well-defined by the subsequent weight fractions (where x_1= Jarosite waste, x_2= clay, x_3 = MPRs);

$0.15 \leq x_1 \leq 0.25$

$0.10 \leq x_2 \leq 0.20$

$0.60 \leq x_3 \leq 0.70$

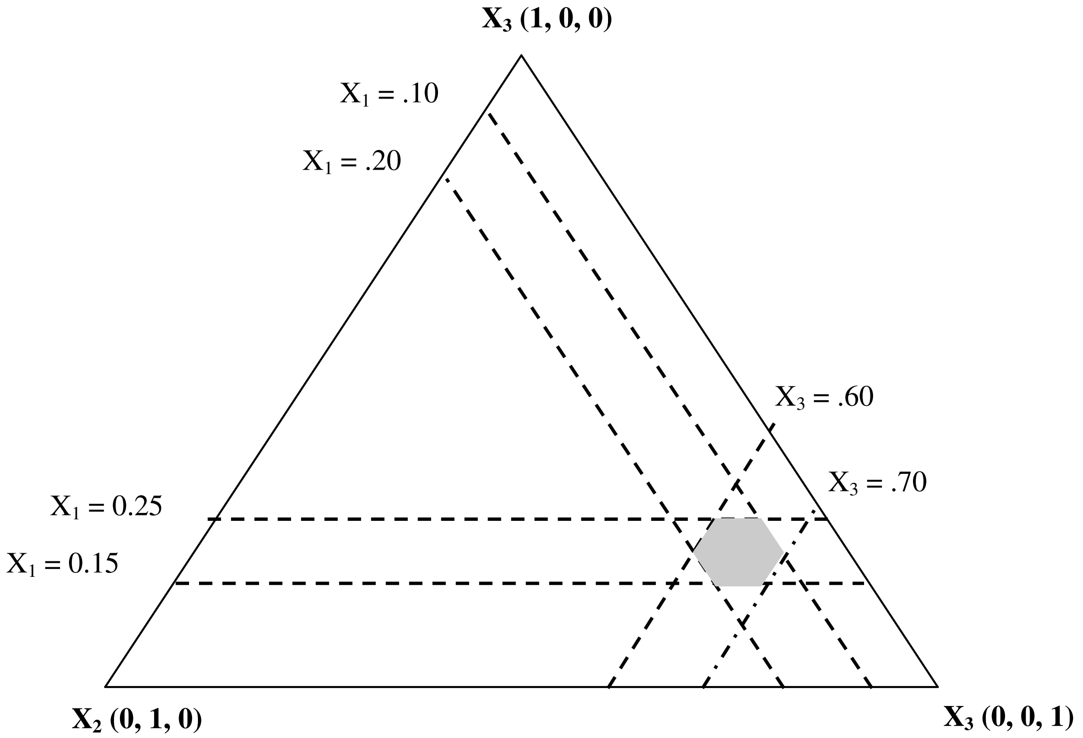

Fig. 1 (b). Example of sub-region of full simplex containing a range of feasible mixtures

2.1.2 Model Fitting and Validation

To authenticate the satisfactory conditions of the selected model quantitatively as well as graphically, the polynomial models reported in the classic mixture approach was used to fit ~~to~~ data by means of least squares techniques and analysis of variance (ANOVA). From the ANOVA significance of the treatment effect can be obtained. The different steps that are involved in model selection along with the fitting are almost the same for polynomials models and the classic mixtures approach.

2.1.3. Optimization

~~Performance~~ The performance of CCB and detoxification of toxic species may depend on the raw materials used, their quantity, concentration, process technique under which CCB ~~were~~ was prepared. Optimization can be accomplished employing the mathematical (numerical) / graphical (contour plot) approaches. The graphical optimization approach is limited where there are only a few responses considered to ascertain the quality of CCB. ~~On the other hand, numerical~~ Numerical optimization needs defining an objective function known as score function~~ / ~~/desirability. This would reflect the levels of each response in terms of minimum (zero) to maximum (one) desirability. The geometric representation of the desirability functions for each individual response is one of the approaches, where *n* is the number of responses to be optimized (Derringer and Suich, 1980):

$$D = (d_1 \times d_2 \times \ldots \times d_n)^{1/n} \qquad (5)$$

Another approach to represent desirability functions is to use a weighted average

$$D = \frac{(w_1 \times d_1 + w_2 \times d_2 + \ldots + w_n \times d_n)}{n} \qquad (6)$$

Here '*n*' *represents* the number of responses while w_1 represents weighting functions varying from 0 to 1.

The Desirability functions can also be expressed mathematically.

On defining the desirability functions for each response, the optimization was done. Also, statistical analysis for the responses compressive strength, water absorption capacity, shrinkage, density and toxic elements leachability (Pb, Cd) in CCB was done. To validate the results, the model was fit to data using analysis of variance (ANOVA) and least least-squares technique, validated and interpreted graphically using contour plot, trace plots, and 3D graph.

2.2 Physico-chemical Characterisation

Standard methods were followed for the analysis of bulk density/ particle density (Veihmeyer and Hendrickson, 1946)and Porosity (Bodman, 1942). Saturated soil pastes international pipette technique was used to measure the water absorption capacity. Electrical conductivity and pH was were measured employing the Orion analyser analyzer (Model 1260, Orion Research Inc., USA) in 1:2 soil suspensions. Laser Diffraction Particle size analyser analyzer Model HELOS Laser diffraction system, Sympatec GMBH, Germany was used to analyse analyze the particle size distribution. For chemical analysis, ground samples were subjected to digestion by microwave digester (QLAB 6000 Microwave Digestion System, Canada) and subsequently the digested samples were filtered employing whatman Whatman filter paper 50. These samples were then analysed analyzed using the Atomic Absorption Spectrophotometer (AAS), Z-5000, Hitachi, Japan with flame and graphite system and hydride generator facilities. In each experiment, high purity water of Elga (Prima 1-3 and Elgastat Maxima, England) system was used.

2.2.1 Mineralogical and Morphological Characterization

The mineralogical investigation was performed by an X-ray diffraction analysis system using an automated powder diffractometer (Model: Philips PW 1710), with Quasar software packages, using a Cu tube (Wavelength of X-Ray (λ) =1.5418 A) and generator settings of 40 KV kV and 30 mA. Different samples were homogenized by grinding in a mortar and pestle for about 10 minutes and were then loaded into an aluminiium sample holder for analysis.

Data was collected at a scanning speed of 0.01 degree 2θ/sec. PC-APD software was used for data smoothing. The samples were scanned in the range of 5^{0} - 70^{0} 2θ. The microstructure characteristics were studied using Scanning Electron Microscope (SEM) Model JOEL JSM-5600, Japan with Energy Dispersive X-ray Spectroscopy (EDS) analysis facilities. Test samples were dispersed in inorganic solvent and spread over on the aluminum stud with silver paint and sputtered with gold before examination in SEM. The Energy Dispersive Spectroscopy spectrum of samples was also recorded, which showed the peak of chemical elements present in the samples. The software of Oxford Model link Pendafet- IC 300 was used for the quantitative estimation by computational method.

2.2.2 Toxicity Leachate Characteristics

The toxicity leachate characteristics of different heavy metals and toxic elements present in the MPRs, Jarosite waste, clay, and CCB were studied following USEPA developed Toxicity Leachate Characteristics Procedure (TCLP) using Zero Head Space Extractor (ZHE), Millipore, USA. Extraction fluid was prepared using acetic acid and 0.1 N NaOH to maintain a pH of 4.93 ± 0.05. The quantity of extraction fluid used was equal to 20 times the weight of the dry solid sample of 25 gm. Primary extraction fluids were extracted from the ZHE at the pressure of 0, 10, 20, 30, 40 and 50 psi (1 PSI = 3.5 kg/cm ^{2}) and leachate was stored at 5° C. Following USEPA procedure, secondary extraction fluids were extracted after agitating the sample pressure barrel from rotary agitators at 30 rpm for 18 h under different pressure. The primary and secondary extraction fluids (leachate) were mixed together and ~~analysed~~ analyzed the content of Ag, As, Cd, Cr, Hg, Ni, Pb, Se, and Zn.

2.3 Development of Ceramic Composite Bricks (CCB)

~~Casting~~ The casting of ceramic composite bricks (CCB) using MPRs with Jarosite waste ~~was~~ experimented in clay system. The well-prepared MPRs with Jarosite waste and clay were solidified/ stabilized (S/S) in rectangular cast cast-iron mold 97.5 cm x 3.5 cm x 3.5 cm). Casting The casting of products (s/s) was done in a hydraulic based hand press under contact pressure. Casted products were subsequently allowed to air dry after the removal from the molds. Thermal stability and strength of s/s of the developed products was were achieved through sintering process. Sintering was done after air air-drying all these s/s products for 15 days (d) and then firing in muffle furnace at 960 ± 2 ^{0} C for ninety minutes. CCB samples were removed from the furnace, when it was reached at room temperature (32 ± 2 ^{0}C) for further studies. The experimental details, raw materials used and experiments identification is shown in **Table S1** of section 2.3 .

2.3.1 Testing mechanical and physical properties of CCB

Standard test methods have been followed to evaluate the mechanical and physical properties (water absorption, shrinkage, and density) of CCB. ASTM standard method were was followed to study the bulk density (ASTM C830-00), shrinkage (ASTM C356-10), water absorption capacity (ASTM C67-60) and compressive strength (ASTM C67-99a) of CCB, which are equivalent to IS 3495(3): 1992. In each case triplicate samples were tested. 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 kg/cm2/min till the ccb failure and the break-point was measured for compressive strength. The compression strength was estimated with regards to maximum load applied corresponding to correspond to its area and expressed in kg/ cm^2.

2.4 Data Analysis

CCB was developed applying a statistically designed experimental approach using Surface Response Methodology (SRM). The Mixture design parameters and their concentration ranges for the CCB Matrix (Jarosite waste-Clay-MPRs) and the details of raw materials component quantity for making s/s and achieving CCB are shown in **Table S2** and **Table S3** of section 2.4. The proportions for the 3-component mixture (Jarosite waste, clay and MPRs) experiment initially were selected in terms of weights. The total weight of the raw materials ~~were~~ was kept constant at 1 kg as required by the model. Since the weight fractions should sum to unity, the raw materials in a mixture experiment are not independent. The parameter levels of the 3 mixture components are shown in **Table S2** of section 2.4.

2.5 Model Fitting and Validation

The polynomial models described in the classic mixture approach were fit to data using analysis of variance (ANOVA) and ~~least~~ least-squares technique. The optimized experimental results (using Jarosite waste and clay soil ratio of one with 15% CCRs) showed that it is possible to make a composite having desirable mechanical properties such as compressive strength (50–81kg/cm^2); water absorption (13–17%); shrinkage (11–32%); and density (1.6–1.8gmcm^{-3}) to use as a construction material. From the ANOVA, significance of the treatment effect was obtained. Sequential F-tests were then performed using linear model and adding terms. The degree of freedom for each input~~s~~ was denoted as DF and the F-statistic was calculated for each type of model and the highest order model with significant terms. Significance was judged by determining the probability that the F-statistic calculated from the data exceeded the theoretical value. When the probability was less than 0.05 (99.9% confidence level) or 0.01 (99.98% confidence level) represent ~~as~~ significant results. For the comparison of the actual error from replication to the residual error to a lack-of-fit test was performed using ANOVA. When residual error is significantly higher than the actual error, the model implies significant lack of fit for which another model was found to be more suitable. The anticipated result during a lack-of-~~-~~fit test was achieved, when the model designated in step 1 not showed significant lack of fit (F test was irrelevant). This showed that the probability was greater (Prob>F) and F value was lesser than the required significance levels at 99.5% confidence level (0.05). To verify the model suitability, statistical analysis was performed and it included root mean square error (RMSE), predicted r^2, adjusted r^2, and predicted error sum of squares (PRESS). The RMSE in this work was the standard deviation linked with experimental error. ~~On the other hand, the~~ The adjusted r^2 was a degree of the variation on the mean explained in the model that was adjusted for various characteristics in the model. The predicted r^2 measured the variation in new data that was elucidated by the model. A simple linear regression technique (least squares) was employed to fit the model to the data exhibiting rough linear relationship. ANOVA was done and F-test along with the lack-of-fit test confirmed the suitability of the used model. After the model adequacy was performed, the assumptions were validated in the ANOVA residual analysis. 'Design Expert' software was subsequently employed to design and investigate the experimental data. In the present study, the program used particular 14 points from a gradient of candidate points. It includes the preeminent points to be fitted in a quadratic polynomial (**Table S3**). The goal was to optimize the raw materials inputs quantity to produce best quality of bricks, which should meet the following criteria:(i) Compressive strength ≥ 25 kg/cm^2; (ii) Water absorption ≤ 20%; (iii) Shrinkage < 15% (iv) Brick density below 1.75 g/cm$^{3;}$ (v) Leachate Concentration of Lead < 5.0 ppm and (VI) Leachate concentration of Cadmium <1.0 ppm. In this paper, due to page limitation, the statistical analysis is described in detail for response brick compressive strength only. The CCB ~~were~~ was tested for their chemical toxicity leachability following USEPA norm and mechanical properties according to the Bureau of Indian Standard (BIS 1077:1992) and assessed their suitability to be used as an engineering brick in construction materials. The impact of application of different waste matrixes on the mineralogical and microstructure characteristics variations was also studied and corroborated to the results in relation to the mechanical strength. In each experiment, minimum four replicate experiments were performed and all data were ~~analysed~~ analyzed statistically.

3. Results and Discussions

3.1 Physico-chemical Characteristics of MPRs, Jarosite waste and Clay

MPRs, Jarosite waste (JW) and clay soil were subjected to their Physico-chemical properties analysis and the properties are shown in **Table 1** of section 3.1. The results showed that MPRs exhibits a fine grain size with particles ranging from nanometers to micrometer. The bulk density of MPRs was quite higher (1.879±0.020 gm/cc) as compared to clay. The porosity of clay and MPRs showed almost in the range of 36-39%. On a contrary, porosity (67.00±0.61%) and water absorption capacity (109.96±0.148) of Jarosite waste was very high as compared to clay and MPRs where in MPRs and clay exhibits relatively lower water absorption capacity. As the pH of Jarosite waste was neutralized using lime at the zinc industry's discharge zone and ~~thus~~ the pH was almost neutral (6.78±0.08), ~~but~~ and the electrical conductivity was extremely high (13.597±0.437 (dS/m) indicating the presence of ions in higher concentration. MPRs showed an alkaline pH (8.360±0.102) and the electrical conductivity was very low (0.2769±1.004) while pH of clay was almost neutral, ~~but~~ the electrical conductivity was higher (6.44±0.305 dS/m) over MPRs. The Electrical conductivity (dS/m) is low as compared to normal clay soil and fly ash and generally it is compared with soil as the soil fertility and water quality contamination depends on the presence of EC and other heavy metals. The electrical conductivity is important for bricks because~~,~~ at the end of the service life is over, we have to dispose~~-~~ safely which should not affect the soil quality as well as it should not leads to leachate~~-~~ of any toxic substance~~/~~/element to the ground~~-~~water and contaminate the soil. ~~Thus~~ ~~it~~ It is important parameters to be considered as Jarosite waste used in the present study is a hazardous waste.

Table 1. Physico-chemical properties of marble waste and Jarosite waste

Parameter	MPRs	JW	Clay

Bulk Density (g/cc)	1.879±0.020	0.984±0.014	1.49±0.079
Specific Gravity	2.516±0.009	2.92±0.07	2.379±0.031
Porosity (%)	39.657±0.388	67.00±0.61	36.317±0.713
Water absorption Capacity (%)	24.15±0.60	109.96±0.148	43.69±0.52
pH	8.360±0.102	6.78±0.08	7.643±0.062
Electrical Conductivity (dS/m)	0.2769±1.004	13.597±0.437	6.44±0.305

Mean of triplicate test results

Table 2 of section 3.2 illustrates the chemical properties of MPRs, Jarosite waste and clay. The major chemical constituents present in Jarosite waste are oxides of iron, ~~sulphur~~ sulfur and zinc (Table 2). The other constituents are calcium, alumin~~i~~um, silicon, lead, and magnesium, and each constituent is present below 7 %. Jarosite waste contain toxic elements like zinc (8.24+0.0755), lead (1.9±0.023%), sulphur (12.23±0.2%), cadmium (317±23.8ppm), chromium (178±24.7 ppm), copper (1043±25.7 ppm), which are far higher than that of MPRs and clay, where more details about the presence of chemical constituents in Jarosite waste, clay and MPRs have been reported and discussed elsewhere (Asokan et al. 2006a, Asokan et al, 2006b, Asokan et al, 2010). The primary chemical constituents in MPRs are oxides of calcium (about 45%) and magnesium (about 5%). There are many trace elements such as oxides of alumin~~i~~um, iron, silica, potassium, carbon, ~~sulphur~~ sulfur are present the MPRs.

Table 2. Chemical properties (%) of MPRs, Jarosite waste, and clay

Parameters	**MRPs**	**JW**	**Clay**
SiO_2	1.73±0.04	6.75±0.412	60.65±0.69
Al_2O_3	1.12±0.09	6.75±0.152	16.22±0.32
Fe_2O_3	1.42±1.94	32.12±0.436	12.43±0.48
MgO	4.41±0.34	1.86±0.068	2.28±0.25
K_2O	0.01±0.00	0.74±0.023	3.22±0.22
CaO	45.40±0.61	6.87±0.151	2.15±0.05

All values are expressed in percentage

The major chemical constituents in clay are oxides of silica (60.65±0.69%) followed by alumina (**Table 2**). More details on the chemical properties of Jarosite waste ~~is~~ are reported elsewhere(Asokan et al., 2010). All these characteristics have been further evaluated and validated from the SEM EDX analysis as reported in **Fig.2** (a & b) of of section 3.1, where the EDX peak shows the chemical element present in MPRs (**Fig.2a**) and Jarosite waste (**Fig.2b**).

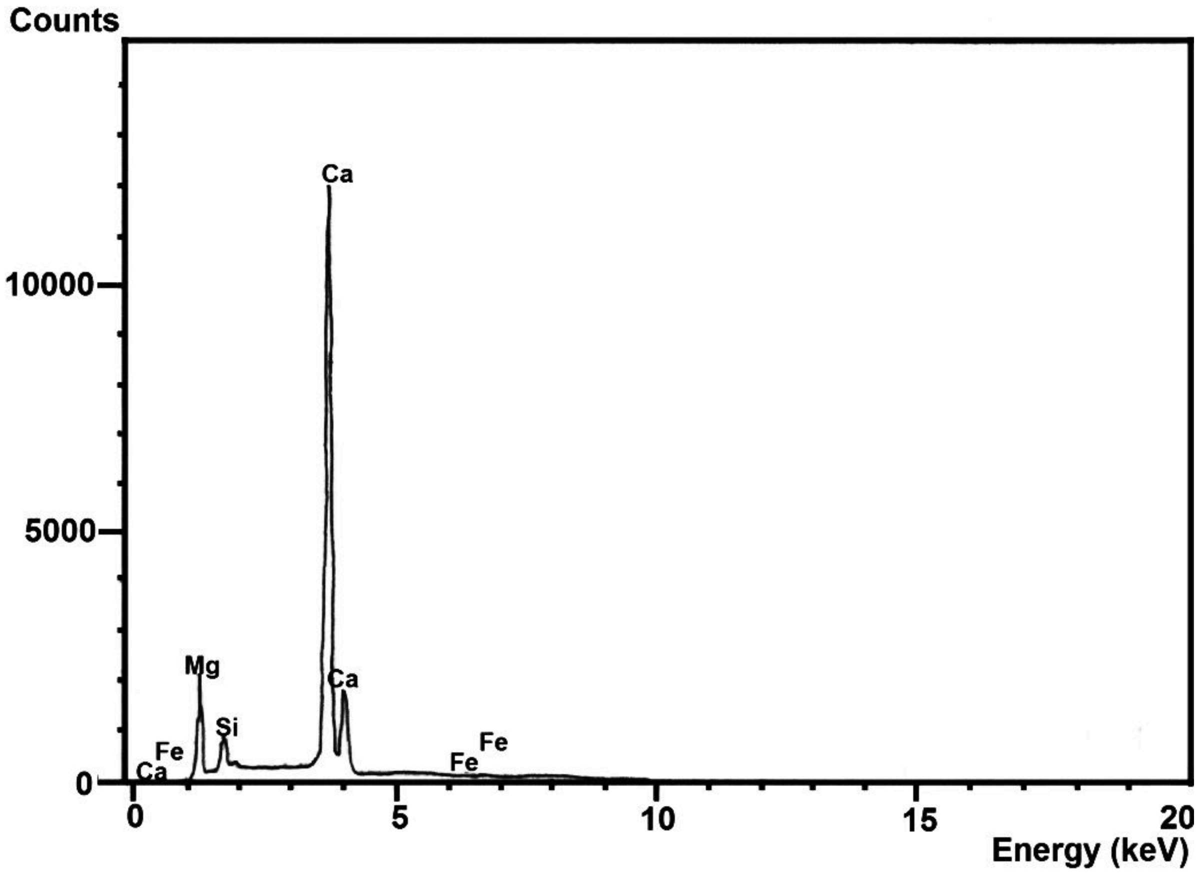

Fig. 2(a). EDX spectrum of marble waste

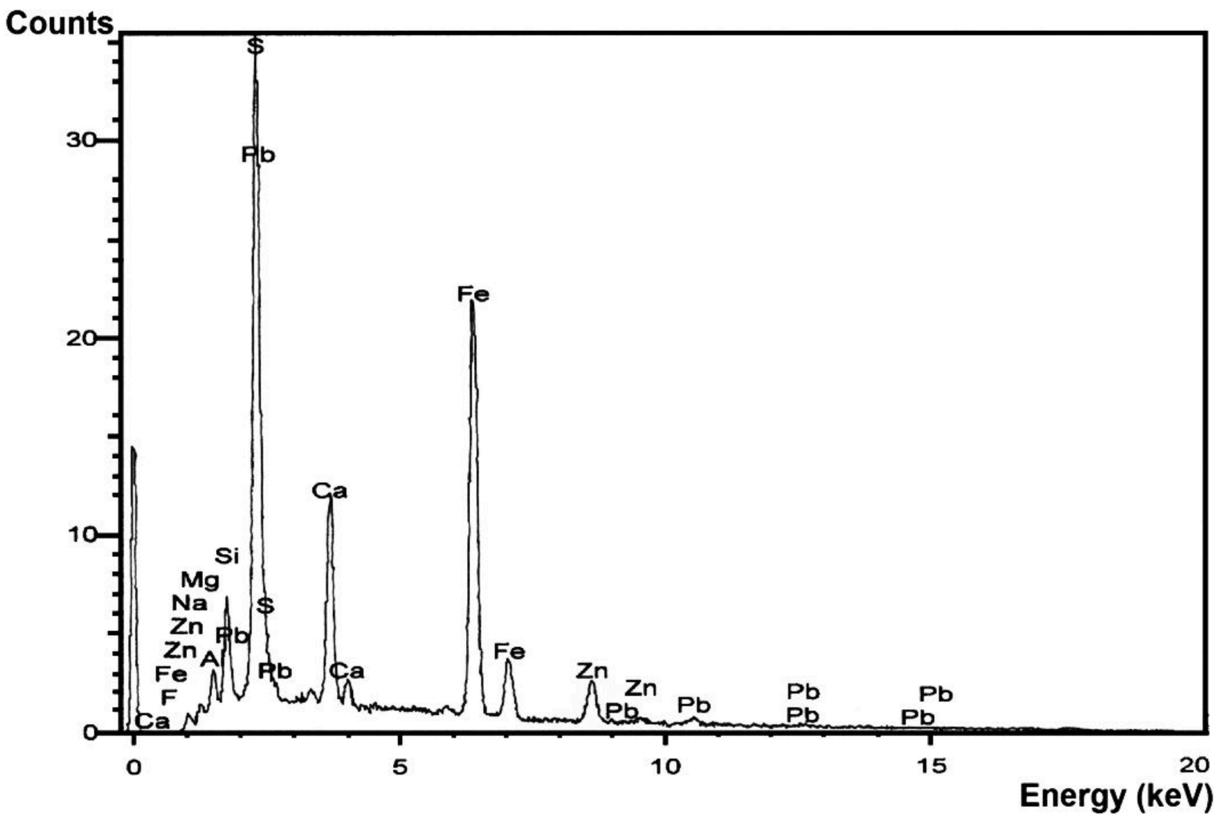

Fig. 2(b). EDX spectrum of Jarosite waste

3.2 Mineralogical Characteristics

The marble processing rejects and residues contain Dolomite (CaMg) $CO_3)_2$), Diopside (CaMg) Si_3, and Wollastorite Wollastonite ($CaSiO_3$). The X-ray diffraction analysis as shown in **Fig. 3(a)** of section 3.2 reveals the foremost mineral phase present in MPRs. Other minerals such as Vaterite ($CaCO_3$) and Calcium silicate ($CaSiO_3$) were also identified in MPRs. The key mineral phases in Jarosite waste were Jarosite (KFe_3 $(SO_4)_{2(}OH)$ $_6$ and Anglesite ($PbSO_4$). Other compounds such as Iron Sulphate Hydrate ($2Fe_2O_3$ SO_3 $5H_2O$), Ammonium Iron sulphate sulfate hydroxide ($NH_4Fe_3(SO_4)(OH)_6$,Iron hydroxide ($Fe(OH)_3$) and Calcium sulphate sulfate ($CaSO_4$)were also present in Jarosite waste and are shown in **Fig. 3(b)** of section 3.2 .This shows the prevalence of OH^- that propels the different constituents to absorb / /expel water from the molecules and were discussed by researchers(Asokan et al., 2010, 2006). Major minerals phases present in clay soil have been shown in **Fig.3(c)** of section 3.2 . Results showed that the dominant phases in clay were

Ferroaetinolite {Calcium Iron Silicate hydroxide – Ca_2Fe_5 (Si_8O_{22}) $(OH)_2$), Vertumnite ($Ca_4Al_4.Si_4O_6$. $(OH)_{24}$. $3H_2O$), Ferroaetinolite (Ca_2Fe_5 $(Si_8O_{22}$ $(OH)_2$), Kaolinite ($Al_2O_3.2SiO_2.2H_2O$) and Cristobalite Quartz (SiO_2).

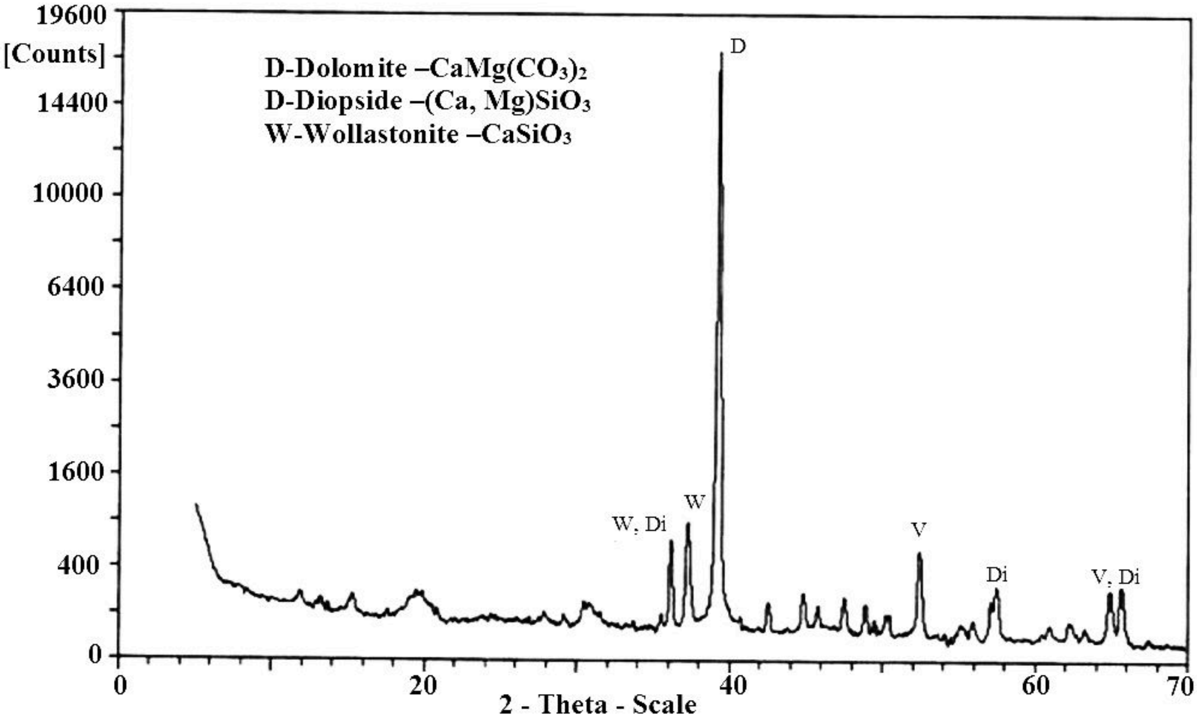

Fig. 3(a). X-ray diffractograms of MPRs

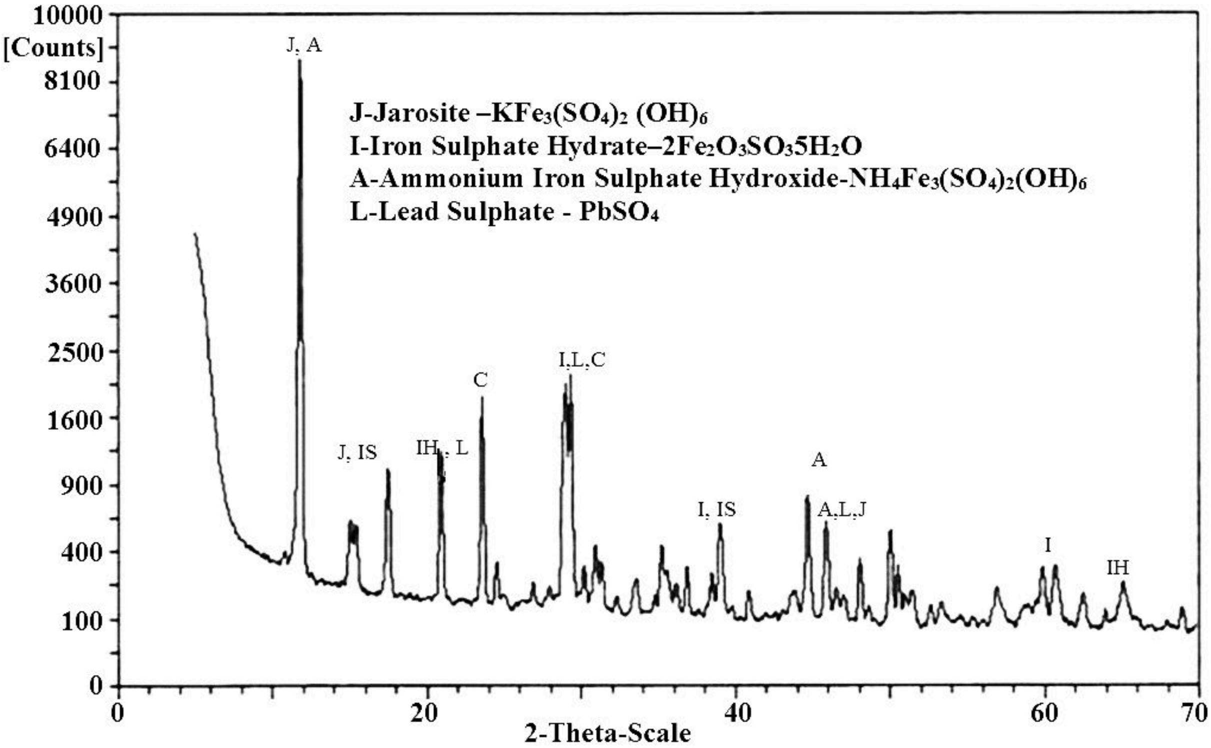

Fig.3 (b). X-~~Ray~~ ray diffractogram of Jarosite waste

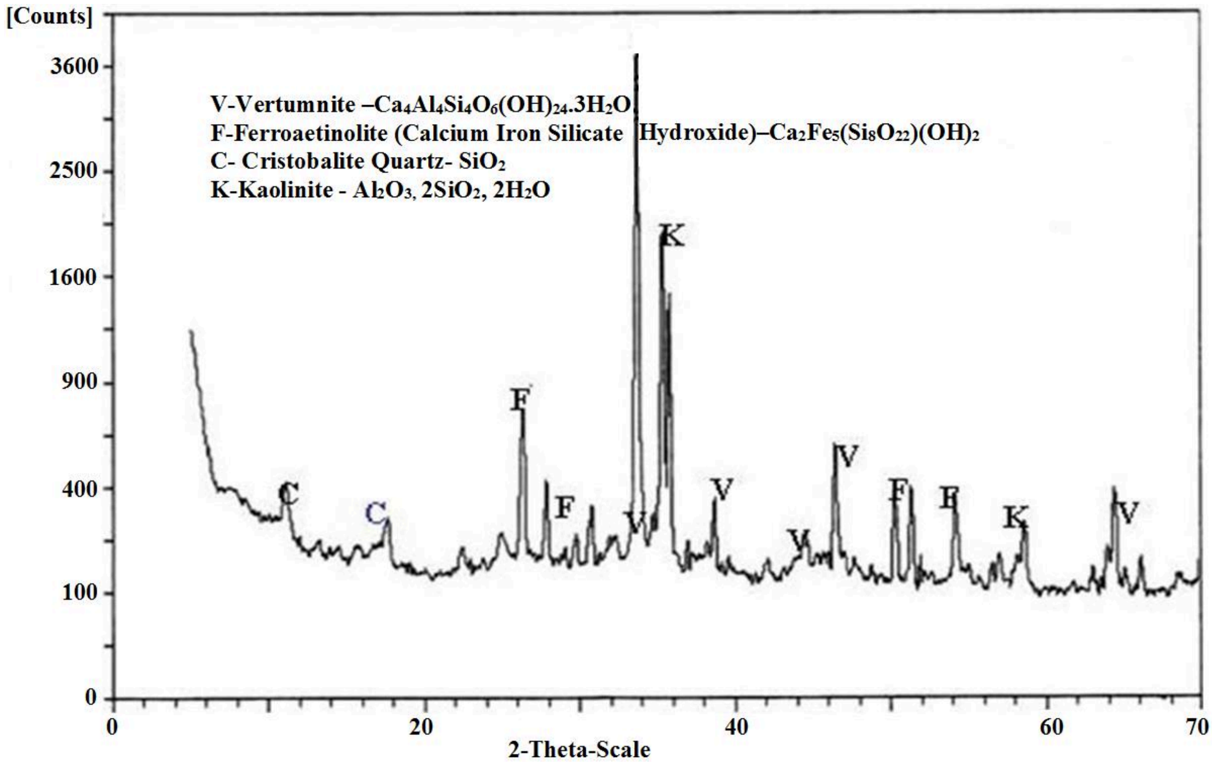

Fig.3(c). X-~~Ray~~ ray diffractograms of clay soil

3.3 Morphological Characteristics

The microstructure of marble processing residues (MPRs) is shown in **Fig. 4 (a)** of section 3.5 **.** Result reveals that MPRs particles exhibit cleavage structure having sharp edges. It was also confirmed from the microstructure that the majority of the particles have irregular shape with solid structure. The particle~~s~~ surface was found to be unsmooth and some of them were angular shape of with solid structure. The microstructure of Jarosite waste is shown in **Fig. 4(b)** of section 3.5 that demonstrates the irregular shape of the particles with multiple humps. Though the surface of Jarosite waste particles was found to be smooth with large lumps, it contains lots of porosity and demonstrates exceedingly swelling / shrinking properties. The particles were made of flaky units with some binder which may be oxides of zinc, ~~sulphur~~ sulfur, calcium /lead and the same was confirmed from the chemical analysis results.

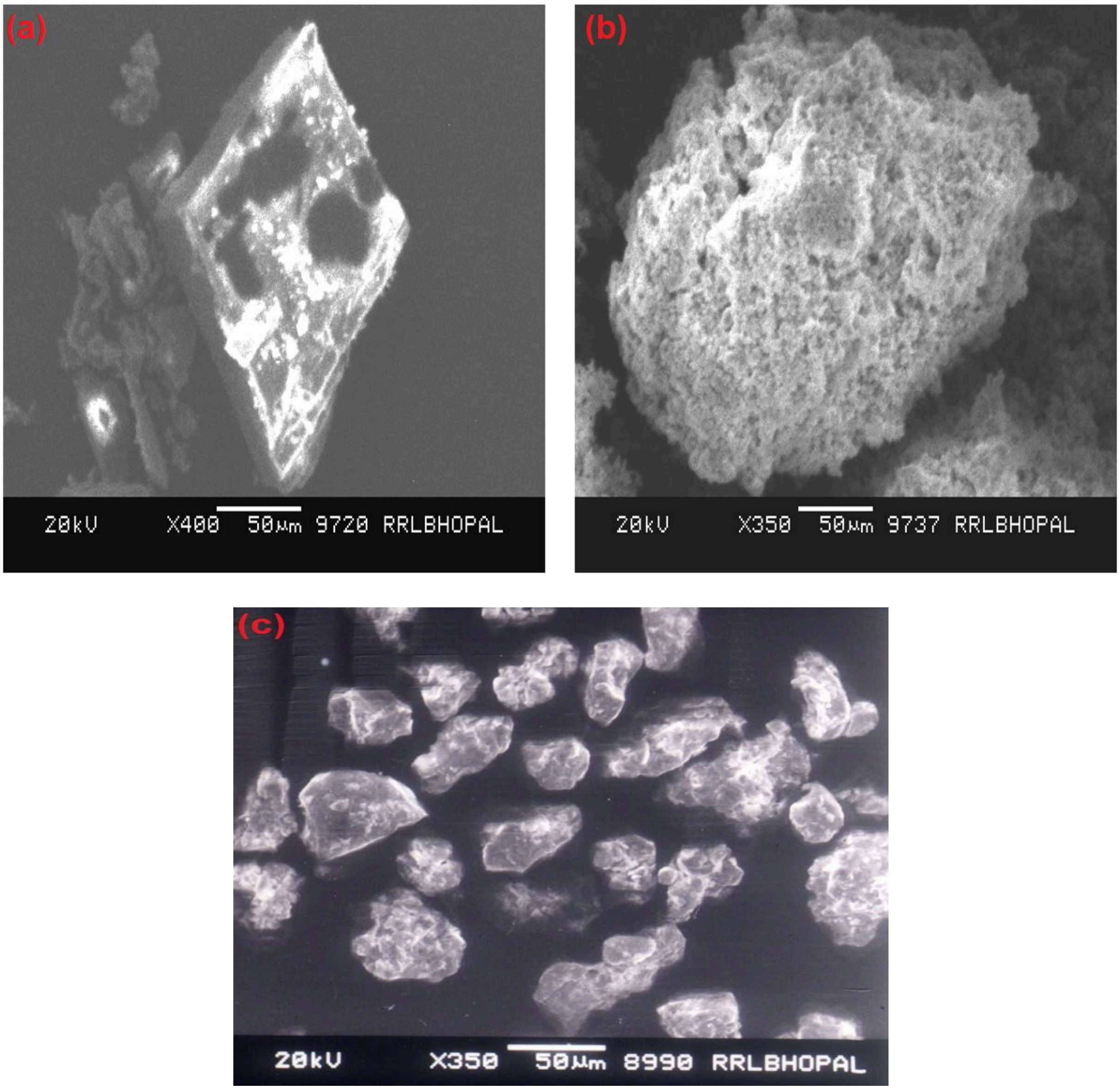

Fig. 4 (a).SEM microstructure of MPRs of different size, shape, and structure; 4(b). SEM microstructure of Jarosite waste particles; 4(c). SEM microstructure of clay soil showing different size, shape, and structure

It can be seen from the SEM microstructure that there is a huge variation in the particle size of Jarosite wastes. The particle surface irregularities indicate that these particles can exhibits good binding characteristics with other extraneous materials. **Fig. 4 (c)** of section 3.5 shows SEM microstructure of clay soil and SEM study reveals that clay particles are solid and irregular in shape having sharp edges. Particles size varied from 2-65 micro-meter and surface was not smooth. Most of the particles have non-uniform shapes; expected to have good packing and bonding with-in the matrix system.

3.4 USEPA TCLP Toxicity Leachate Characteristics of MPRs, Jarosite waste, and Clay

Table 3 of section 3.4 shows the toxicity leachate concentration of MPRs, Jarosite waste and clay along with the permissible limits and USEPA hazardous waste numbers. It is evident from the results that the concentration of almost all the toxic elements for example Pb, Cd, Ni, Ag, As, Cr, Se, and Zn in MPRs was lower than that of Jarosite waste / /clay and were below the TCLP toxic limits recommended by USEPA and falls under non-hazardous waste category.

Table 3. Toxicity characteristics leachate concentration in MPRs, Jarosite waste, and clay extracted as per the US EPA TCLP norms

Jarosite / additives		**Leachate concentration of toxic elements**							
		Pb	Ni	Cd	Zn	Ag	As	Cr	Se
MPRs	R1	0.15	1.34	0.010	< 4	3.09	2.66	21.20	2.07
MPRs	R2	0.15	1.30	0.010	< 4	3.09	2.44	22.12	1.06
MPRs	R3	0.13	1.42	0.012	< 4	2.88	2.28	22.07	1.98
Mean		0.14	1.35	0.011	< 4	3.02	2.46	21.80	1.70
SD		0.01	0.06	0.001	< 4	0.12	0.19	0.52	0.56
JW	R1	36.8	3.71	27.000	356.0	77.82	3.70	63.60	2.95
JW	R2	35.2	3.46	26.500	360.0	78.54	2.85	64.57	1.78
JW	R3	35.62	3.15	28.500	358.0	79.2	3.34	63.88	2.86
Mean		35.87	3.44	27.333	358.0	78.52	3.30	64.02	2.53
SD		0.83	0.28	1.041	2.0	0.69	0.43	0.499	0.65
Clay	R1	0.16	3.95	0.030	< 4	2.69	1.63	11.30	1.22
Clay	R2	0.26	3.10	0.032	< 4	2.83	1.37	13.21	0.99

Clay	R3	0.22	2.94	0.028	< 4	2.94	1.46	12.88	1.02
Mean		0.21	3.33	0.030	< 4	2.82	1.49	12.46	1.08
SD		0.05	0.54	0.002	< 4	0.13	0.13	1.02	0.13
US EPA Limit ppm		5.0	70.0	1.0		5.0	5.0	5.0	1.0
US EPA HW Number		D008	D012	D006		D011	D004	D007	D010

Values for the concentration of Pb, Ni, Cd, and Zn are expressed in ppm and the rest (Ag, As, Cr, Se) are in ppb.

US EPA HW Number – United State Environmental Protection Agency Hazardous waste Identification Number.

MPRs used in this study confirmed that they were nontoxic and were in compliance with the permissible limit. Most of the elements including nickel, chromium, silver, arsenic and selenium concentrations in Jarosite waste were also below the USEPA toxic limits (**Table S4**). ~~But t~~The concentration of lead (34.85±0.83 ppm) and cadmium (27.333±1.041ppm) was extremely higher than that of the US EPA TCLP limits. These results confirmed that the Jarosite waste falls under the hazardous waste category.

3.5 Effect of MPRs on the Mechanical Properties of CCB

The s/s composite brick specimens were developed before and after sintering, following the mix design using different proportionate of MPRs. The impact of different matrix composition on the performance of ceramic composite bricks (CCB) in terms of compressive strength, shrinkage, water absorption, and density is reported in **Table 4** of section 3.5.

Table 4. Impact of different matrix composition on the performance of CCB

Experiment Trial 5	Jarosite waste: Clay Ratio	Jarosite waste (g)	Clay (g)	MPRs (g)	Comp strength (kg/cm^2)	Water absorption (%)	Shrinkage (%)	Density (g/cc)
1	1:1	500	500	00	65.40	15.90	12.26	1.74
2	1:1	425	425	150	52.80	16.65	4.20	1.62
3	1:1	350	350	300	49.60	17.93	3.45	1.57
4	1:1	275	275	450	46.12	22.65	2.73	1.44
5	2:1	666.66	333.33	00	84.90	17.26	21.70	1.79
6	2:1	566.666	283.333	150	35.24	20.44	7.05	1.58
7	2:1	466.67	233.33	300	31.70	21.86	4.83	1.49
8	2:1	366.66	183.33	450	29.86	24.50	2.12	1.43
9	3:1	750	250	00	140.80	14.51	31.36	1.91
10	3:1	637.5	212.5	150	35.70	19.94	10.55	1.55
11	3:1	525	175	300	32.70	21.20	5.64	1.49
12	3:1	412.5	137.5	450	29.86	23.84	1.81	1.43
13	4:1	800	200	00	125.80	14.50	38.08	1.93
14	4:1	680	170	150	29.98	20.95	13.19	1.53
15	4:1	560	140	300	29.20	23.30	6.79	1.49
16	4:1	440	110	450	23.15	24.57	1.51	1.41

3.5.1 Compressive Strength

The effect of different concentrations of MPRs with Jarosite waste in the clay matrix system on the compressive strength of ceramic composite bricks (CCB) and water absorption behavior is shown in **Fig. 5 (a-b)** and **TableS5** of section 3.5.1 . Results revealed that CCB made out of 15% MPRs with equal ratios of Jarosite waste and clay resulted in a compressive strength of 52.8 kg/cm^2, which is higher than that of the BIS specification (< 35 kg/cm^2) meeting the quality standard for use- in construction application. With increase in quantity of MPRs with maintaining equal ratios of Jarosite waste and clay, there was decrease in the compressive strength of CCB and minimum compressive strength was 46.12 kg/cm^2 with 45% MPRs incorporation.

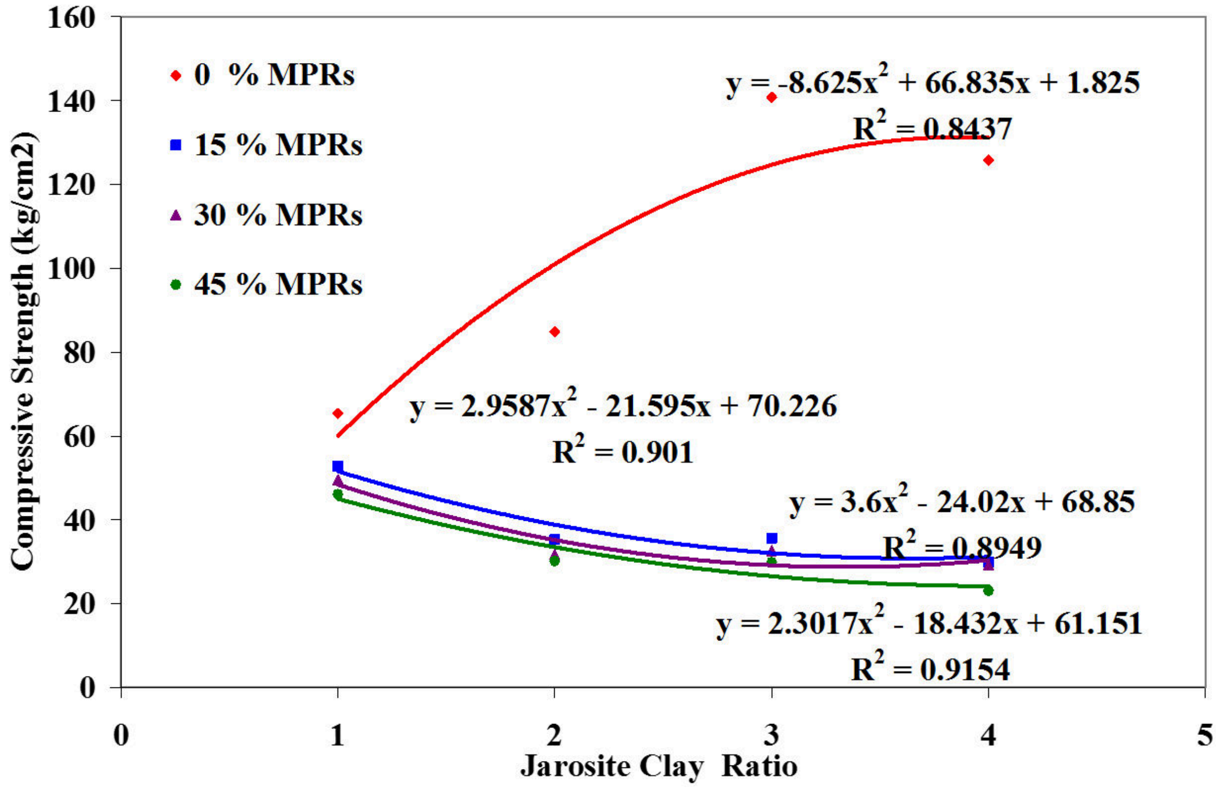

Fig. 5 (a). Effect of MPRs on compressive strength of CCB

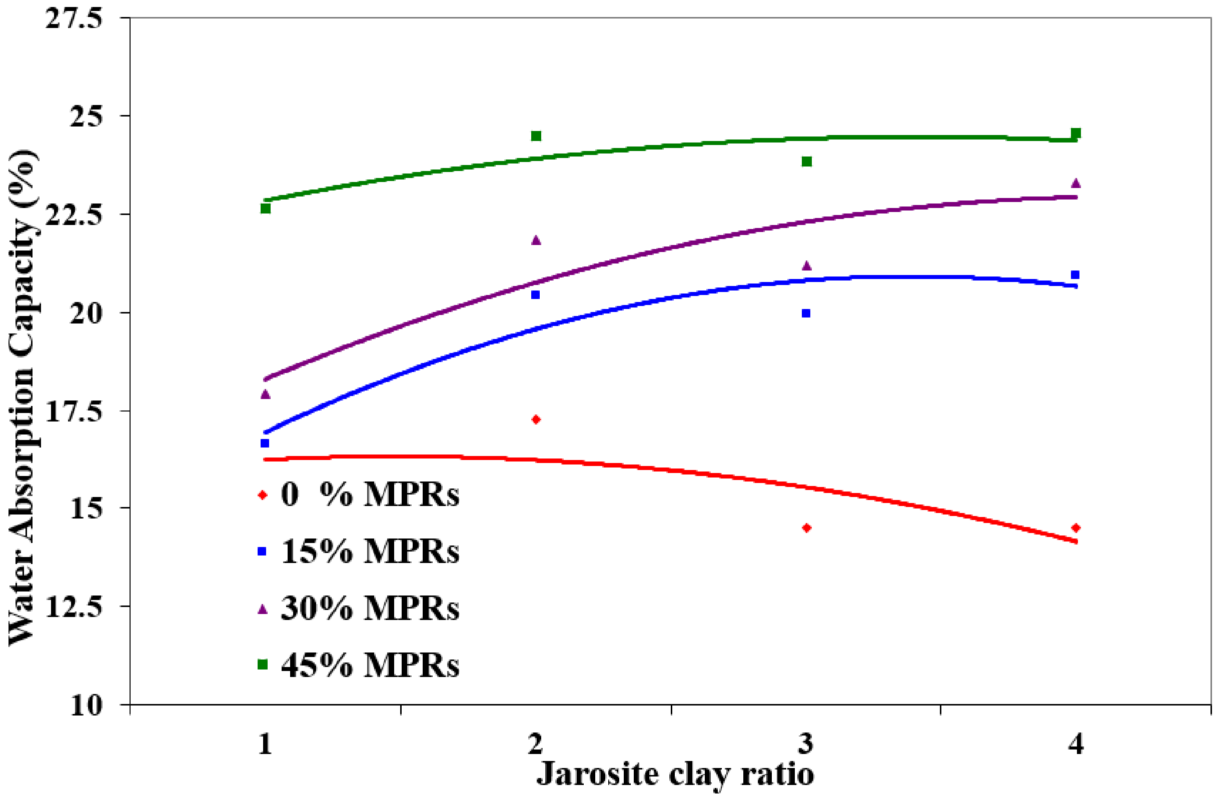

Fig. 5 (b). Effect of MPRs on water absorption of CCB

Without MPRs, the ceramic composite bricks made of Jarosite waste and clay alone resulted in higher compressive strength, very high shrinkage which might probably be due to the formation of a considerable amount of liquid phase within the fine particles. It might have possibly reduced the porosity under the capillary tension forces in the fine pores. Nevertheless, maintaining the MPRs integration (15-45%) and increasing Jarosite waste by reducing clay content decreased the compressive strength of CCB. Wherein minimum compressive strength (23.15 kg/cm^2) was recorded using a 4:1 ratio of Jarosite clay with 45% MPRs and maximum compressive strength (140.8 kg/cm^2) was recorded using 3:1 ratio of Jarosite clay without MPRs (**Table 4**). The trend on the distinction of compressive strength of CCB and the impact of application of MPRs with Jarosite waste and clay ratio can be seen from the **Fig. 5 (a)** of section 3.5 . Linear regression equitation was fitted for the response compressive strength data of CCB and this confirms statistically that the compressive strength of CCB decreases with increasing Jarosite clay ratio as well as increasing the MPRs concentration. The r^2 values were 0.915 for 45% MPRs incorporation with varying Jarosite clay ratios. The r^2 values specify a good fit of data with the equations that describes the relationship between the compressive strength of CCB and influence of different raw materials. Thermal decomposition of carbonates during the process, also contributes to the development of a micro-porosity which affects the quality of bricks. During firing, the decomposition of $CaCO_3$as well as its transformation into CaO might have resulted in a notable increase in microspores space contributing to the reduced compressive strength of CCB with increase in concentration of MPRs.

3.5.2 Water Absorption and Shrinkage

The water absorption capacity of CCB and the relationship between the impact of the addition of different concentration and ratio of matrixes are shown in **Fig. 5 (a)** and **Table 4** of section 3.5.1. Results revealed that with MPRs application, the achieved minimum water absorption capacity was 16.65 % when Jarosite waste clay ratio was maintained one with 15% MPRs (**Table 4**)). It is evident from the results that increase in MPRs in CCB, increased the wastter absorption capacity and maximum water absorption (24.57%) was recorded with 45% MPRs addition (**Fig.5 a**). It is important to note that, with increase in ratio of Jarosite to clay, water absorption capacity decreased, but and the shrinkage was increased. **Fig. 5 (c)**) of section 3.5.2 shows the effect of different concentrations of MPRs on shrinkage of CCB in Jarosite waste and clay system. Maximum shrinkage was recorded (38%) in the CCB made out of 4:1 ratio of Jarosite waste and clay without MPRs (**Table 4**). When MPRs were applied, the shrinkage was found to be reduced and minimum shrinkage (1.51%) was attained with maximum (45%) MPRs application in 1:1 ratio of Jarosite waste and clay matrix (**Fig. 5 c**).

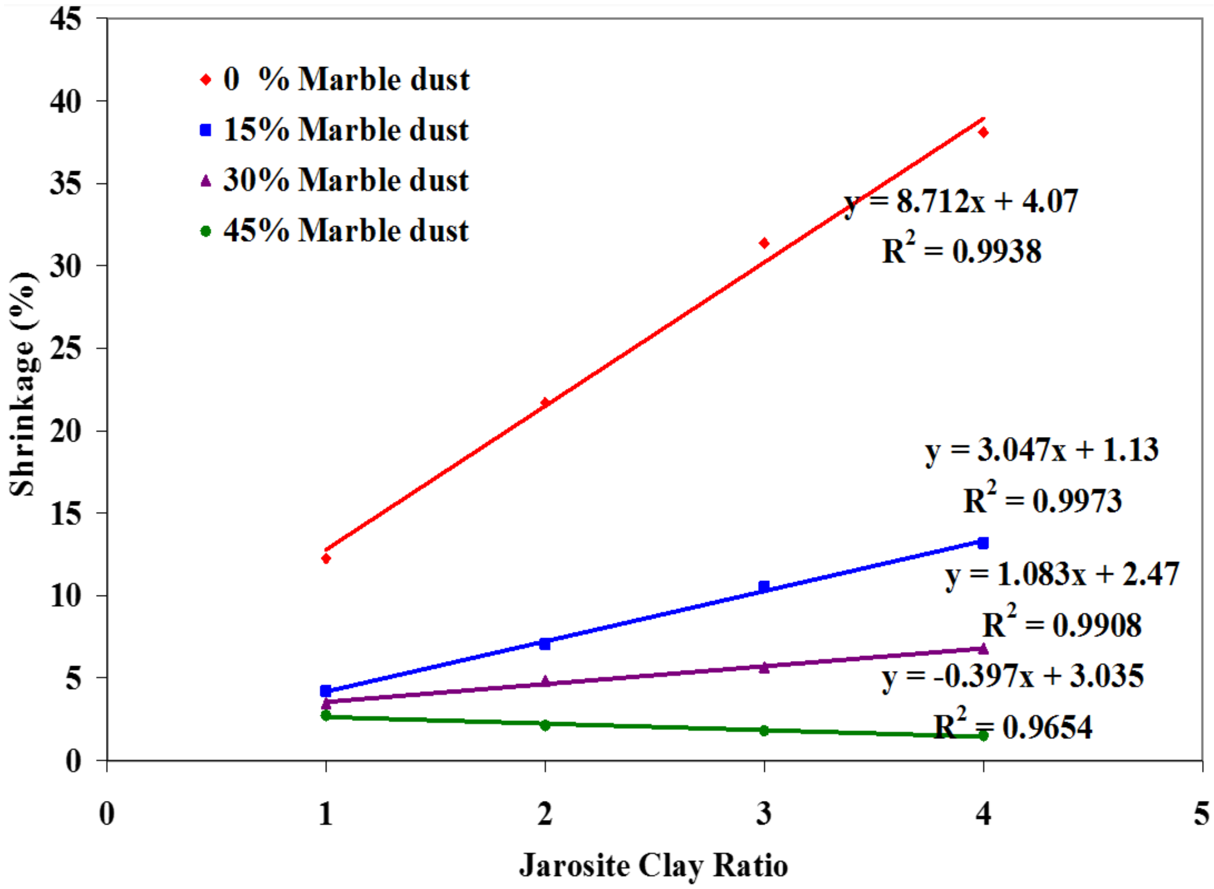

Fig. 5 (c). Effect of MPRs on shrinkage of CCB

The correlation coefficient (r^2) values from the regression equations fitted for the response water absorption (**Fig. 5a**) and shrinkage (**Fig. 5 b**) indicate a very good fit of data, which satisfactorily describe the relationship between MPRs, Jarosite waste and clay matrix system and shrinkage of CCB. As compared to all combinations, MPRs application (15%) not reduced the shrinkage of CCB and improved finished quality. Carbonates strongly influence the porosity resulting in improvement in texture and physical-mechanical properties of CCB. The morphology of MPRs might have also greatly influenced the porosity in CCB. The carbonates in MPRs and clay facilitates the formation of crevice and pores when the bricks were fired at about 960ºC. This analysis has been supported ~~with~~ by the earlier studies that the nonappearance of carbonates contributes to the constant reduction in porosity (Cultrone et al., 2004). The major chemical constituent in MPRs is $CaCO_3$ and decomposition of such carbonates influences micro-porosity during sintering under crystallization process. The transformation of $CaCO_3$ into CaO greatly affected CCB towards increase in water absorption capacity and reduced shrinkage.

3.5.3 Density

The impact of different matrix composition on the density of CCB is shown in **Table 4** and **Fig. 5d** of) of section 3.5.3 .

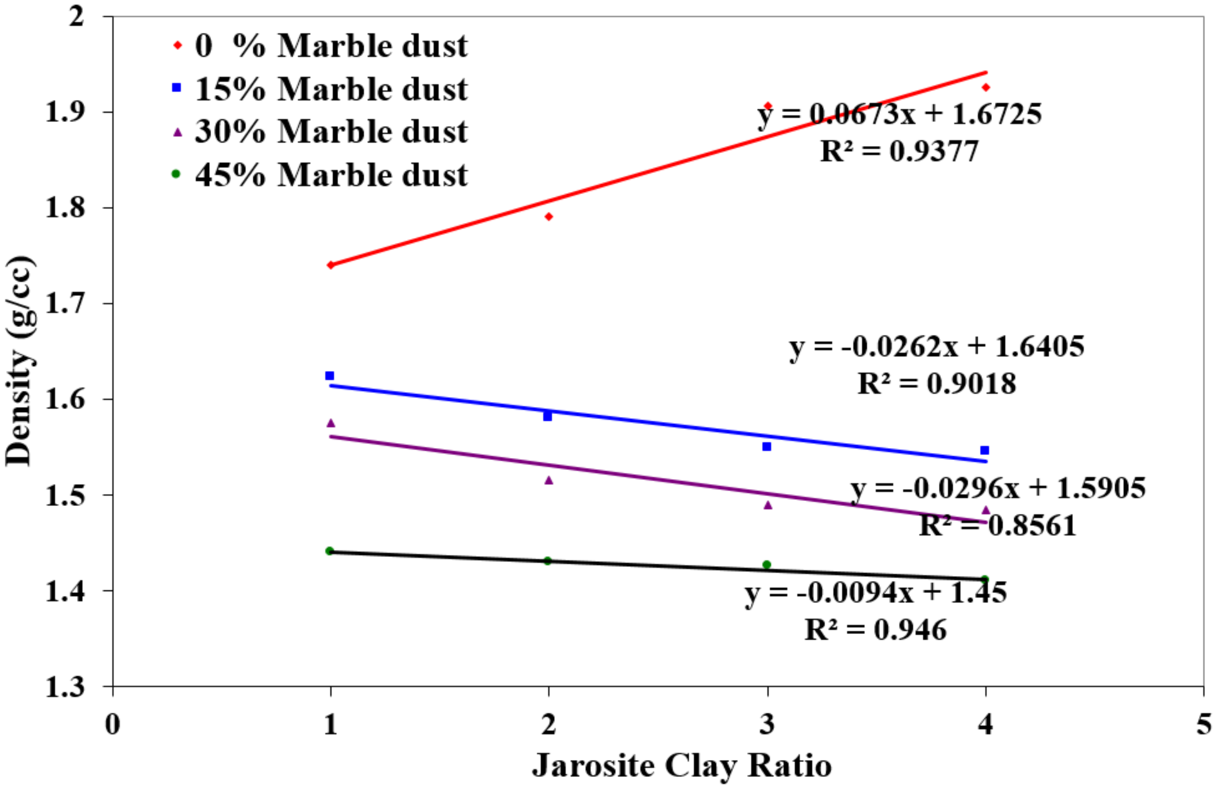

Fig. 5 (d) Effect of MPRs on the density of CCB

It is obvious from the results that MPRs application (0-45%) reduced the density of CCB and minimum density (1.41gm/cc) was with maximum MPRs (45%) application in the Jarosite waste and clay matrix system. With varying ratios of Jarosite waste and clay matrix (1:1 – 4:1) in the CCB, maximum density (1.93 gm/cc) was recorded with a maximum concentration of Jarosite waste in clay system (Jarosite waste clay ratio 4:1) without MPRs. The outcome of present experimental programme and the results obtained from the design expert model corroborating density, shrinkage water absorption capacity, and compressive strength of CCB developed using MPRs, Jarosite waste and clay matrix system were summarized and analysed analyzed (**Table 4** and **Figs.5 a-d**). Results revealed that with increase in concentration of MPRs, compressive strength of CCB decreased and water absorption capacity increased. But tThe shrinkage and density substantially decreased. The CCB developed using 15% - 45% of MPRs with different ratio of Jarosite and clay (1:1- 4:1) matrix system resulted in 23.13-52.8 kg/cm^2 compressive strength. The variation in the quality of CCB has been attributed to the substantial differences in the composition / /concentration of mineral phases in different waste matrixes. The findings of the present study confirm that high proportion of calcite in MPRs attributes to the creation of more pore size in CCB due to its high high-temperature decomposition and the release of CO_2 resulting in reduced density, shrinkage, compressive strength and increased in water absorption capacity, which is also supported by earlier performed work (Cultrone et al., 2004).

3.6 Effect of MPRs on Mineralogical Properties of CCB

To study the effect of sintering on the s/s composite made out of MPRs, Jarosite waste and clay matrix, XRD analysis was done for selective samples in which the most desired results (mechanical strength and toxicity leachate limits) were achieved. **Fig. 6(a)**) of section 3.6 shows XRD analysis results of s/s green (unfired green bricks) developed using MPRs (15%) with Jarosite waste clay matrix ratio of 1. It was observed from the results that major mineral phases in the s/s products are Dolomite {Ca Mg $(CO_3)_2$}; Lead Carbonate Hydroxide {$2PbCO_3Pb\ (OH)_2$} and Ammonium Calcium Sulphate Hydrate {$NH_4)2[(CaSO_4)_5\ (OH)_6$}.Riccardi *et al.,* (1999) reported that in "Ca-rich sample the intensity of the calcite reflections decreases as the firing temperature increases (Riccardi et al., 1999). At temperatures of 850ºC the gehlenite is present together with hematite, whereas the wollastonite is recorded" only in highest temperature fired products. In the present study, as shown in **Fig. 6(b)** of section 3.6 , there was were a changes in the mineral phase of s/s composites after firing at 960^o C and formation of new phases could be recorded. The identified mineral phases after high temperature firing in the CCB were Dolomite {Ca Mg $(CO_3)_2$}; Alumina {Al_2O_3}; Hematite {Fe_2O_3} and Quartz {SiO_2}. The feldspar was found to show a single reflection in the samples with Ca deficient specimen having a larger peak than in Ca-rich sample due to the compositional changes, while temperature increases.

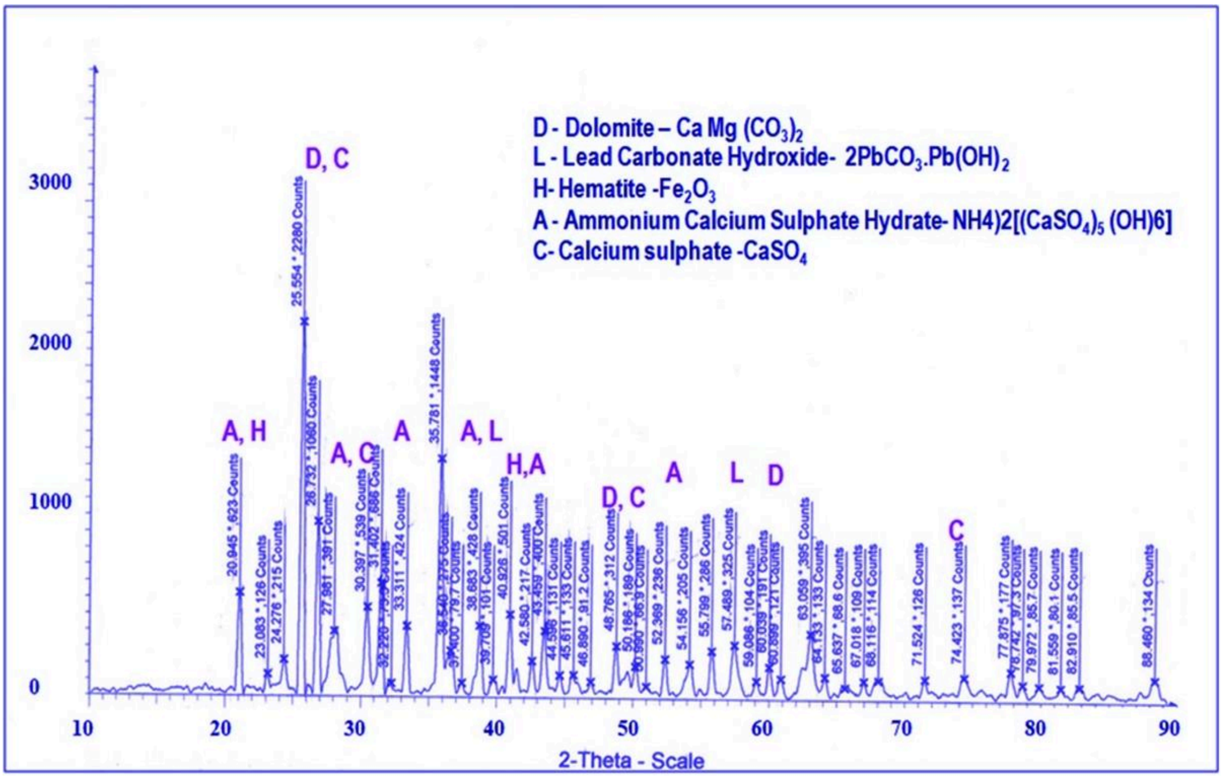

Fig. 6 (a). XRD analysis of solidified unfired green composite products developed using Jarosite waste clay ratio 1:1 with 15% marble waste

CaO is expected to migrate over wider domains resulting in an amplification of the stability field of gehlenite. The reaction kinetics ~~as well as occurrence of new phases~~, as well as the occurrence of new phases, is controlled by ~~the~~ dehydration and decarbonation reactions. It could be concluded from the study that in CCB, sintering behavior is significantly dependent on the parameters such as quantity, composition, and grain size distribution. This leads to the foundation of transitory liquid phases that facilitates the densification of the main crystalline phases, anorthite, hematite, magnetite, dolomite, calcite and or zinc ferrite. The quality of s/s green products fabricated using MPRs, Jarosite waste and clay matrix ~~has~~ have undergone substantial changes owing to the firing in the presence of several phase constituents in the matrices. It has resulted in the loss of K^+ and OH^- groups. ~~Similar~~ A similar phenomenon has been observed in the case of CCB as MPRs ~~is~~ are rich in calcium oxide~~,~~ when it was mixed with Jarosite waste and clay matrices/ minerals. S/S products, in the presence of humidity, CaO rapidly reacted and ~~was~~ were transformed into portlandite ($Ca(OH)_2$).

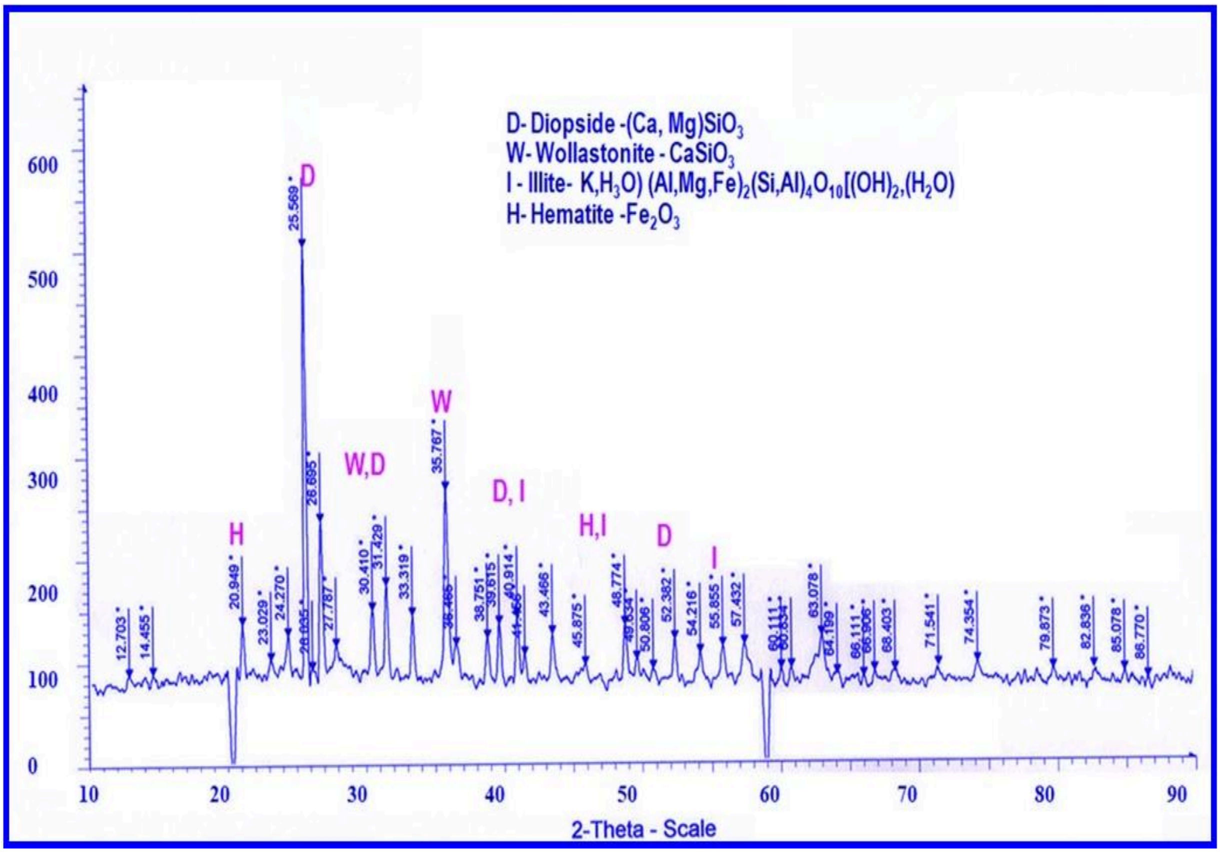

Fig. 6(b). XRD analysis of solidified sintered composite products developed using Jarosite clay ratio 1:1 with 15% marble waste

This reaction was exothermal and caused a substantial increase in volume. ~~T~~There was no shrinkage in CCB developed using MPRs with Jarosite waste and clay matrix. As supported by Cultrone et al., (2004), the reaction kinetics is as follows (Cultrone et al., 2004):

$$\underset{CaCO_3}{\text{Calcite}} \xrightarrow[\Delta T]{CO_2 \uparrow} \underset{CaO + H_2O}{\text{lime}} \longrightarrow \underset{Ca(OH)_2}{\text{portlandite}} \quad (6)$$

The decomposition of dolomite occurs as per the following equation:

Dolomite lime periclase (7)

$$CaMg(CO_3)_2 \xrightarrow{\Delta T} CaO + MgO + 2CO_2 \quad (8)$$

Prominent crystallization pressure was found to be exerted by the newly formed portlandite in the confined spaces of the CCB rich in CaO, which usually occurs in ceramics employing raw materials rich in carbonates.

3.7 Effect of MPRs on Microstructure Properties of CCB

Fig. 7(a-f) of section 3.7 displays the SEM microstructure of CCB's— internal surface developed using MPRs (15% and 30%) with Jarosite waste and clay matrix ratio of 1, 2 and 3. CCB was prepared using different ratios of Jarosite waste and clay with 15% and 30% MPRs. In Fig. 7, the details are: (a) 1:1 ratio of Jarosite waste and clay with 15% MPRs; (b) 1:1 ratio of Jarosite waste and clay with 30% MPRs; (c) 2:1 ratio of Jarosite waste and clay with 15% MPRs ; (d) 2:1 ratio of Jarosite waste and clay with 30% MPRs ; (e) 3:1 ratio of Jarosite waste and clay with 15% MPRs ; (f) 3:1 ratio of Jarosite and clay with 30% MPRs. MPRs mainly consists of CaO and firing CaO at ~~high~~ high-temperature results in better blending of Jarosite waste clay matrix. In the CCB developed using 15% MPRs with 1:1 ratio of Jarosite waste clay matrix, the texture of the surface was found to be compacted, well densified, solid, monolithic and waste matrices were found well bonded with each other. When MPRs ~~was~~ were used at 15% along with Jarosite waste clay matrix, the internal section of the bricks showed good binding, plain surface and slightest pore space could also be seen. As a result, water absorption capacity of bricks was found to be least as compared to the products developed with 30 % and 45 % MPRs application. **Fig. 8 (a-c)** of section 3.7 displays the morphological (SEM) structure of the internal surface of s/s sintered products fabricated using Jarosite waste clay ratio of 1 and 2 in which no additives were applied.

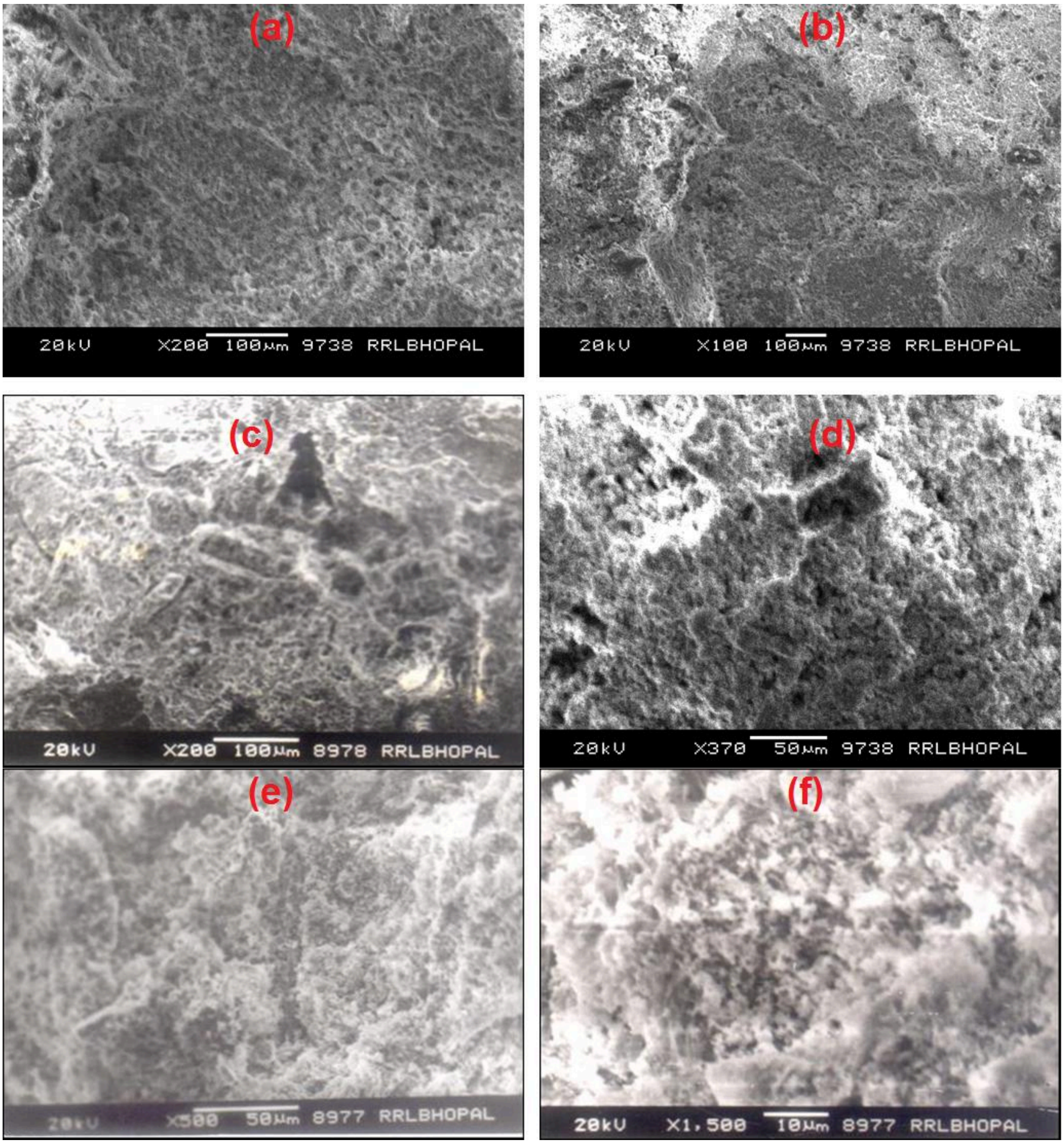

Fig. 7 SEM microstructure of fracture surface of CCB

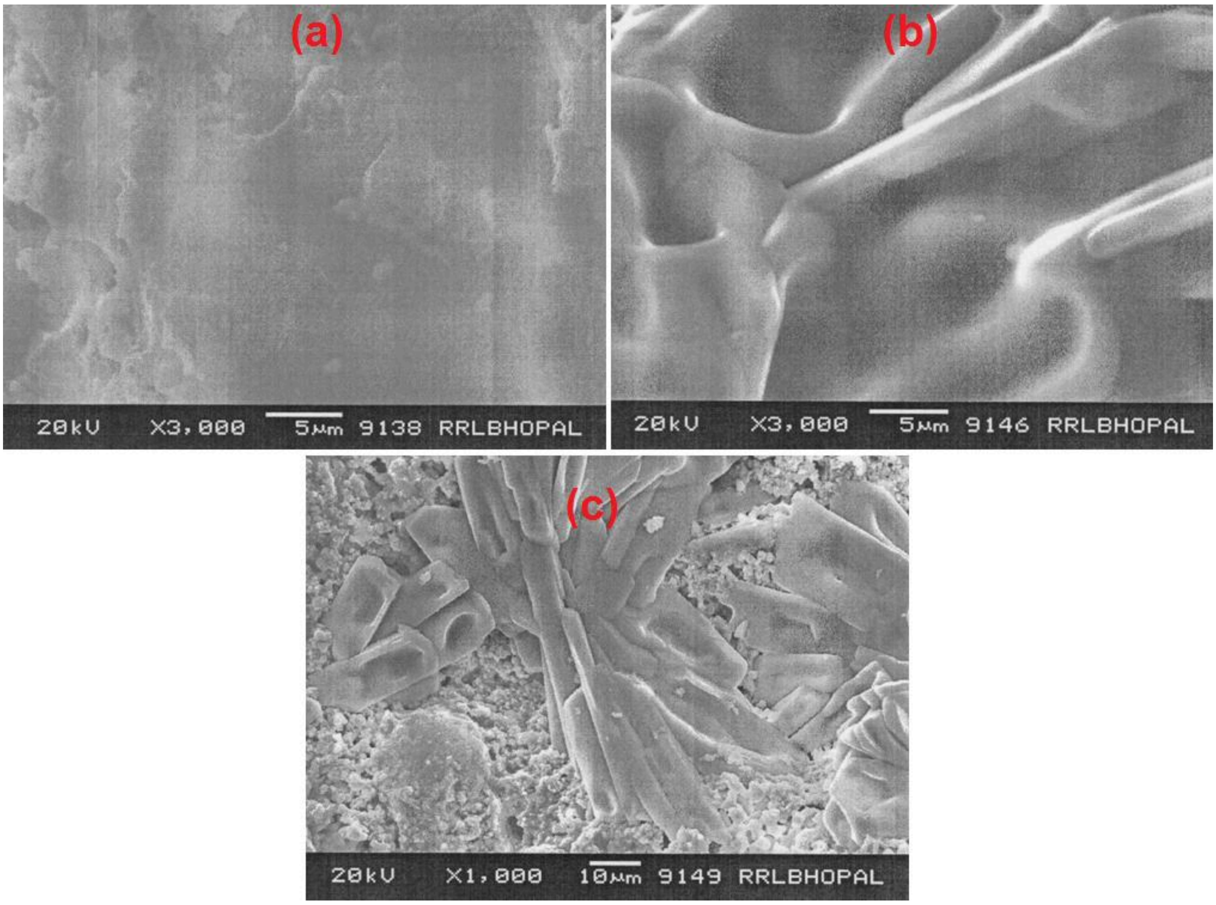

Fig. 8 SEM microstructure of fracture surface of s/s sintered products developed from different ratios of Jarosite waste and clay without additives (a) 1:1 ratio of Jarosite waste and clay (b) 2:1 ratio of Jarosite waste and clay (c) 3:1 ratio of Jarosite waste and clay.

Due to the fine texture of Jarosite waste, there is significant densification of the product and no pore space could be seen. The shrinkage was optimum and the products did not meet the requisite properties (toxicity leachate concentration) as recommended by the USEPA standard for use in engineering application.

3.8 Effect of MPRs on Toxicity Leachate Concentration in CCB

To investigate the potential of MPRs as additives in immobilizing hazardous Jarosite, the TCLP approach was followed as a tool in confirming the environmental significance of toxic substances in the wastes matrixes. **Table 5** of section 3.8 shows the comprehensive results on the effect of MPRs, Jarosite waste and clay matrix on leachate concentration of the most critical elements such as Ag, Cd, Pb and Se in CCB.

Table 5. Effect of MPRs, Jarosite waste and clay matrix on toxicity leachate concentration in CCB

Sample ID	**Quantity (g) of s/s sintered matrices**			**TCLP leachate concentration (ppm)**			
	Jarosite waste	**clay**	**MPRs**	**Ag**	**Cd**	**Pb**	**Se**
1M	500	500	0	2.51	0.316	10.45	0.246
2M	**425**	**425**	**150**	**0.061**	**0.291**	**3.84**	**0.224**
3M	**350**	**350**	**300**	**0.04**	**0.256**	**2.81**	**0.207**
4M	275	275	450	0.028	0.23	1.76	0.188
5M	666.66	333.33	0	2.6	0.378	11.8	0.27
6M	566.666	283.333	150	0.15	0.347	4.08	0.246
7M	466.67	233.33	300	0.096	0.316	3.11	0.233
8M	366.66	183.33	450	0.061	0.277	2.11	0.213
9M	750	250	0	2.71	0.71	13.465	0.293
10M	637.5	212.5	150	0.276	0.518	4.38	0.267
11M	525	175	300	0.211	0.47	3.46	0.254
12M	412.5	137.5	450	0.15	0.421	2.52	0.236
13M	800	200	0	2.82	0.741	15.3	0.317
14M	680	170	150	0.401	0.592	4.71	0.287
15M	560	140	300	0.316	0.539	3.91	0.273
16M	440	110	450	0.241	0.495	2.96	0.254
Raw Jarosite waste (ppm)				78.51	27.33	35.87	2.53

Results from the study revealed that there was a significant decrease in the leachate concentration of lead in CCB with MPRs application. It is obvious from the results that in the

Jarosite waste clay matrix composite sintered brick system, the maximum concentration of Ag leachability was 2.82 ppm where no MPRs ~~was~~ were applied. The leachability of Ag in this CCB, sample (**Table 5**), was lower than that of USEPA recommended limit (5 ppm) and the concentration of Lead was recorded as 15.3 ppm, which is quite higher than that of USEPA standard limits (i.e. 5ppm). ~~But, i~~In all cases, the leachate concentration of all critical toxic elements in CCB was remarkably reduced as compared to the initial concentration of lead in Jarosite waste (78.51 ppm). It is recorded from the results (**TableS6**) that with the increment in the concentration of Jarosite waste, there is considerable increase in the lead content in CCB. The CCB developed with Jarosite waste clay matrix ratio 1, 2, 3 and 4 resulted in ~~lead~~ leachate of~~-~~ lead 10.45 ppm, 11.8 ppm, 13.465 ppm, and 35.87 ppm~~ respectively~~, which was higher than the USEPA standard confirming it as hazardous nature. ~~But, t~~The leachate concentration of all these elements was low in the CCB developed with incorporation of MPRs, which has confirmed the non-hazardous nature of CCB. Results revealed that through the sintering process under solid-state reaction, Jarosite mineral's toxic elements were detoxified and immobilized through complexing in the calcium silicate matrix. The leachate concentration of other toxic elements such as Ag, As, Cd, Co, Cu, Cr, Ni in the CCB with incorporation of MPRs (15-30%) under optimized conditions ~~was~~ were recorded as below the USEPA prescribed standard confirming non-hazardous materials (**Table 6**).

Table 6. Mixture design parameters with responses of CCB

	Component	Component	Component	Response	Response	Response	Response
Run order	**A:Jarosite waste (g)**	**B:Clay (g)**	**C:MPRs (g)**	**Comp. Strength (kg/cm^2)**	**Water Abs. (%)**	**Shrinkage (%)**	**Density (g/cc)**
10	395.00	278.75	326.25	36.4986	21.6019	1.20686	1.55419
5	275.00	500.00	225.00	56.298	17.4042	4.93337	1.69279

13	275.00	275.00	450.00	62.6037	20.3158	4.51261	1.54597
3	800.00	110.00	90.00	95.1573	16.3918	31.8146	1.9482
9	657.50	218.75	123.75	59.738	19.3763	15.6145	1.76205
4	500.00	500.00	0.00	64.2422	19.488	13.1416	1.73207
2	275.00	275.00	450.00	61.2037	22.0158	4.61261	1.49597
11	800.00	110.00	90.00	95.1573	16.3918	31.8146	1.9482
14	500.00	500.00	0.00	62.1322	17.218	12.1416	1.69921
1	440.00	110.00	450.00	18.3033	24.6452	2.10036	1.48196
6	515.00	282.50	202.50	37.7824	20.9435	4.88401	1.63995
12	275.00	500.00	225.00	58.258	15.6142	4.73337	1.64279
8	650.00	350.00	0.00	84.7985	17.4845	20.6217	1.77608
7	620.00	110.00	270.00	24.8051	20.9703	9.04665	1.67207

As reported and discussed in the previous section, the quality of CCB developed using 15-30 % MPRs with a 1:1 Jarosite waste clay ratio met the mechanical strength for use in engineering applications as burned clay building brick as recommended by Indian Standard (IS 1077:1992) specification. The toxicity leachability results confirmed that MPRs was a potential resource in immobilizing / detoxifying hazardous Jarosite waste as well as contributed towards attaining quality products for use in building construction applications. ~~Earlier~~ An earlier study on MPRs applications for hydrothermal solidification of clay –quartz mixture showed that calcined marble dust could be employed as a substitute source of active CaO and hydrated phase contributed to the improvement in the strength of s/s samples suitable as new building material(Sarkar et al., 2006). Since the hydrothermal s/s process involves considerable energy for calcinations to obtain lime from $CaCO_3$, the present study showed that MPRs could be used ~~not only~~ for manufacturing sintered bricks. ~~but also it~~ It greatly influenced– and acted as catalyst for immobilizing hazardous Jarosite waste (Montanaro et al., 2001).

In summary, although the incorporation of MPRs decreased the compressive strength but and it contributed to reduce reducing shrinkage and density significantly. Whereas the CCB developed using 15% MPRs with 1:1 Jarosite waste clay matrix ratio showed a mean compressive strength of 54.61 kg/cm^2, which is acceptable quality for use in construction purpose. This combination could be an intermediate and optimum condition in which the product met all desirable mechanical properties for use in building construction applications. The element leachate concentration were was within the USEPA recommended safe limits. **Table 5** shows the summary of the optimized conditions in achieving optimal quality of MPRs, Jarosite waste, and clay matrix composite products (CCB) for safe utility in construction application.

3.9 Model Validation in Optimizing CCB Quality and Waste Matrixes Concentration

In the present paper, among several responses evaluated and analyzed, the model was fit to data for the response compressive strength using analysis of variance (ANOVA) and least least-squares techniques. The validated and graphically interpreted contour plot, trace plots and 3D graph can be used to predict the effect of response variables (quality) of composite bricks with varying concentration of MPRs and Jarosite waste in clay matrix system.

3.9.1 Model Validation in Optimizing CCB

The experimental conditions for mixture model and responses compressive strength, water absorption, shrinkage, and density are shown in **Table 6** of section 3.9.1. The polynomial models described in classic mixture approach were fitted to data employing least squares techniques and analysis of variance (ANOVA). From the ANOVA results, the significance of the treatment effect was obtained. The results of ANOVA for compressive strength are displayed in **Table S4**. From this table, the row with source “Quadratic” indicates that the coefficients of the quadratic model terms are not equal to zero as indicated by a low value (< 0.05) of "Prob > F" also called as p-value. The associated p-values (Prob > F) are interpreted when the true coefficient equals zero. The row with source "Special Cubic" the special cubic coefficients contrast from zero. Since the "Prob >F" of 0.0481 is less than 0.05, the special cubic terms were also included in the model. Similarly, the cubic coefficients are required in the model. The residual coefficients are not required as "Prob > F" of 0.945 exceeds the value 0.05.The lack of fit value indicates the lack of fit with respect to pure error. The lack of fit value should be non-significant (Prob F > 0.05), to fit the data to the model. So, a A lack of fit test was carried out using ANOVA. For compressive strength, the lack-of-fit test (**Table S5**) for the special cubic model gives "Prob > F" equal to 0.945, which is not significant indicating the experimental data fit the model. **Table S6** shows the model summary statistics for the response compressive strength. It shows that the special cubic model provides a "Predicted r^2" values of 0.9970 which is in excellent agreement with the "Adjusted r^2" of 0.9985.

3.9.2 Process Optimization

Response trace plots and contour plots are used to interpret graphically the validated model results. **Fig. 9** of section 3.9.2 shows the response trace plots for compressive strength. The response trace plot comprises of 3 overlaid plots, one for each constituent of the CCB namely Jarosite waste, clay, and MPRs. The plot demonstrates the "effect" of variation of each component on compressive strength. Results revealed that with the increment in the amount of Jarosite waste, there is an increase in the compressive strength. The effect was higher with the higher amount yielding higher strength. MPRs application reduced compressive strength and minimum was with maximum use (45%) of MPRs. **Fig. 10** of section 3.9.2 depicts the response contour plots for compressive strength of CCB. From these figures, it is apparent that as in case of trace plots, increase in concentration of Jarosite waste increased compressive strength. Addition The addition of clay increased the compressive strength up to a certain level with slight decrease in compressive strength at higher concentrations. This confirms that high plasticity soil alone cannot be a very good candidate in making good quality bricks and MPRs as well as Jarosite waste considerably influenced the improvement in the performance of CCB. **Fig.11** of section 3.9.2 shows the 3D graph of compressive strength. It reveals that the response of each characteristics changes with change in constituents. Sintering influenced the texture along with structure leading to the substantial changes in the mechanical properties of the CCB. The sintering efficiency was found to be dependent on the presence and content of SiO_2, CaO, and PbO, along with the alkaline oxides in MPRs. Jarosite waste and clay matrix system which contributed in to the Jarosite waste phase transformation resulted in densification and transformation into main crystalline phases, hematite and magnetite, and calcium silicate compound. Desirability functions were used to discover the optimum mixture proportions by Numerical optimization.

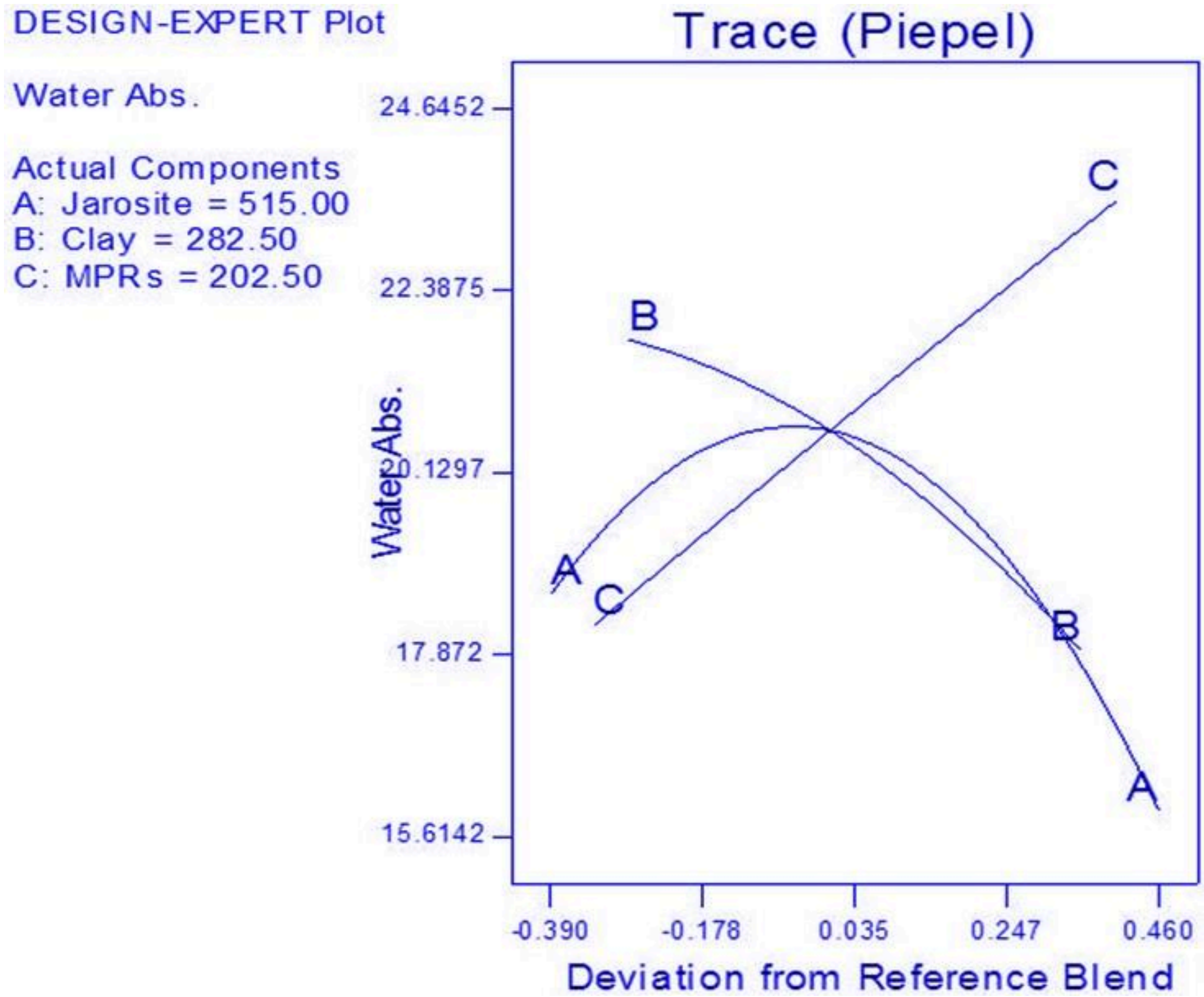

Fig. 9 Response trace plot for compressive strength of CCB

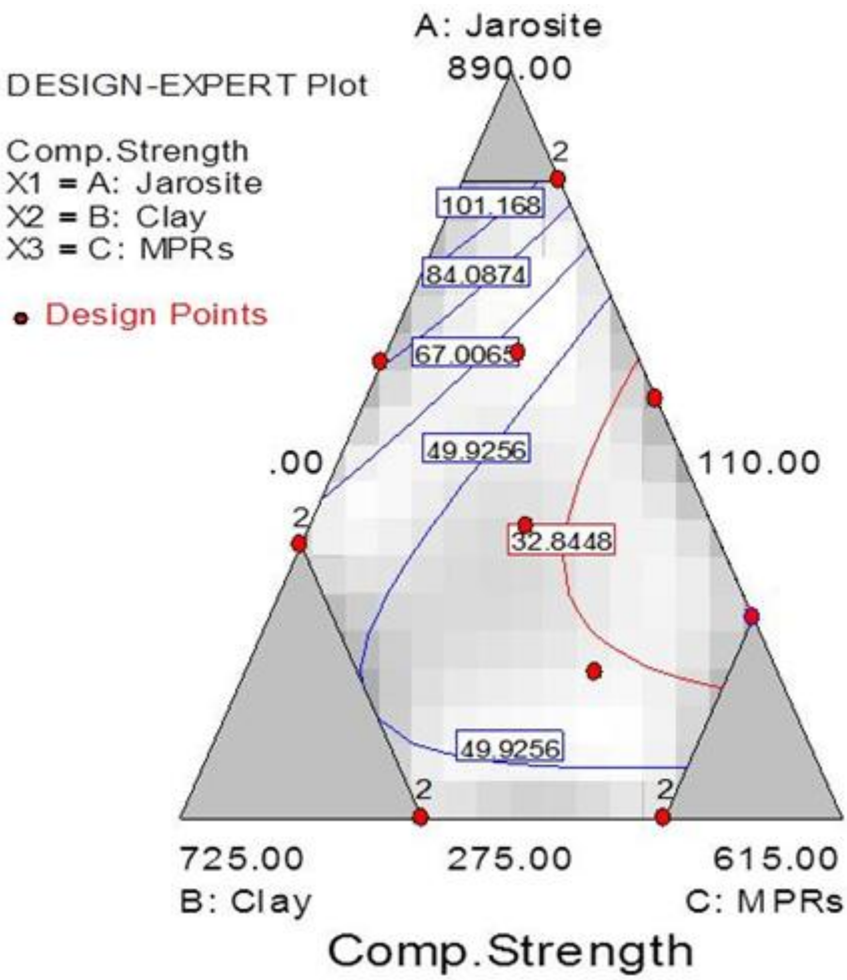

Fig. 10. Response trace plot for compressive strength of CCB

The desirability function values vary between 0 and 1. The desirability value for brick compressive strength is between 18.3 and 95.15 (kg/m^2) and 0 otherwise. **Table S7**shows the constraints and parameter range for desirability function. Based on the model prediction, the optimum mix design which maximizes the brick properties are shown in **Table 7** of section 3.9.2. The model predictions for brick properties at a given set of brick and the overall desirability value for these brick mixtures were 1, 0.52 and 0.788. The optimized mix design of the mixture approach model is 275g Jarosite waste; 321.21g Clay; 403.79g MPRs in which the response Compressivestrength resulted in 60.24 kg/cm^2; water absorption 20.13%; shrinkage 3.92 % and density 1.55 g/cm^3. These predicted results were compared with the actual experimental results and established that the response characteristics are in very good agreement with each other.

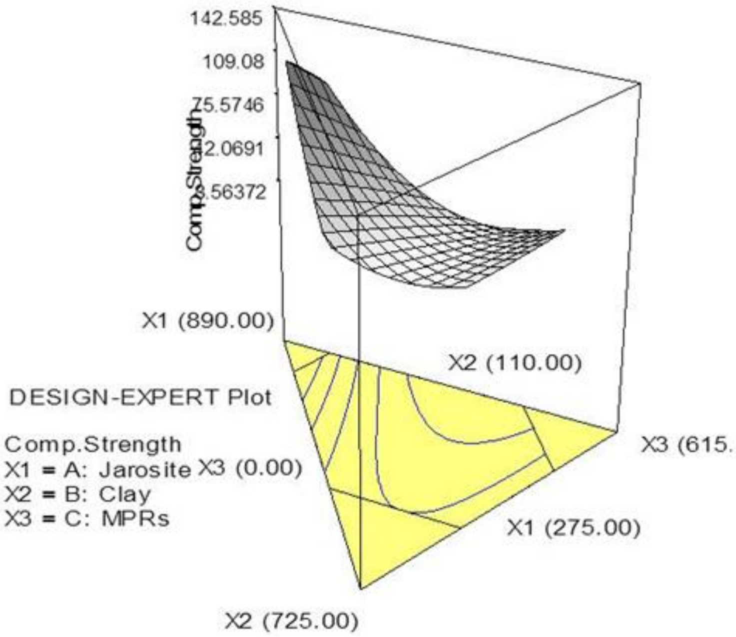

Fig. 11 Response 3D graph for compressive strength of CCB

Table 7. Optimum Mix design to maximize the brick properties

Number	Jarosite waste (g)	Clay (g)	MPRs (g)	Comp. Strength (kg/cm^2)	Water Abs. (%)	Shrinkage (%)	Density (g/cc)	Desirability	
1	275.00	321.21	403.79	60.2467	20.1301	3.92915	1.5514	0.788	Selected
2	668.44	150.15	181.41	47.2889	19.7845	14.642	1.75118	0.520	
4	276.53	273.47	450.00	61.3518	21.2195	4.4735	1.51731	1.000	

Table 8 of section 3.9.2. shows the leachate concentration of toxic elements in CCB under optimized conditions. Integration of MPRs (15% MPRs) with a 1:1 Jarosite waste clay matrix ratio showed intermediate conditions to achieve desirable quality of CCB in terms of

mechanical strength and toxicity leachate point of view to use CCB as alternative materials to burned clay bricks.

Table 8. Leachate concentration of toxic elements in CCB under optimized conditions

Sr. No.	Elements	MPRs (15%) with 1:1 Jarosite waste clay ratio	USEPA Limit(ppm)
1.	Pb	3.84±0.027	5.0
2.	Cd	0.291±0.007	1.0
3.	Ni	4.14±0.16	70.0
4.	Ag	0.061±0.01	5.0
5.	Cr	< 0.0005	5.0
6.	As	0.384±0.036	5.0
7.	Se	0.224±0.046	1.0

All the values are in ppm

4. Opportunity for sustainable manufacturing of CCB

Bricks have been traditionally used as major construction materials in civil infrastructure and housing sector. To meet the demand in the society, exploitation of natural resources, especially the clay minerals leads to damaging the environment and eco-system. ~~Currently~~ The available fired bricks are expensive, ~~it~~ they involve huge energy for production~~,~~ while firing at high temperature and not much attracted by ~~end~~ end-users. The builders, architects, and consumers are exploring the scope for newer and alternative materials to traditional fired bricks for construction, civil infrastructure, and other building applications. ~~Increasing~~ The increasing price of bricks, non-availability of natural clay, manufacturers and user agencies are looking for new materials to overcome the present issues on traditional bricks on a competitive technical and economic ~~prospective~~perspective. The developed CCB in the present program~~me~~ is expected to meet the ~~end~~ end-users' requirement as well as it paves a way for effective use of waste resources as a raw material~~s~~ in making composite bricks equivalent and better in quality than~~–~~ that of traditional bricks~~.~~. Presently, India produces about 550 million tons of inorganic wastes annually. This huge quantity of wastes creates major environmental danger both for living and non-living systems internationally. The major sources of such wastes are marble wastes, fly ash, red mud, metallurgical wastes including Jarosite waste. To address these alarming challenges, the CCB developed in the present study would provide innovative solutions with great commercial ~~opportunity~~ opportunities for effective use of inorganic wastes and organic wastes in manufacturing ~~value~~ value-added hybrid green composite bricks in a sustainable manner.

Conclusions

Multidisciplinary research work was performed in the present study using an integrated approach to investigate and understand the characteristics of MPRs, hazardous Jarosite wastes and clay soil. Subsequently, these waste materials were converted into harmless sustainable ceramic composite bricks (CCB). The findings of the present study showed that application of MPRs reduced the plasticity, improved the quality of CCB and acted as catalyst to immobilize toxic substance in CCB made out of complex wastes.~~,~~ The Jarosite waste served as a raw material to partially replace clay in making CCB. The statistically design experimental results confirmed that addition of 15-30 % MPRs with 1:1 Jarosite clay matrix is an intermediate condition to have satisfactory compressive strength (49.62-52.8kg/cm^2), water absorption (16.65-17.93%), shrinkage (3.45-4.2%) and density (1.57-1.63g/cc) in which toxicity leachate concentration was within the USEPA safe limit as well as CCB meeting the desirable quality as per IS standard to be used in building construction. The toxicity leachate studies also demonstrated that the leachate concentration of toxic elements in the CCB developed using15-30 % MPRs with Jarosite waste clay matrix ratio 1 were found to be below the USEPA TCLP toxicity limits and CCB meeting all desirable quality, equivalent to that of burned clay bricks. From the RSM model, it is evident that the predicted results were compared with the experimental data and confirmed that the response characteristics are identical.

Realization of this technology will provide multiple solutions on multidisciplinary subject for multifunctional applications. Commercial exploitation of findings of this study will create new employment, contribute to enhance economy & provide holistic solutions for Jarosite waste and marble waste safe and effective utilization globally.

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