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Research Article

Re-use of fluoride contaminated bone char sludge in concrete

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ABSTRACT

Managing sludge generated by treating groundwater contaminated with geogenic contaminants (fluoride, arsenic, and iron) is a major issue in developing nations. Their re-use in civil engineering applications is a possible pathway for reducing the impact on the geo-environment. This paper examines the re-use of one such sludge material, namely, fluoride contaminated bone char sludge, as partial replacement for fine aggregate (river-sand) in the manufacture of dense concrete specimens. Bone char sludge is being produced by defluoridation of contaminated groundwater in Nalagonda District, Andhra Pradesh, India. The impact of admixing 1.5–9% sludge contents on the compression strength and fluoride leaching potential of the sludge admixed concrete (SAC) specimens are examined. The compression strengths of the SAC specimens are examined with respect to strength criteria for manufacture of dense, load-bearing concrete blocks. The fluoride release potential of the SAC specimens is examined with respect to standards specific to disposal of treated leachate into inland surface water.

1. Introduction

Management of sludge generated by treatment of groundwater contaminated with geogenic contaminants (fluoride, arsenic, and iron) is a major issue in developing nations. Frequently, the sludge is stored in a pit or disposed on ground leading to possible contamination of surface water and groundwater sources. Re-use of geogenic sludge materials in manufacture of bricks are being explored as pathways for minimizing their impact on the geo-environment [1–4]; similar to studies made with industrial/municipal sludge [5–7].

Besides brick manufacture, waste materials (fly ash, bottom ash, blast furnace slag, waste foundry sand, industrial sludge, construction and demolition wastes, mine tailings, waste-gypsum) are being increasingly explored as replacement of natural aggregates in concrete [8–17]. The present study examines the feasibility of re-use of fluoride-contaminated bone char sludge as partial replacement for fine aggregate (river-sand) in concrete specimens. The compressive strengths of the sludge admixed concrete (SAC) specimens are examined with respect to strength requirements of load-bearing, dense concrete blocks. The fluoride concentrations released by SAC specimens in leachability tests are examined with respect to standards specified for disposal of treated leachate into inland surface water. Standards for treated leachate are considered as SAC blocks represent a variety of chemically treated waste.

2. Production of bone char sludge

Bone char sludge is produced by defluoridation of contaminated groundwater in Nalagonda District, Andhra Pradesh, India. The fluoride concentration in the groundwater samples of this region range from 4 to 6 mg/L. The permissible limit for fluoride concentration in drinking water is 1.5 mg/L [18]. Defluoridation of contaminated groundwater is hence performed by employing bone char-based community defluoridation system, which has a capacity to treat 1,25,000 L of fluoride-contaminated water using 50 kg of bone char [19].

Bone char is a blackish, porous, granular material, prepared by heating ground bone in a furnace, without or with only limited admission of atmospheric oxygen at 550 °C for about 4 h. Bone charcoal is composed by 57–80% of calcium phosphate [mainly as hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$)], 6–10% of calcium carbonate and 7–10% of activated carbon [20]. Bone char removes fluoride from contaminated groundwater by replacement of hydroxyl ions by fluoride ions according to the chemical reaction [20]:

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^- \quad (1)$$

Measuring the fluoride concentrations in the treated water samples monitored the defluoridation capacity of the bone char-based community defluoridation system in Nalagonda District. After the defluoridation capacity of bone char is exhausted the spent bone

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char is removed from the defluoridation system and stored in sealed bags as bone char sludge [19]. This study examines the impact of partial replacement of fine aggregate (river-sand) with bone char sludge on the engineering and environmental integrity of dense concrete specimens.

3. Methodology of study

3.1. Materials

The bone char sludge (natural water content = 3%) from Nalagonda District, Andhra Pradesh, India, was used in the study. The total mass content of fluoride in bone char sludge sample was determined to be 10.2 mg/g of sample. The total mass content of fluoride was determined by dissolution of the bone char sludge sample in 4 M caustic soda solution (NaOH) using microwave digestion method. Ordinary Portland cement was used in the preparation of concrete specimens. Crushed gravel (maximum particle size 12.5 mm) was used as coarse aggregate while, river-sand served as the fine aggregate (maximum particle size 4.75 mm).

3.2. Tests on bone char sludge

Particle size distribution [21], X-ray diffraction analysis, pH (solids to solution ratio 1:2.5) and electrical conductivity (solids to solution ratio 1:2) measurements were performed with the bone char sludge sample. The TDS of the sludge sample was estimated from the measured EC value. The bone char sludge was also subjected to leaching tests using a variety of extracting fluids.

In the ASTM water leach test [22], crushed samples of bone char sludge was agitated with distilled water (pH 5.6). After equilibration, the solids + solution mix was filtered and the filtrate analyzed. In the TCLP (toxicity characteristics leaching procedure) test [23], bone char sludge sample was agitated with the TCLP extractant. After equilibration, the solids + solution mix was filtered and the filtrate analyzed. The TCLP extractant was prepared by adding 5.7 mL of glacial acetic acid to 500 mL of distilled water, followed by addition of 64.3 mL of 1 molar NaOH solution and diluting the entire mix to a volume of 1 L. The resultant fluid has pH of 4.9. In the third category of leaching test, the bone char sludge was agitated with 0.001N and 001N HCl solutions and 0.001N and 0.01N NaOH solutions. After equilibration, the solid + solution mixes were filtered and analyzed.

In all the three category of leaching tests, a solid:solution ratio of 1:20 (particle size < 9.5 mm) and an agitation period of 18 h were used. After equilibration, filtrates in all leaching tests were analyzed for pH, EC and fluoride ion concentration (measured using fluoride ion selective electrode).

3.3. Tests on sludge admixed concrete specimens

3.3.1. Strength measurements

The concrete specimens (dimensions 100 mm × 100 mm × 100 mm) used in the study are representative of dense concrete blocks used as load-bearing units. The dense concrete blocks are expected to have minimum average compressive strengths of 4–5 MPa [24]. Various proportions of the waste were investigated by adding 1.5%, 3%, 6%, and 9% bone char sludge to the concrete mix on dry mass basis. The bone char sludge was added to concrete mix as replacement for river-sand. Concrete mix with 0% waste material served as the control mix. The mix proportions of all concrete mixes were based on a weight proportion of 1:3:6 (cement:sand:gravel content), representing the proportion for nominal concrete mix [25]. Typically, the control concrete mix comprised of 250 g of cement, 750 g of river-sand and 1500 g of coarse aggregate/gravel. The mix constituents were thoroughly hand-mixed till a mass of uniform color and consistency was obtained. The concrete specimens were prepared by manual compaction at near constant slump values that ranged between 25 and 30 mm. BIS 456 [25] suggests slump values ranging from 25 to 75 mm for low workability concrete. Water/cement ratios of 1.06, 1.13, 1.2, 1.35 and 1.43 maintained the near-constant slump values (25–30 mm) at sludge contents of 0, 1.5%, 3%, 6% and 9% respectively. Slump tests on concrete mixes containing varying sludge contents (0–9%) were performed in accordance with BIS 1199 procedure [26]. During preparation of the concrete specimens, each mix was placed in a mold in three layers and each layer was thoroughly tamped 25 times with suitable tamper [26] until the mold was filled up and then the excess mix was removed with a trowel. Three specimens were prepared at each sludge content.

The SAC specimens were de-molded after 24 h and cured in a water tank at room temperature for 28 days. To verify the fluoride released by the SAC specimens during curing period, fluoride concentrations in the water tanks were monitored periodically (Fig. 1). Measurements revealed that 0.19, 0.42 and 0.8 mg/L of fluoride is released from 0, 3% and 9% SAC specimens after 28 days of curing (Fig. 1), which is much lower than the standard specified for

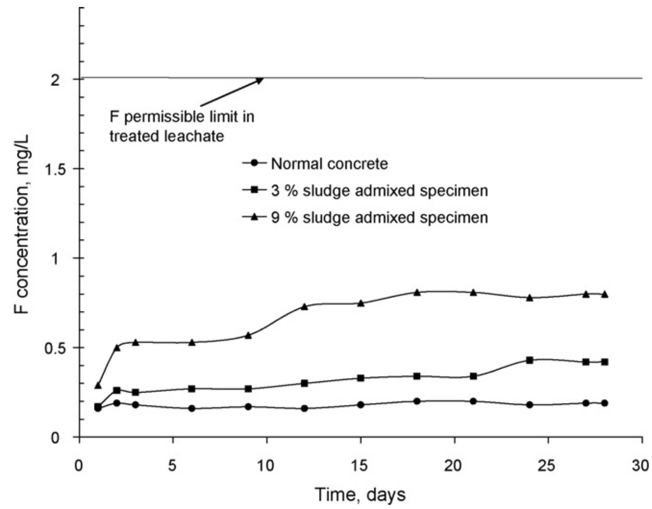

Fig. 1. Fluoride release during curing of concrete and SAC specimens.

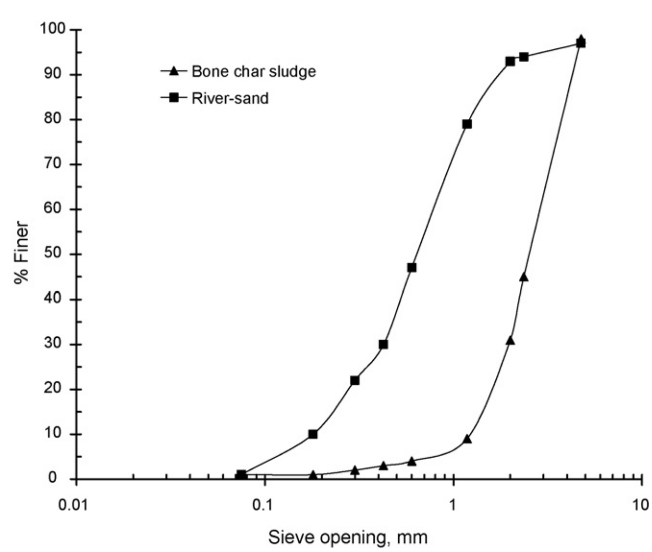

Fig. 2. Particle size distribution of bone char sludge and river-sand specimens.

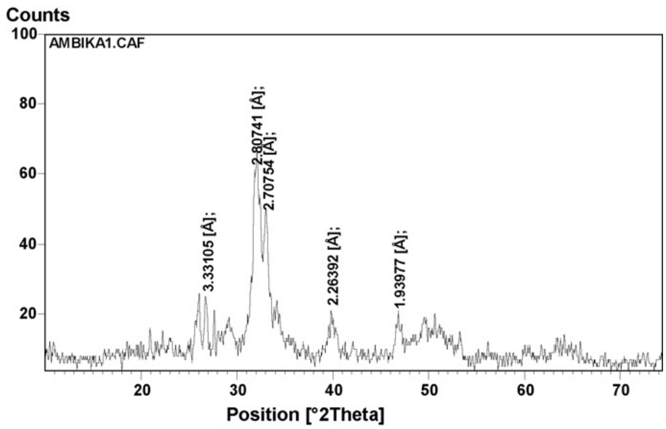

Fig. 3. X-ray diffraction pattern of bone char sludge.

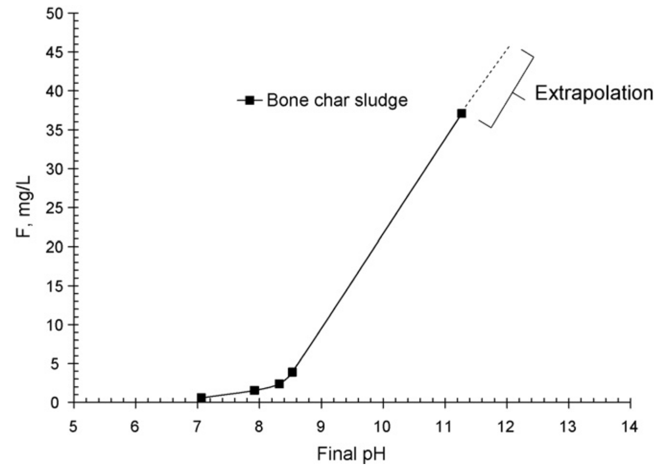

Fig. 4. Fluoride released by bone char sludge as function of pH.

disposal of treated leachate into inland surface water (2 mg/L). After 28 days of curing, compressive strengths were determined in a strain-controlled testing machine at strain rate of 1.25 mm/min. The average of three strength determinations is reported for each SAC specimen.

3.3.2. Water leach and TCLP tests

Water leach and TCLP tests were performed with crushed samples of concrete (0% sludge content) and SAC specimens (1.5–9% sludge contents) as described in Section 3.2. The alkaline nature (pH > 12) of the concrete and SAC specimens warranted their extraction with an acidic extractant fluid. This extractant fluid was prepared by diluting 5.7 mL glacial acetic acid to a volume of 1 L with distilled water. The resultant fluid has pH of 2.9.

4. Results and discussion

4.1. Bone char sludge

The bone char sludge sample is constituted by sand sized particles (4.75–0.075 mm) with bulk of the particles (70%) having particle sizes varying between 4.75 and 2 mm (Fig. 2). The bone char sludge has alkaline pH of 8.4 and total dissolved solids (TDS) concentration of 200 mg/L. X-ray diffraction pattern of the bone char sludge sample (Fig. 3) reveals it to be composed of carbonate hydroxyl apatite fluorian mineral [chemical formula—$Ca_{10}(PO_4)_5CO_3(OH)F$]. Strong peaks corresponding to this mineral are observed at d-spacings of 2.81, 2.71, 2.26 and 1.94 Å. Presence of quartz impurity in the sludge sample is revealed by a strong peak at 3.33 Å (Fig. 3).

The bone char sludge samples released fluoride concentrations of 2.7 and 0.52 mg/L in the water leach test and TCLP test respectively. Distilled water has initial pH of 5.6 and is characterized by final pH of 8.3 after contacting with the bone char sludge sample. Likewise, the acetate buffer used in the TCLP test is characterized by initial and final (after equilibration with bone char sludge) pH values of 4.9 and 5.6 respectively. Distilled water leachate is characterized by larger fluoride concentration (2.7 mg/L) than the TCLP leachate (0.52 mg/L) presumably for the following reasons. The alkaline pH of distilled water is consequence of leaching and release of hydroxyl ions from the bone char sludge sample. A greater amount of fluoride is released in this alkaline environment apparently from occurrence of following reaction:

$$Ca_{10}(PO_4)_6F_2 + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 2F^- \qquad (2)$$

The importance of hydroxyl ion concentration in releasing fluoride ions is illustrated by the leaching tests performed on bone char sludge samples with hydrochloric acid (0.001N HCl and 0.01N HCl) and caustic soda solutions (0.001N and 0.01N NaOH). The results are illustrated in Fig. 4 that plots the amounts of fluoride released as function of final pH of the leachate. 0.01N hydrochloric acid solution, characterized by final pH of 7.0, leaches minimal fluoride concentration of 0.58 mg/L from the sludge specimen. On the other hand, the strongly alkaline 0.01N caustic soda solution with an abundance of hydroxyl ions, (final pH 11.3) extracts 37.1 mg/L of fluoride from the sludge sample.

4.2. Influence of admixing sludge on compressive strength

Fig. 5 plots the variations in compressive strengths of the concrete (0% sludge content) and SAC specimens (1.5–9% sludge contents) as function of the sludge content. The figure shows that admixing 1.5% sludge content does not improve the compressive strength. Admixing 3% sludge content maximizes the compressive strength of the SAC specimens. Presumably, maximum strength mobilization occurs at 3% sludge content as maximum dry density of 2.22 Mg/m^3 is attained at this sludge content (Table 1). It may be noted that the concrete specimen and SAC specimens more than satisfy the compressive strength requirement for load-bearing blocks (4–5 MPa—BIS 2185). The possible reasons for maximum compressive strength development at 10% sludge content are examined.

Fig. 2 compared the particle size distributions of bone char sludge and fine aggregate (river-sand) specimens. The figure

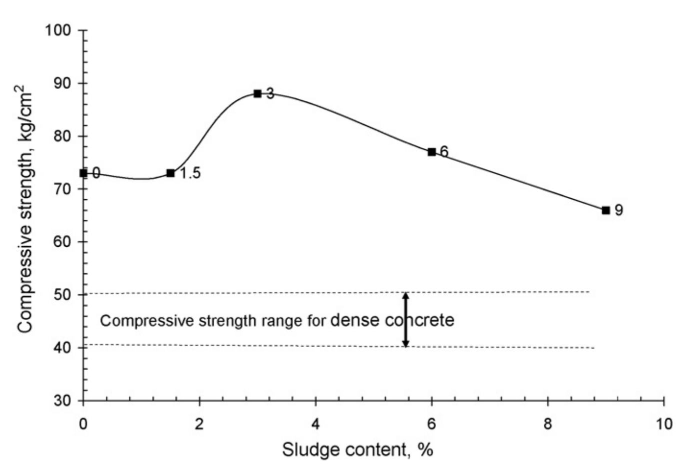

Fig. 5. Variation of compressive strength of SAC specimens with sludge content.

Table 1
Material properties of SAC specimens.

Specimen	Water/cement ratio	Slump value (mm)	Dry density[a] of 28-days cured specimen (Mg/m^3)	Compressive strength[a] (MPa)
Concrete	1.06	25	2.09	7.3
1.5% SAC	1.13	28	2.08	7.2
3% SAC	1.2	27	2.22	8.8
6% SAC	1.35	29	2.16	6.8
9% SAC	1.43	28	2.02	6.6

[a] Average of three specimens.

showed that at a given % finer value, the bone char sludge contains coarser sand-sized particles than the river-sand specimen. The scanning electron micrographs in Figs. 6 and 7 shows the bone char sludge specimen is comprised of angular particles, while, the river-sand by rounded grains. Fig. 8 shows the SEM of 90% river-sand + 10% bone char sludge mix, which is representative of river-sand-bone char sludge ratio in the 3% SAC specimen. The figure shows that the relatively, finer river-sand particles fill the gaps between the coarser bone char sludge particles. Apparently optimum packing of voids is mobilized at 3% sludge content imparting a higher dry density and maximum compressive strength to the 3% sludge admixed concrete (SAC) specimen.

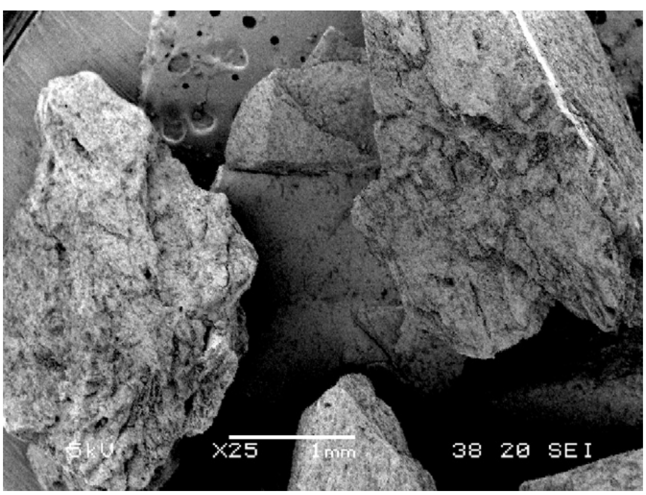

Fig. 6. SEM of bone char sludge specimen.

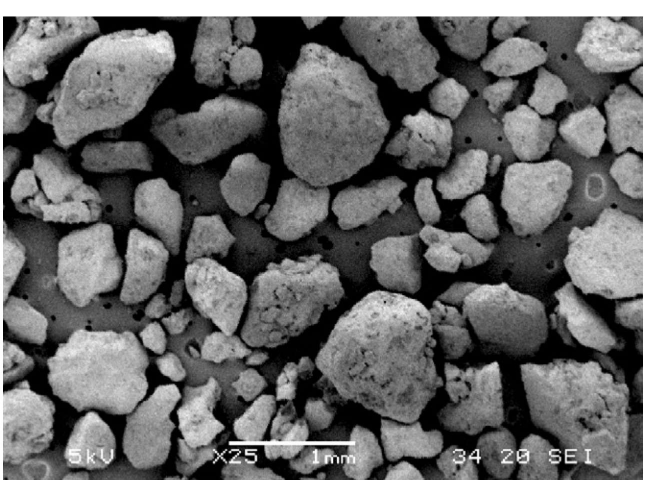

Fig. 7. SEM of river-sand specimen.

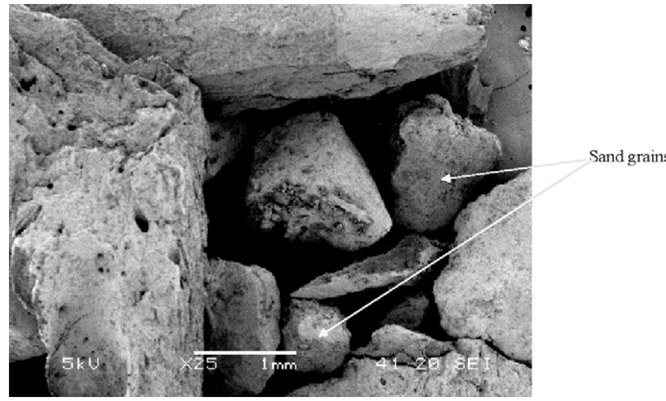

Fig. 8. SEM of 90% river-sand + 10% bone char sludge mix.

4.3. Fluoride leachability tests

Fig. 9 compares the fluoride released by the concrete and SAC specimens in the water leach and TCLP tests. The figure firstly shows that 0.19–0.43 mg/L of fluoride is released by concrete specimens (0% sludge content) in the water leach and TCLP tests respectively. Partial replacement of river-sand by sludge though increases the fluoride released by the SAC specimens (0.34–0.84 mg/L in water leach tests and 0.47–1.51 mg/L in TCLP tests), the values released are much lower than the standard specified for disposal of treated leachate into inland surface water (2 mg/L). The data in Fig. 9 suggest that partial replacement of river-sand with bone char sludge will not degrade the strength or environmental integrity of concrete specimens. Fig. 9 shows that the TCLP extractant (pH 2.9) extracts relatively greater amount of fluoride than distilled water (5.6) from the SAC specimen of given sludge content.

The fluoride release by bone char sludge was earlier inferred to be a function of the final pH of the leachate with larger amounts of fluoride release occurring in the alkaline pH range. The water test leachates of the 1.5–9% SAC specimens are characterized by pH of 12.0. Plot in Fig. 4 suggests that bone char sludge will release 45 mg/L of fluoride at pH of 12.0 or calculations in Eq. (3) show that 0.9 mg of fluoride will be released by 1 g of sludge material at this alkaline pH as

$$\text{Amount of fluoride released/g of sludge at pH 12} = \frac{45\ \text{mg} \times 100\,\text{mL}}{1000\,\text{mL} \times 5\,\text{g}} \quad (3)$$

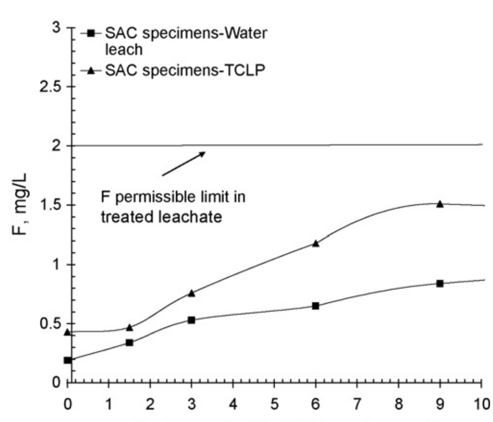

Fig. 9. Fluoride released by SAC specimens in water leach and TCLP tests.

Table 2
Fluoride release potential of SAC specimens in water leach tests.

SAC specimen	Mass of sludge in 5 g of specimen	Fluoride release by 5 g of specimen at pH 12 – mg of fluoride/5 g of specimen		F retention efficiency (%) (from Eq. (5))
		Theoretical value	Experimental value	
1.5%	0.075	0.068	0.029	57
3%	0.15	0.14	0.054	61
6%	0.30	0.27	0.056	79
9%	0.45	0.41	0.073	82

The average (of three specimens) final dry density, volume (1000 cm^3) of the SAC specimens and weight proportion of cement: sand: gravel (1:3:6) content was used to calculate the mass of bone char sludge present in 5 g of 1.5%, 3%, 6% and 9% SAC specimens used in the water leach tests (Table 2). These mass values were in turn used to obtain the theoretical amounts of fluoride release by varying amounts of bone char sludge present in the 1.5%, 3%, 6% and 9% SAC specimens. The theoretical amount of fluoride release is calculated as

$$F_{\text{theoretical}} = \frac{0.9\ \text{mg} \times m_S}{1\ \text{g}} \quad (4)$$

where 0.9 mg represents amount of fluoride released by 1 g of sludge at pH 12 and m_S is the mass of sludge present in 5 g of 1.5%, 3%, 6% and 9% SAC specimens (Table 2). Data in Table 2 shows that the experimental amounts of fluoride released by 5 g of SAC specimens in the water leach tests are generally far lesser than the theoretical values. These results indicate that partial replacement of river-sand by bone char sludge in the manufacture of dense concrete specimens reduces the fluoride release potential of the encapsulated sludge material. The difference between theoretical and measured fluoride release values of a SAC specimen can be construed to represent its efficiency for fluoride retention with a larger difference implying lesser fluoride release by the SAC specimen; mathematically it is represented as

Fluoride retention efficiency

$$= \frac{F_{\text{theoretical release}} - F_{\text{experimental release}}}{F_{\text{theoretical release}}} \times 100\% \quad (5)$$

The fluoride retention efficiencies of the SAC specimens increase with the amount of sludge present in the SAC specimens (Table 2); the trend of results apparently suggest that a stronger chemical stabilization of the fluoride contaminant in the concrete matrix occurs at larger sludge contents.

5. Conclusions

X-ray diffraction pattern of the bone char sludge sample revealed it to be composed of carbonate hydroxyl apatite fluorian mineral. The fluoride release potential by bone char is dependant on the pH of the extraction fluid. Alkaline solutions extract greater amounts of fluoride owing to replacement of fluoride in the mineral lattice by hydroxyl ions from leachate. Experimental results demonstrated that the concrete specimen (0% sludge content) and SAC specimens (1.5–9% sludge content) more than satisfy the compressive strength requirement for load-bearing concrete blocks (4–5 MPa). Further, admixing 3% sludge content maximized the compressive strength amongst the SAC specimens. Dry density and SEM measurements suggested that optimum packing of voids is mobilized on partial replacement of river-sand by 3% sludge content that in turn imparted maximum compressive strength to this sludge admixed concrete specimen. Water leach and TCLP tests with the SAC specimens showed that these specimens release much lower amounts of fluoride than specified for disposal of treated leachate into inland surface water (2 mg/L). Calculations also revealed that partial replacement of river-sand with bone char sludge in the manufacture of dense concrete specimens reduces the fluoride release potential of the encapsulated sludge material. Consideration of compressive strength and leachability results suggest that partial replacement of river-sand by bone char sludge does not degrade the strength or environmental integrity of concrete specimens.

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