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Characterization studies of tannery sludge, flyash and GGBS

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This work focuses on characterization of CETP tannery sludge, flyash and GGBS and the properties of the CETP tannery sludge is compared with flyash and GGBS using a variety of techniques, including Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) analysis, X-Ray diffraction (XRD) and X-ray fluorescene spectroscopy. Heavy metal composition in the sludge, flyash and GGBS is given by XRF studies. SEM diagrams for cross sectional area of the samples were taken. The mircroscopic images of GGBS, flyash and tannery sludge are found to be flaky, spherical and granular respectively. XRD studies proved that GGBS is amorphous due to the presence of amorphous silica and alumina. The tannery sludge and flyash is found to be crystalline with minority of amorphous phase. In this study, Fourier Transform Infrared Spectrophotometry (FTIR) provides a quick and relatively inexpensive method for identifying, quantifying and to determine the frequency of functional groups tannery sludge, flyash and GGBS. This research quantified the resemblance of the characteristic properties of the flyash GGBS and tannery sludge.

Keywords: CETP tannery sludge, flyash, GGBS, XRF, SEM, XRD, FTIR analysis.

Introduction

As India is one one of the developing countries in the world there is a need to exploit every bit of natural source. Because of development in the industrialization and urbanization, a lot of wastage has been dumped into the environment polluting the natural resources[1]. Safeguarding our natural resources have reached to a point of crisis due to unplanned urbanization and industrialization[2]. Solid waste from tanneries, coal mining and metal industries seems to be one of the main cause in the depletion of surface and subsurface of the soil. The problem of environmental pollution on account of essential industrial growth is the problem of disposal of industrial wastes, whether solid, liquid or gas. All these three types of wastes have the potential of ultimately polluting land. Polluted soil in addition to other effects, directly affects ground water not only in industrial areas but also in agricultural fields, as well as the beds of rivers, creating secondary source of pollution[3,4]. Human health is mainly affected due to toxic hazards generated through the unskilled and unprotected handling of chemicals, and treated hides and skins[5] from tanneries, coal mining and as well as from iron and steel industry. Dumping these wastes in the lands has posed a serious disposal and ecological problem to environment in addition to occupying a large tract of scarce cultivable land. Although the beneficial use of flyash and GGBS in concrete, brick making, soil stabilization treatment and other applications have been recognized, only a small quantity is being utilized in our country currently in such applications. It is unfortunate that there are no reliable estimates from the above mentioned industries, of the quantity and types of hazardous wastes generated.

Materials and methods:

The materials such as tannery waste, ground granulated blast furnace slag (GGBS), flyash were used for this studies.

Chemicals and collection of materials:

The CEPT sludge samples were collected from common tannery effluent treatment plant, Ranipet, India. The tannery waste collected from the tannery effluent treatment plant was dried in an oven for nearly 2 h to remove the moisture from the sample. The dried samples were powdered well and sieved well and stored for further testing of the sample. Ground granulated blast furnace slag comprises mainly of calcium oxide, silicon di-oxide, aluminium oxide, magnesium oxide was purchased commercially. The flyash used for this study was collected from Lignite Thermal

Power Plant, Neyveli, Tamilnadu. As the flyash is obtained from lignite, this falls under the category of high calcium flyash i.e. Class C flyash. The flyash is sieved through 50 μm standard sieve and used for the analysis.

Physicochemical properties of tannery sludge, flyash and GGBS:

Table 1. Characterization of the CEPT tannery waste

Parameter	Tannery sludge	Flyash	GGBS
Colour	Brownish	Grey	Off white
Specific gravity	2.56	2.2	2.9

Instrumental analysis:

X-Ray Fluorescence shows that the heavy metal composition in the tannery sludge, flyash and GGBS. X-Ray diffraction is a powerful nondestructive technique for characterizing the sludge, flyash and GGBS. It provides information on structures, phases and the peak intensities are determined by the distribution of atoms within the lattice. Consequently, the X-ray diffraction pattern is the fingerprint analysis of periodic atomic arrangements in the tannery sludge flyash and GGBS. FTIR analysis is carried out for the all three samples to find the absorption features which result from the detection of vibrational modes, i.e. lattice vibrations and/or molecular group vibrational modes. Qualitative identification of the individual samples is possible because they have characteristic absorption bands in the midrange of the infrared, wave numbers 4000 to 400 cm^{-1}. Samples were analyzed in a 4500 FT-IR with a diffuse reflectance attachment from wave numbers 4000–400 (cm^{-1}).

Results and discussion

FTIR analysis:

The FTIR spectra obtained for the flyash, GGBS, and tannery waste is illustrated in Figs. 1a, 1b and 1c. The most important transsmission bands of flyash are at 3432 cm^{-1}, 1661 cm^{-1}, 1454 cm^{-1}, 1112 cm^{-1}, 681 cm^{-1}, 455 cm^{-1}. In flyash, a large broad band at 3432 cm^{-1} is attributed to the presence of the O-H stretching frequency of Si-OH group. The band at 1661 cm^{-1} assigned to C=O vibration. A less intense peak at 1454 cm^{-1} is assigned to the stretching vibration of O-C-O in $CaCO_3$ confirms the presence of lime in flyash. An intense band at 1112 cm^{-1} corresponds to the asymmetric stretching of Si-O-Si or Al-O-Si group. The peak at 681 cm^{-1} is sharp and less intense, corresponds to Si-O-Si and Al-O-Si symmetric stretching vibration. The strong peak at 455 cm^{-1} is due to the in-plane bending of Si-O-Si or O-Si-O group.

The FT-IR spectrum of tannery sludge presented in Fig. 1c contains the stretching vibration at 3747 cm^{-1} and is related to O-H group. Absorption band at 3630 cm^{-1} may be assigned to the group calcium hydroxide. A broad peak at 3296 m^{-1} may be assigned to chromate group. A very weak absorption band near 2360 m^{-1} is related to C=O bond stretching. The peak at 1676 cm^{-1} may be correlated to Si-O-H bending mode of vibration. The intense band at 1458 cm^{-1} is the characteristic peak of calcium assigning (ν_3) vibrational mode. The very weak and broad at 1107 cm^{-1} and 1077 cm^{-1} may be assigned to sulphates and chromium sulphates. The very sharp peak at 873 cm^{-1} may be assigned to Al-O stretching vibration. A weak and less intense absorption band is found at 606 m^{-1} may be assigned to C=S bond stretching vibration of sulphides and (ν_4) vibrational mode of sulphates. The band centered around 750 cm^{-1} shows the alkaline (Na, K) content in sample. A less

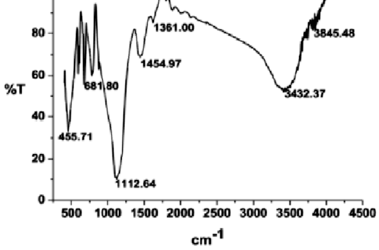


Fig. 1a. Flyash

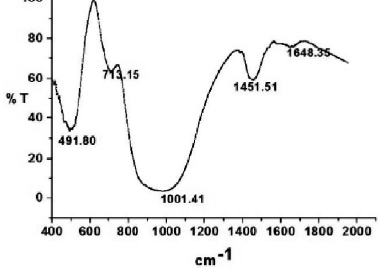


Fig. 1b. GGBS

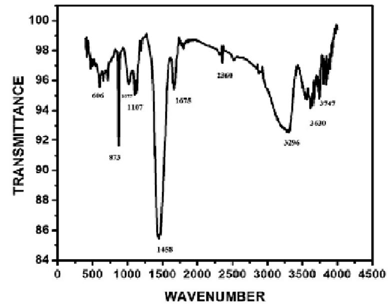


Fig. 1c. Tannery waste.

intense peak around 550 cm^{-1} and 720 cm^{-1} is assigned to the trivalent chromium present in the tannery sludge. As the trivalent chromium content in the sludge is very less the peak intensity is found to be very less.

The FT-IR analysis of GGBS presented in Fig. 1b shows a broad weak band at 1648 m^{-1} is due to the presence of both species C-O stretching and N-O asymmetric stretching indicative of carbonates and nitrates. The broad and less intense band at 1451 cm^{-1} is assigned to the ν_3 vibrational mode of calcium carbonates. The weak absorption at 720 cm^{-1} is assigned to the the in-plane bending (ν_4) mode of CO_3^{2-} group. The strong band at 1001 cm^{-1} is assigned to the characteristic peak of sulphates of calcium and may also be assigned to the Si-O and Al-O bond. The strong absorption band at 491 cm^{-1} of the spectrum shows the bending frequency of Si-O bond. Hence, the spectral details confirms the characteristic features, usually absorption features, which can be related qualitatively.

XRD analysis:

The XRD of the tannery sludge, flyash and GGBS were analysed. The X-ray diffraction pattern of flyash illustrates the crystalline phases present in the flyash namely, quartz and mullite.

Mullite (alumina silicate) shows peaks at 25.5°, 27.2° of 2θ values. The quartz exhibits peaks at 21°, 26.7°, 36.5°, 50.4°, 59.9°, 68.1° of 2θ values. The presence of amorphous phases is identified as a broad diffraction "hump" in the region between 10 to 20 degrees (2θ). The hametite shows a very less intense peak near 32.5°, 36°, 51.5°, 57.5° of 2θ values. The 2θ value at 62.5° shows the magnetite form in the flyash. GGBS shows the amorphous nature and there is no well defined peak found in XRD. The amorphous vitreous phase of GGBS is attributed to the presence of amorphous silica and alumina. In the tannery sludge the high intense peak at 29.4°, 26.5°, 31.7° of 2θ shows the monoclinic phase of calcium sulphate hemihydrates and gypsum. 36.1° shows the chromium oxide peak in the sample. Sharp peaks denote the crystalline with amorphous nature of the sludge sample.

XRF analysis:

The average concentration of major metal ions, such as Cr, Cd, Pb and Fe, in the sludge, flyash and GGBS is confirmed by the XRF analysis (Table 1).

Heavy	Chemical compostion (%)		
metals	Flyash	GGBS	Tannery waste
Mo	0	0.08	0.06
Nb	0.03	0.05	0.06
Zr	0.07	0.05	0.02
Fe	7.38	0.67	0.54
Mn	0.3	0.43	0
Cr	0	0	3.77
Ti	0.42	0.54	0.20

SEM analysis:

The microstructure of precursors was analyzed using scanning electron microscope (SEM) (Fig. 3).

The microstructure of flyash is appeared to be a glassy, hollow, spherical vitreous particles of different sizes namely

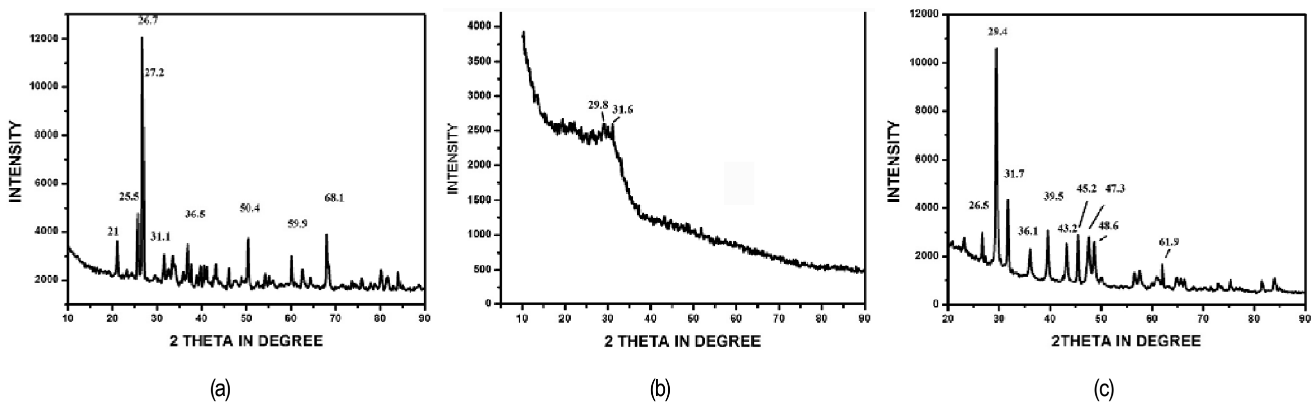
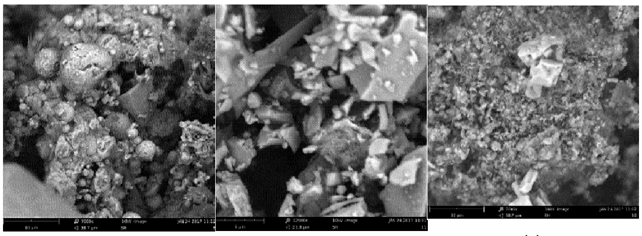


Fig. 2. XRD analyist of (a) flyash, (b) GGBS and (c) tannery waste.



(a) (b) (c)

Fig. 3. SEM images of (a) Flyash, (b) GGBS and (c) tannery waste.

microspheres which are contained by the large cenosphere particles (thin walled hollow spheres) formed during the combustion process. The resulting macro particles are named as "plerosphere". Crystalline phase is also observed due to the crystals of mullite and iron in the microstructure analysis of flyash. Furthermore, surface texture appears to be smooth and dense to highly porous with coatings, such as magnetite. The microstructure of slag appears to be flaky, crystalline particle with smooth edges and angles. The surface is enriched with coating of silica. The surface texture of tannery waste appeared to be smooth, granular, dense to highly porous morphology is seen and the surfaces had sometimes coating of chromium.

Conclusion

The characteristic studies carried out for flyash, GGBS and tannery waste concludes the following points. Based upon data recorded in FTIR analysis, it can be concluded that Si-O-Si, Al-O-Si groups are present both in flyash and GGBS. A strong peak is obtained in the figure print region of flyash FTIR spectra confirms the presence of lime in flyash. Like wise in tannery sludge a less intense band is obtained for the carbonates and high intense absorption band is found for sulphates of calcium. A less intense peak near 720 cm^{-1} and 550 cm^{-1} confirms the presence of chromium in tannery sludge. It can be concluded that the presence of calcium in sludge may find its application in binding with geopolymers as already flyash and GGBS play a vital role in geopolymerisation process. Further the XRD analysis of all the three samples proves that the GGBS contains maximum amount of amorphous silica or alumina. In flyash and tannery sludge both crystalline and amorphous phases exists which proves that tannery sludge can be utilized for geopolymerisation process with GGBS and flyash. XRF analysis concludes that a rich iron content in flyash proves the presence of hametite structure in it and chromium content in tannery sludge. From the microscopic structure, it can be concluded that different morphologlical structure is seen in all the three samples. This research quantified the resemblance of the characteristic properties of the flyash, GGBS and tannery sludge with appropriate proportion of certain additives can be proportioned to meet the strength and workability requirement in Geotechnical application.

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