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Evaluation of physical stability and leachability of Portland Pozzolona Cement (PPC) solidified chemical sludge generated from textile wastewater treatment plants

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ABSTRACT

The chemical sludge generated from the treatment of textile dyeing wastewater is a hazardous waste as per Indian Hazardous Waste Management rules. In this paper, stabilization/solidification of chemical sludge was carried out to explore its reuse potential in the construction materials. Portland Pozzolona Cement (PPC) was selected as the binder system which is commercially available cement with 10–25% fly ash interground in it. The stabilized/solidified blocks were evaluated in terms of unconfined compressive strength, block density and leaching of heavy metals. The compressive strength (3.62–33.62 MPa) and block density (1222.17–1688.72 kg/m^3) values as well as the negligible leaching of heavy metals from the stabilized/solidified blocks indicate that there is a potential of its use for structural and non-structural applications.

1. Introduction

Rapid urbanization and industrialization in India during the last few decades have resulted in the arduous task of finding means to manage the waste generated. There has been a significant increase in the industrial sectors such as pesticides, drugs and pharmaceuticals, textiles, dyes, fertilizers, tanneries, paint and chlor-alkali which have a major potential for the generation of hazardous waste containing heavy metals, cyanides, pesticides, complex aromatic compounds (such as Polychlorinated Biphenyls) and other chemicals, which are highly toxic, flammable, reactive, corrosive, or have explosive properties.

The physico-chemical treatment of dyeing wastewater from textile units leads to the generation of large quantity of chemical sludge which is inorganic and non-biodegradable in nature. The dyestuff present in the wastewater gets precipitated in the form of settleable sludge slurry in the presence of coagulants such as lime and ferrous sulphate. The chemical sludge contains inert solids, polymer solids, precipitated dye products, metal salts and other chemicals. The sludge is considered hazardous as per Indian Hazardous Waste (Management, Handling and Transboundary Movement) Rules, 2008 under Schedule I, category no. 34 [1]. Presently large quantities of chemical sludge remain disposed at CETP (Common Effluent Treatment Plant) premises and awaiting disposal at landfill.

Hazardous waste treatment and disposal technologies have been developed to handle several types of wastes and new technologies are still emerging. Stabilization/solidification (S/S) is a technology used for treating industrial solid wastes containing toxic constituents to prevent their dissolution and release to the environment [2]. It had been used for decades as a final treatment step prior to the disposal of both radioactive and chemical hazardous wastes. Solidification refers to techniques that encapsulate the waste in a monolithic mass of high structural integrity. Solidification does not necessarily involve a chemical interaction between the waste and solidifying agents but may mechanically bind the waste into a monolith. Contaminant migration is restricted by decreasing the surface area exposed to leaching and/or isolating the surface within the impervious capsule. Stabilization refers to techniques which reduce the hazard potential of waste by converting the contaminants into their least soluble, mobile or toxic form. It is used extensively for the treatment of sludge and contaminated soils containing toxic metals and organic constituents, incinerator residues and bulk wastes from power plants [3,4]. It is used widely because of their simple operation, cost effectiveness and their desirable characteristics [5,6]. The most common binder systems used in S/S systems are alkaline matrices such as lime and Portland cement. These are inexpensive, incorporate wet wastes and their alkalinity

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greatly reduces the solubility of many inorganic toxic or hazardous metals. The S/S matrix can also be modified using additives such as fly ash, soluble silicates, slag and clay.

In S/S process using cement, water reacts chemically with cement to form hydrated silicates and aluminates resulting in a solid monolithic mass. Hydration of di- and tricalcium silicates forms C-S-H gel also known as tobermorite and crystalline calcium hydroxide. The C-S-H gel is responsible for the strength development after the initial setting of the mixture.

Real wastes are complex mixtures with contrasting physical and chemical properties that are difficult to characterize. The synergistic or antagonistic effects of multiple component mixtures can influence both hydraulic or pozzolonic activity. Several heavy metal salts have been implicated in the inhibition of hydration process with consequent retardation in the setting and curing of cement/waste matrix and thus reduction in strength development [7,8].

Ansari and Thakur [9] carried out some studies on textile chemical sludge which was collected from the drying beds of the effluent treatment plant of a local textile unit engaged in the production of bleached and dyed/printed cotton, polyester cotton and viscose fabrics. They performed the studies by mixing sludge with the clay so that it can be reused as some brick material. The semi-dried sludge was mixed in the proportion of 0, 15, 30 and 45%. The maximum percentage of semi-dried sludge that can be mixed with clay for making bricks was 45%. The physical properties of sludge and clay were determined, which indicated that the durability of bricks made from the pure clay is more than that of the sludge–clay mixture. However, the quality of sludge–clay mixture can be further improved by igniting the sludge at 600 °C before mixing with the sludge.

Baskar et al. [10] carried out the feasibility studies of chemical sludge collected from the textile wastewater treatment plants in clay bricks. The sludge was used in proportion (0–30%) in the clay bricks and bricks found to satisfy the criterion for shrinkage and weight loss properties for quality bricks. Compressive strength was found to decrease with increase in waste and increase with increase in firing temperature. The maximum amount of sludge that can be added is in the range of 6–9% having the compressive strength values between 4.25 and 3.54 N/mm^2 satisfying the Bureau of Indian Standards (BIS) norms.

One such study was also conducted by Balasubramanian et al. [11] who explored the use of textile sludge in the construction materials both for structural and non-structural applications. They explored the possibility of using sludge up to 30% as partial replacement of cement. The cement–sludge blocks failed to fulfil the criteria for structural applications. However, the strength and other parameters met the BIS for non-structural applications like flooring tiles, pavement blocks and bricks. Pudji and Rahmi [12] carried out the stabilization of textile sludge containing heavy metals using cement, lime, organic matter and soil as a blank to bind the textile sludge. Analysis of the leachate was carried for the parameters like COD, pH, heavy metals and gas for every two weeks. The heavy metal analysis of leachate showed stabilization that 20% cement had bound heavy metals except for copper and nickel. The stabilization using organic matter and lime gave good results in binding heavy metals except the copper. COD content was also found to be low in the leachate.

Though these researchers in India have attempted to carry research studies on textile chemical sludge for different aspects using different binder systems; there is no comprehensive study available on chemical sludge from textile wastewater treatment plants covering all the aspects including characterization and microstructural examination of sludge, treatability studies using different binder systems such as OPC and PPC containing fly ash, leachability studies as well as the toxicity assessment. We have tried to carry out such a comprehensive study covering many of such aspects such as detailed physico-chemical characterization and microstructural examination of chemical sludge, stabilization/solidification of sludge using OPC and PPC (cement containing fly ash), leachability studies for heavy metals and toxicity assessment using fish bioassay. This manuscript covers the solidification/stabilization of chemical sludge using PPC (Ordinary Portland Cement with fly ash interground in it), leachability and microstructural examination of untreated raw sludge samples as well as stabilized/solidified sludge samples. We are further in the process of publishing the findings of our Ph.D. research in the renowned national and international journals.

Therefore, the main aim of this study is to explore the possibility of chemical sludge, generated from effluent treatment plants treating the textile dyeing wastewater, to be used in construction material. Solidification of chemical sludge was carried using Portland Pozzolona Cement (PPC) as the binder system. The effectiveness of solidified samples was assessed by measuring physical (unconfined compressive strength and block density) and chemical characteristics (leachability of heavy metals) and microstructural examination of untreated sludge as well as treated stabilized/solidified samples using XRD and SEM studies.

2. Methods and materials

2.1. Chemical sludge and binder system

The sludge was obtained from CETP in Balotra located at Barmer district of Rajasthan state in Western India. The CETP receives wastewater mainly from cotton dyeing and printing units. Standard sampling procedures were adopted. Samples of sludge were collected in wide mouth polypropylene jars and refrigerated at 4 °C for storage and transportation. In the laboratory, the sludge was dried in a hot air oven for 24 h at 100 °C. After drying, the sludge was powdered in a ball mill and then was passed through 212 μ BSS sieve. The chemical sludge was dark green in colour and slightly odorous in nature. The chemical sludge was characterized for various physico-chemical parameters and heavy metals using standard analytical methods as recommended by Bureau of Indian Standards (BIS), APHA methods [13] and CPCB manual on hazardous waste characterization [14] and USEPA SW-846 [15]. The physico-chemical properties and heavy metals of CETP sludge are shown in Table 1.

Table 1
Physico-chemical characterization of chemical sludge generated from the treatment of textile dyeing wastewater at Balotra.

Parameter	Value
pH	8.70
Electrical conductivity (mS/m)	6.90
Moisture content (%)	10.50
Total solids (%)	89.50
Total volatile solids (% of dry solids)	36.60
Total fixed solids (% of dry solids)	63.40
Total organic carbon (%)	11.20
Calorific value (kcal/kg)	991.57
Density (kg/m^3)	916.23
Specific gravity	0.94
Cd (mg/kg on dry wt. basis)	5.17
Cu (mg/kg on dry wt. basis)	225.48
Zn (mg/kg on dry wt. basis)	186.47
Ni (mg/kg on dry wt. basis)	89.67
Co (mg/kg on dry wt. basis)	11.20
Pb (mg/kg on dry wt. basis)	44.75
Cr (III) (mg/kg on dry wt. basis)	231.45
Cr (VI) (mg/kg on dry wt. basis)	BDL[a]

[a] Below detection limit.

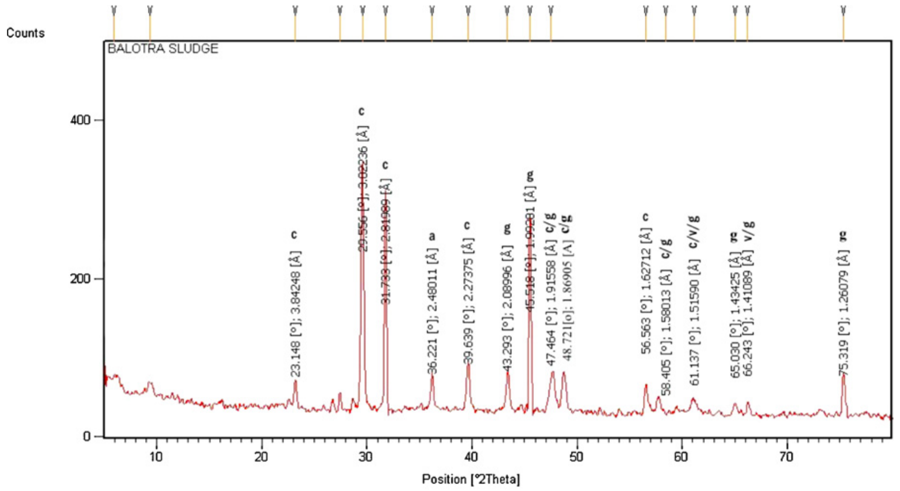

Fig. 1. XRD pattern of chemical sludge from Balotra CETP. C: calcite ($CaCO_3$); v: vaterite ($CaCO_3$); a: calcium hydroxide ($Ca(OH)_2$); g: gypsum ($Ca(SO_4)(H_2O)_2$).

2.1.1. X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) examination of chemical sludge

The XRD patterns of chemical sludge are given in Fig. 1. The XRD patterns reveal the presence of main compounds such as $CaCO_3$ (calcite), $CaCO_3$ (vaterite) and small amounts of calcium hydroxide $Ca(OH)_2$ and gypsum ($Ca(SO_4)(H_2O)_2$). The presence of calcium compounds as well as gypsum in XRD patterns of sludge further confirms that the sludge has a possibility to be used in construction materials.

The scanning electron micrographs of chemical sludge are given in Fig. 2. The sludge particles are in the form of agglomerates with diameter varying from 1 to 40 μm showing the predominance of spherical particles.

2.1.2. X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) of Portland Pozzolona Cement (PPC)

Portland Pozzolona Cement (PPC) of grade 43 confirming to IS 1489 (Part 1): 1991 [16] was used as the binder system. PPC is commercially available cement with 10–25% fly ash interground in it. Mortar cube steel moulds of 70.6 mm × 70.6 mm × 70.6 mm were used for casting the cement–sludge mixture. The XRD pattern of hardened Portland Pozzolona Cement (PPC) containing fly ash is shown in Fig. 3. The crystalline phases of portlandite and di- and tricalcium silicates were detected. The peaks of tricalcium aluminate were also detected. A minor hydrate product called “gehlenite hydrate”, $2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}8H_2O$, which is formed from Al from fly ash was also observed. This compound is reported to form from Al in the fly ash as given in the literature by Glasser [17]. There is also a broad and diffuse hump that appears between 27° and 35°. This could either be the glass structure of fly ash or the formation of poorly crystalline calcium silicate hydrate.

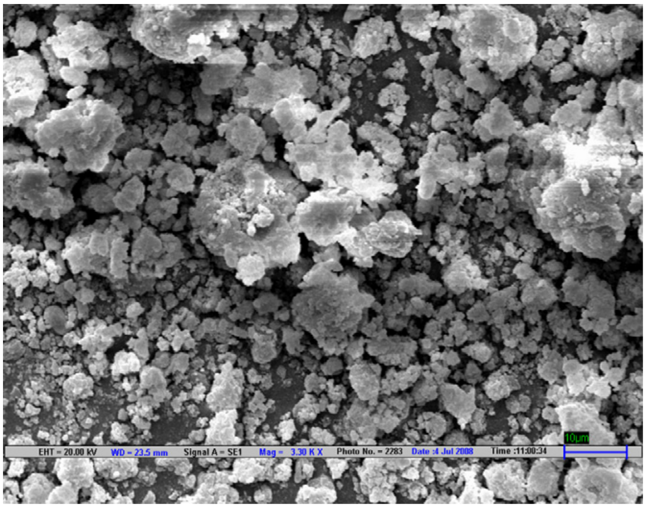

Fig. 2. SEM of sludge from Balotra CETP (at 3300× magnification).

SEM of hardened PPC also reveals a dense microstructure with normal hydration products portlandite and needle like ettringite crystals spread over the surface with the inclusion of some spherical structures of fly ash in it (Fig. 4).

2.2. Preparation and casting of cement–sludge blocks

Distilled water was used in preparing the cement–sludge cubes. The block cubes were prepared as per the BIS IS 4031(6) [18]. The mixture for each cube was placed on a nonporous plate. The recipe was mixed with the trowel until the mixture was of uniform colour. Water was slowly added into the dry mix to promote hydration. The mixture was then mixed at high speed for 3 min upon attainment of pre-determined water–cement ratio and to get a uniform colour of the mixture. While assembling the mould, thin film of petroleum jelly was applied at joints to prevent waste leakage during vibration. Thin film of mould oil was applied in interior faces of the mould for easy removal of solidified cubes after curing. The mixture was poured into the mould and compacted for the removal of entrained air with the help of a prodding rod after casting each layer. Filled moulds were kept in moist condition for 24 h at room temperature (27–29 °C) and relative humidity of 92%. The cubes were then removed from the mould and placed submerged in water in a tray. The water in the tray was changed every 7th day and the temperature was maintained at 27 ± 2 °C. The cubes were subjected to 14-days and 28-days water curing to allow the progressive strength development. Each sample ratio was prepared in triplicate. The sample ratio prepared is as given in Table 2.

2.3. Evaluation of solidified/stabilized blocks

2.3.1. Physical characteristics

After curing the blocks were subjected to unconfined compressive strength (UCS) determination test. Compressive strength is

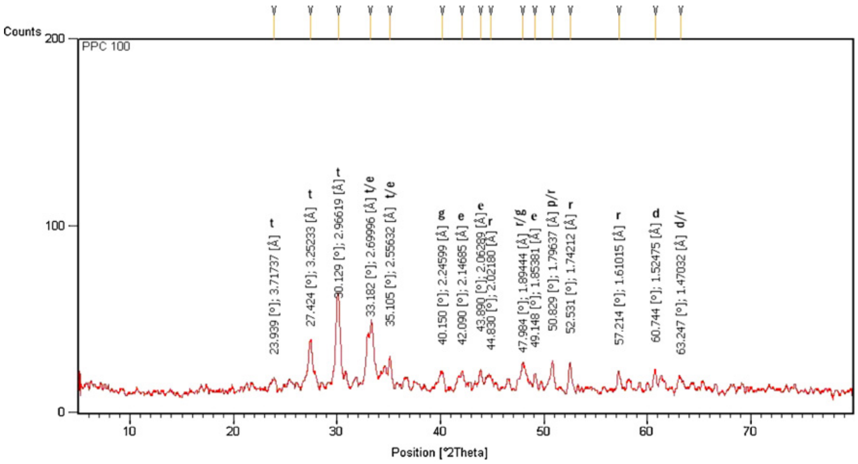

Fig. 3. XRD pattern of hardened Portland Pozzolona Cement (PPC). p: portlandite ($Ca(OH)_2$); t: tricalcium silicate (Ca_3SiO_5); d: dicalcium silicate (Ca_2SiO_4); e: ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$); r: tricalcium aluminate ($Ca_3Al_2O_6$), g: gehlenite hydrate ($Ca_2Al_2SiO_7\cdot 8H_2O$).

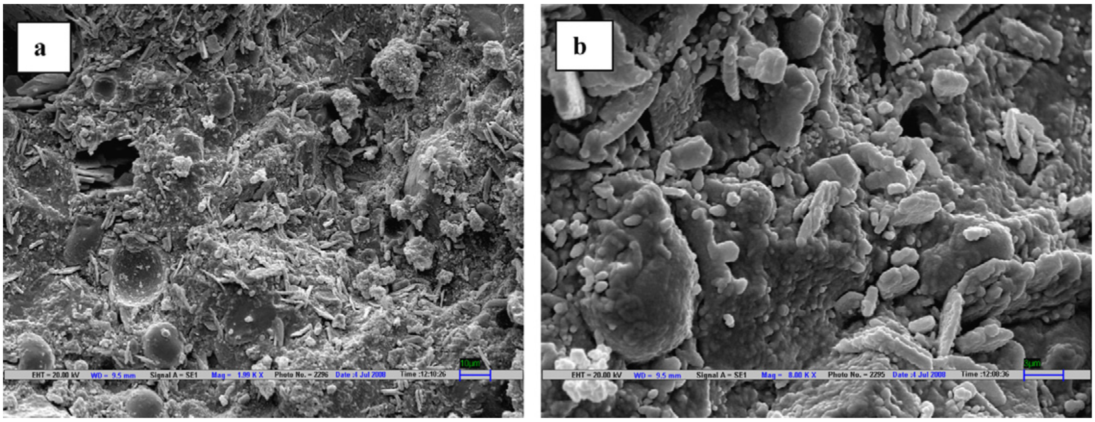

Fig. 4. Scanning Electron Micrograph (SEM) of hardened Portland Pozzolona Cement (PPC) at different magnifications (a) 2000× and (b) 8000×.

the capacity of the material to withstand axially directed pushing forces. When the limit of compressive strength is reached, the material is crushed. The test samples were compressed between the platens of a compressive strength testing machine by a gradually applied load. The load was gradually and steadily applied starting from zero at a rate of 35 N/mm^2/min. UCS values of cement–sludge paste cubes were measured by compression testing machine as per BIS IS 4031(6) [18]. Total maximum loads were recorded at the point of fracture and the compressive strength was determined using the formula. The measured compressive strength of the cubes was calculated by dividing the maximum load applied to the cubes during the test by the cross-sectional area; using the formula,

Table 2
Nomenclature for Sludge/ PPC mixtures studied.

Nomenclature	Description
PPC as binder system in 14 days water curing	
PPC-CN-14-W	0% Sludge, 100% PPC, 14 days water curing
PPC-30-14-W	30% Sludge, 70% PPC, 14 days water curing
PPC-40-14-W	40% Sludge, 60% PPC, 14 days water curing
PPC-50-14-W	50% Sludge, 50% PPC, 14 days water curing
PPC-60-14-W	60% Sludge, 40% PPC, 14 days water curing
PPC-70-14-W	70% Sludge, 30% PPC, 14 days water curing
PPC as binder system in 28 days water curing	
PPC-CN-28-W	0% Sludge, 100% PPC, 28 days water curing
PPC-30-28-W	30% Sludge, 70% PPC, 28 days water curing
PPC-40-28-W	40% Sludge, 60% PPC, 28 days water curing
PPC-50-28-W	50% Sludge, 50% PPC, 28 days water curing
PPC-60-28-W	60% Sludge, 40% PPC, 28 days water curing
PPC-70-28-W	70% Sludge, 30% PPC, 28 days water curing

$$\mathrm{fm} = \frac{P}{A}$$

where fm is the compressive strength (in N/mm^2), P is the total maximum load (in N) and A is the area of loaded surface (in mm^2).

Compressive strength was calculated by taking the average of three replicates for each test. The block density was also measured as per the BIS specification code IS 2185 (Part I): 2005 [19]. Blocks were dried to constant mass heated to approximately 100 °C. After cooling the blocks at room temperature, the dimensions of each block were measured in centimetres and the overall volume computed in cubic centimetres. The samples were then weighed in kilograms and density of each block was calculated. Triplicate of the blocks were taken for the measurement and the average density was taken for the three blocks.

2.3.2. Leaching characteristics

Toxicity Characteristics Leaching Procedure (TCLP) of USEPA, method 1311 of SW-846 [20] was used to conduct leaching of the crushed waste material. After 28 days of curing, the samples of cubes were crushed to <9.5 mm in size. Extraction fluid # 1 (acetic acid–water solution at pH 2.88) at a liquid-to-solid ratio of 20:1 was added to crushed cube sample and tumbled end-to-end at room temperature for 18 h in stainless steel extraction bottles at 28–30 rpm. At the end of the extraction, the leachate was filtered through a 0.45 μm membrane filter to remove suspended solids. The leachate was directly analysed on atomic absorption spectrometer (AAS) for the heavy metals.

3. Results and discussions

(1) The compressive strength of solidified blocks varied between 2.78–17.42 MPa for 30%, 40%, 50%, 60% and 70% sludge addition after 14 days of water curing and 3.62–33.37 MPa after 28 days of water curing. The maximum compressive strength was found in case of control i.e. 44.26 MPa after 14 days of water curing and 63.69 MPa after 28 days of water curing. As the percentage of sludge was increasing in PPC–sludge blocks, the compressive strength was decreasing. The compressive strength data is given in Table 3.

The decrease in compressive strength might be due to the presence of certain compounds like salts of zinc and lead in the sludge which might have deleterious effect on the hydration reactions responsible for the strength development. They lead to the formation of a membrane around cement particles with the precipitation of calcium hydroxyzincate ($CaZn_2(OH)_6{\cdot}2H_2O$) that can prevent the water and ion transport required for cement hydration [6,7,21]. This retardation of cement hydration causes a decrease in strength development. Coating of tricalcium silicate with $3CaO{\cdot}SiO_2{\cdot}(C_3S)$ of cement with Pb or complexation of Pb might have also caused retardation in cement hydration [22,23].

The UCS of PPC–sludge blocks was in the range of 3.62–33.37 MPa (Fig. 5). The UCS values for 11 classes of common burnt clay bricks range 3.5–35 MPa (IS 1077: 1992) [24]. Thus the PPC–sludge blocks (UCS: 3.62–33.37 MPa) were conforming to 9 classes of bricks and fly ash bricks (UCS: 6.86–24.5 MPa). They also compare well with other building materials like hollow and solid concrete blocks having strength requirements of 4 and 5 MPa (IS 2185 (Part I): 2005) [25] and hollow and solid light weight concrete blocks having strength requirements of 8.5 and 12.5 MPa (IS 2185 (Part II): 2005) [26], soil based blocks having strength requirements of 2 MPa (IS: 1725-1982) [27], lime-pozzolona concrete blocks for paving having strength requirements of 3.5 MPa (IS: 10360-1982) [28]. Therefore considering the strength requirements of these construction materials, the cement–sludge blocks fulfil the requirements for most of the materials for non-structural purposes.

Table 4
Block density of cement–sludge blocks with PPC as binder system in water curing.

Block ID	Block density (kg/m^3)	
	14 days	28 days
0% Sludge, 100% cement	1930.90	1991.77
30% Sludge, 70% cement	1669.59	1688.72
40% Sludge, 60% cement	1448.74	1465.96
50% Sludge, 50% cement	1457.05	1435.35
60% Sludge, 40% cement	1321.36	1346.68
70% Sludge, 30% cement	1236.38	1222.17

(2) The block density of cement–sludge blocks varied between 1236.38–1669.59 kg/m^3 after 14 days of water curing and 1222.17–1688.72 kg/m^3 after 28 days of water curing (Table 4). The maximum block density was found for the control, i.e. 1930.90 kg/m^3 after 14 days of water curing and 1991.77 kg/m^3 after 28 days of water curing. The block density after 14 and 28 days of curing were nearly the same. This indicates that it is not affected by the duration of curing once it has been hardened properly. The block density was decreasing as the percentage of sludge was increasing in PPC–sludge blocks as sludge had less density as compared to PPC (Fig. 6).

The block density for cement–sludge blocks compares well with reported block density requirements for cellular light weight concrete (800–1800 kg/m^3), lime based blocks (1000 kg/m^3), hollow and light weight concrete blocks (1600 kg/m^3), hollow and solid concrete blocks (1800 kg/m^3).

(3) The heavy metal concentrations in the leachate were compared with the USEPA regulatory limits and were found to be negligible compared to the stipulated limits. There is insignificant leaching of heavy metals from the cement–sludge blocks. The pH values and heavy metal concentrations of leachates are given in Table 5. The high pH values suggest alkaline nature of the sludge samples. The pH value decrease is far more rapid in the case of blocks made with increasing volume of sludge samples with PPC as compared to Ordinary Portland Cement (OPC). This is due to the reduction of free $Ca(OH)_2$ by reaction with fly ash which is more silica rich than cement. The reaction is similar to an acid–base reaction in which more acidic components of fly ash reacted with alkaline $Ca(OH)_2$ thus resulting in a slightly decreased pH. But the principal reaction product, i.e. C-S-H was itself sufficiently soluble to condition a high pore fluid pH. The percent reduction is also mentioned in Table 4 with Pb (62–68%), Cd (14–57%), Cr (45–100%), Cu (31–82%), Ni (33–56%), Co (35–71%) and Zn (63–81%).

Table 3
Compressive strength data of cement–sludge blocks with PPC as binder system in water curing.

Block ID	Sludge (g)	Cement (g)	Total wt. (g)	Water (ml)	$\frac{\text{Water}}{\text{Sludge+Cement}}$	Compressive strength (MPa)
PPC-CN-14-W-1	0	700	700	140	0.20	44.26
PPC-30-14-W-1	180	420	600	150	0.25	17.42
PPC-40-14-W-1	240	360	600	165	0.28	10.81
PPC-50-14-W-1	300	300	600	190	0.32	8.63
PPC-60-14-W-1	360	240	600	214	0.36	4.88
PPC-70-14-W-1	420	180	600	220	0.36	2.78
PPC-CN-28-W-1	0	700	700	145	0.20	63.69
PPC-30-28-W-1	180	420	600	163	0.25	33.37
PPC-40-28-W-1	240	360	600	170	0.28	19.53
PPC-50-28-W-1	300	300	600	185	0.32	11.43
PPC-60-28-W-1	360	240	600	205	0.36	7.65
PPC-70-28-W-1	420	180	600	210	0.36	3.62

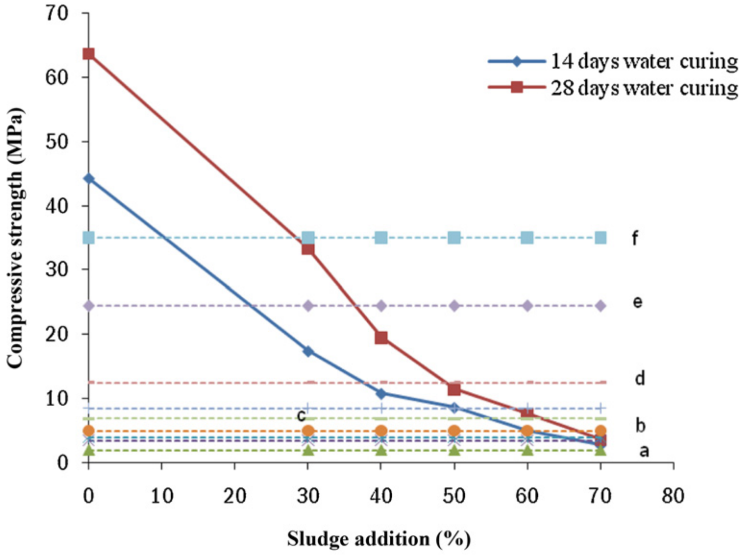

Fig. 5. Compressive strength of PPC–sludge mixtures in water curing. (a) Soil based blocks having strength requirements of 2 MPa; (b) lime-pozzolona concrete blocks for paving having strength requirement of 3.5 MPa; (c) hollow and solid concrete blocks having strength requirements of 4 and 5 MPa; (d) hollow and solid light weight concrete blocks having strength requirements of 8.5 and 12.5 MPa; (e) fly ash bricks having strength requirements of 6.86 and 24.5 MPa; (f) common burnt clay building bricks having strength requirements of 3.5–35 MPa.

(4) The XRD pattern of PPC with 40% sludge replacement reveals the peaks of unreacted di- and tricalcium silicates along with the peaks of ettringite (Fig. 7). Portlandite peak was totally absent in the XRD pattern indicating the hydration retardation due to the addition of chemical sludge. The peaks of gehlenite hydrate were also observed.

The SEM of PPC with 40% sludge loading is shown in Fig. 8. The sludge could be seen everywhere coating on both the surface of cement clinkers and fly ash. Cement hydration is normally a self inhibiting process and largely controlled by the permeability of the gelatinous coating around the cement clinkers. The deposition of chemical sludge on the surface of the clinkers and fly ash results in dense coating and this could be the cause for the hydration retardation of both cement clinker and fly ash.

3.1. Cost estimation of solidification/stabilization vs present mode of disposal

The accepted option as per the Hazardous Waste Management rules is the disposal of chemical sludge to the secured landfill. At present, the only available landfill in Rajasthan is located in Udaipur. This is very far from small scale industrial clusters at Balotra and Pali making the sludge disposal a costly option. This is also not environmentally benign as the sludge has potential to contaminate soil and groundwater if not properly managed at the landfill site.

Assuming that landfill would be available in the neighbourhood and nominal cost of disposal at Rs. 500 per tonne of sludge, the cost of sludge management is compared with alternative scenario, i.e. reuse of sludge. In the alternative scenario, if reuse of chemical sludge in the construction material is opted for, the benefits and

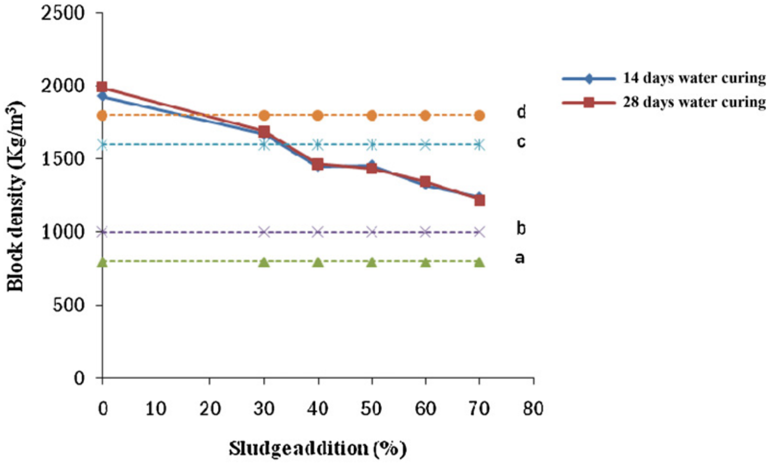

Fig. 6. Block density of PPC–sludge mixture in water curing. (a) Cellular light weight concrete (CLC) blocks with density requirements varying from 800 to 1800 kg/m^3; (b) lime based blocks having density requirements of 1000 kg/m^3; (c) hollow and solid light weight concrete blocks having density requirements of 1600 kg/m^3; (d) hollow and solid concrete blocks having density requirements of 1800 kg/m^3.

Table 5
Heavy metal concentrations in TCLP leachate in PPC–Sludge solidified blocks in water curing.

Sample ID	Leachate pH	Pb (mg/l)	Reduction (%)	Cd (mg/l)	Reduction (%)	Cr (mg/l)	Reduction (%)	Cu (mg/l)	Reduction (%)
Untreated sludge	7.52	0.76		0.07		0.56		0.49	
PPC-CN-14-W-1	11.39	BDL	–	BDL	–	BDL	100.00	BDL	–
PPC-30-14-W-1	11.88	0.24	68.42	0.05	28.57	BDL	100.00	0.11	77.55
PPC-40-14-W-1	11.49	0.24	68.42	0.03	57.14	BDL	100.00	0.13	73.47
PPC-50-14-W-1	10.67	0.27	64.47	0.06	14.29	BDL	100.00	0.18	63.27
PPC-60-14-W-1	9.89	0.27	64.47	0.04	42.86	BDL	100.00	0.27	44.90
PPC-70-14-W-1	7.06	0.25	67.11	0.04	42.86	BDL	100.00	0.30	38.78
PPC-CN-28-W-1	11.72	BDL	–	BDL	–	BDL	BDL	BDL	–
PPC-30-28-W-1	11.66	0.26	65.79	0.05	28.57	0.31	44.64	0.09	81.63
PPC-40-28-W-1	11.67	0.25	67.11	0.04	42.86	BDL	BDL	0.12	75.51
PPC-50-28-W-1	10.89	0.26	65.79	0.05	28.57	BDL	BDL	0.18	63.27
PPC-60-28-W-1	9.65	0.27	64.47	0.05	28.57	BDL	BDL	0.25	48.98
PPC-70-28-W-1	6.78	0.29	61.84	0.04	42.86	BDL	BDL	0.34	30.61
Limits		5.0[a]		1.0[a]		5.0[a]		130[b]	

Sample ID	Leachate pH	Ni (mg/l)	Reduction (%)	Co (mg/l)	Reduction (%)	Zn (mg/l)	Reduction (%)
Untreated sludge	7.52	0.43		0.34		0.52	
PPC-CN-14-W-1	11.39	BDL	–	BDL	–	BDL	–
PPC-30-14-W-1	11.88	0.21	51.16	0.11	67.65	0.11	78.85
PPC-40-14-W-1	11.49	0.19	55.81	0.10	70.59	0.19	63.46
PPC-50-14-W-1	10.67	0.24	44.19	0.17	50.00	0.13	75.00
PPC-60-14-W-1	9.89	0.26	39.53	0.18	47.06	0.10	80.77
PPC-70-14-W-1	7.06	0.29	32.56	0.21	38.24	0.11	78.85
PPC-CN-28-W-1	11.72	BDL	–	BDL	–	BDL	–
PPC-30-28-W-1	11.66	0.21	51.16	0.11	67.65	0.17	67.31
PPC-40-28-W-1	11.67	0.22	48.84	0.20	41.18	0.14	73.08
PPC-50-28-W-1	10.89	0.24	44.19	0.15	55.88	0.10	80.77
PPC-60-28-W-1	9.65	0.24	44.19	0.22	35.29	0.12	76.92
PPC-70-28-W-1	6.78	0.28	34.88	0.22	35.29	0.15	71.15
TCLP limits		2.0[c]		N/av		500[b]	

BDL, below detection limit.

[a] USEPA TCLP limits.

[b] 100 times the drinking water standards assuming that 100 times dilution would occur before the leachate could reach the drinking water.

[c] German leachate quality standards.

savings will be considerable. A portion of Portland cement could be replaced by chemical sludge. The replacement can be done either directly at the concrete batch plant or during the production of blended cements or in cement concrete tile manufacturing plant. This would mean a considerable amount of savings for the construction company. Since chemical sludge is a waste at CETP, it is available free of cost. Hence the cost of sludge will depend on the transportation cost from the CETP. The processing cost of sludge is the other associated cost. If the lead distance is less, considerable savings in the construction cost can be achieved. If the environmental degradation costs, i.e. cost of ground water contamination due to leaching or land degradation cost are considered, then the actual savings will be much higher. In that case, the sludge use will be justified even for distance greater than 100 km.

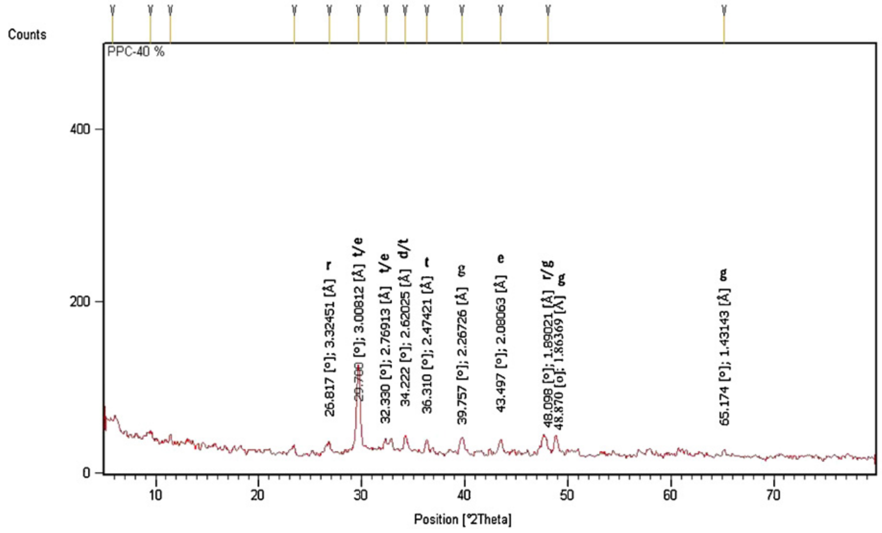

Fig. 7. XRD pattern of PPC with 40% sludge loading. t: tricalcium silicate (Ca_3SiO_5); d: dicalcium silicate (Ca_2SiO_4); e: ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$); r: tricalcium aluminate ($Ca_3Al_2O_6$), g: gehlenite hydrate ($Ca_2Al_2SiO_7\cdot 8H_2O$).

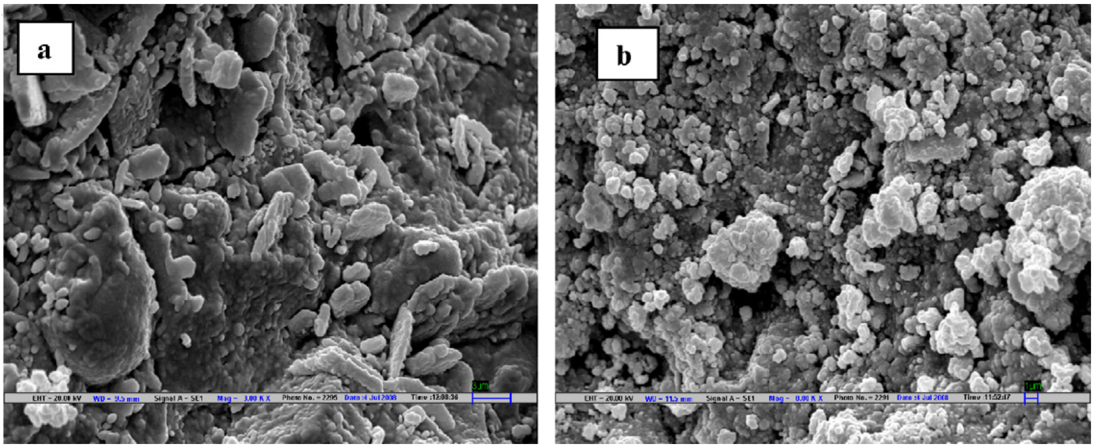

Fig. 8. Scanning Electron Micrograph (SEM) at × 8000 magnification (a) hardened PPC (b) hardened PPC with 40 % sludge addition.

4. Conclusions

The results show that stabilization/solidification is an effective method for the management of chemical sludge generated from wastewater treatment plants in textile dyeing units. The study led to the following conclusions:

- The compressive strength was decreasing as the proportion of sludge in solidified blocks was increasing.
- The physical engineering data show that the unconfined compressive strength of the sludge–PPC blocks ranged between 2.78–17.42 MPa after 14 days of water curing and 3.62–33.37 MPa after 28 days of curing. The compressive strength was increasing as the blocks were cured for more number of days.
- The block density ranged between 1236.38–1669.59 kg/m^3 after 14 days of water curing and 1222.17–1688.72 kg/m^3 after 28 days of water curing. It was nearly the same after 14 days and 28 days of curing showing that it is not affected by the number of days of curing.
- The physical engineering data were comparable with the different standards of construction materials indicating that the chemical sludge has a potential to be reused for the construction purpose after stabilization/solidification.
- The heavy metal concentrations in the leachate was found to be less than the stipulated USEPA TCLP limits showing that leaching of heavy metals from stabilized/solidified materials was not significant. Different types of leaching tests such as long term leaching tests of sludge are proposed to be conducted in future to have a better understanding of leaching process and the leaching mechanism involved in the S/S.
- The microstructural studies of solidified/stabilized chemical sludge were also conducted using XRD and SEM tests. In case of normal hardened PPC containing fly ash, distinct peaks of portlandite dominated the XRD pattern along with the other peaks of smaller intensity, i.e. ettringite and unreacted silicates. A minor hydration product called "gehlenite hydrate" which is Al from fly ash is observed. There is a clear growth of hexagonal AF$_t$ needles supporting the hydration process in the hardened cement.
- There is a modification of XRD and SEM patterns in the PPC with 40% sludge addition. There is a less development of portlandite peaks and the relative development of ettringite peaks increased. The intensity of unreacted di- and tricalcium silicates indicating the retardation of cement hydration is also increased.

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