A Study on Utilization of Treated Spent Liquor Sludge with Fly Ash by Making Cement Concrete Hollow Cavity Bricks

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***Abstract*- This solid waste may contaminate surface run-off and surface water. In stainless steel pickling industries, a lot of sludge is generated and disposal of above sludge as per Act of Hazardous Waste (Management & Handling) Rules, 1989 is not easy. In the normal practice, the sludge is being disposed off on both sides of roads and railway tracks to fill low lying areas. This causes a severe problem, because during rains, the entire toxic compound (leachate) goes into ground and pollutes the ground water. Seeing the above problem, a study is taken for utilization of pickling sludge with fly ash to avoid the problem of disposal. Cement concrete hollow cavity bricks can be made and compressive strength of cement concrete hollow cavity brick is found to increase with addition of 7.5% TSLS (treated spent liquor sludge) and 15% fly ash as a partial replacement of cement. Formation of C-S-H gel may be contributing to increase in compressive strength.**

Keywords- Hazardous Waste; Pickling; Sludge; Brick

I. INTRODUCTION

Rapid industrialization of India led to geometrical rise in the level of air, water, space, noise and land pollution. One of India's major concerns is the increasing level of land pollution, which is largely due to the uncontrolled disposal of industrial solid and hazardous waste. With rapid Industrialization, the generation of industrial solid and hazardous waste has increased appreciably and the nature of waste generated has become complex. Their impacts on the ecological bodies are noticeable.

TABLE I LIST OF HAZARDOUS WASTE

S. No.	Process	Hazardous Waste
12	Metal Surface Treatment, such as etching, staining, polishing, galvanizing, cleaning, degreasing, plating etc.	12.1 Acid residues 12.2 Alkali residues 12.3 Spent bath/Sludge containing sulphide, cyanide and toxic metals 12.4 Sludge from bath containing organic solvents. 12.5 Phosphate Sludge 12.6 Sludge from staining bath 12.7 Copper etching residues 12.8 Plating metal sludge 12.9 Chemical Sludge from waste water treatment.

Waste is classified by USEPA as hazardous waste if it exhibits any of the following-corrosivity, ignitability, reactivity, and toxicity. Other characteristics such as carcinogenicity, bioaccumulation and photo toxicity, etc. are also classified as hazardous [1].

One of the major environmental problems of the steel industry comes from pickling plant waste. Steel finishing operation such as pickling, galvanizing, plating, etc. involves a surface cleaning process to eliminate scale, rust and dust. This process is carried by immersion of steel in hot acidic solution. Pickling solutions are specifically listed in hazardous waste (Management & Handling), amendment rules 2002 [2]: (Table I).

II. LITERATURE REVIEW

Vijay and Shiorwala [3], had carried out study on pickling sludge by using toxicity characteristics leaching procedure (TCLP) for pickling and electroplating sludge. Their conclusions and recommendations as based on detailed analysis of sludge and leachability characteristics by TCLP test are as follows.

1) Since the high leachability of heavy metals like chromium, nickel, cobalt, iron and copper in Sludge, it requires proper sludge management including waste minimization, metal recovery and safe disposal of sludge.
2) The waste generated for metal pickling and electroplating industries is identified as hazardous solid waste as per Indian standards.
3) Conversion of metal containing solid waste into building materials uses stabilization and solidification techniques.
4) Detoxification studies of hazardous waste carry out under physical engineering and durable property test.
5) Care is taken for handling such type of sludge in electroplating and metal pickling industries for avoiding health hazards.

Asavapisit and Chotklang [4] had worked on solidification of electroplating sludge using alkali activated pulverized fuel ash as cementitious binder. This work included the potential for utilization of alkali-activated PFA as solidification binder to treat electroplating sludge. The sludge was solidified using 30 wt.% of lime and 70 wt.% of

PFA. Two alkali activators, Na_2SiO_3 and Na_2CO_3 were added at 0, 4, 6, and 8 wt.%. Results showed that early strength development of lime-PFA cements with Na_2SiO_3 and Na_2CO_3 was considerably higher than those without it. Addition of electroplating sludge resulted in reduced strength. The strength reduction was greater when 4% Na_2SiO_3 activator was used than when 8% Na_2CO_3 activator was used. A higher pH of Na_2SiO_3 solution (pH=13.5) compared to that of Na_2CO_3 Solution (pH=11.9) resulted in resolubilisation of metal hydroxides from the electroplating sludge which competed with calcium ion for soluble silicate.

Many studies on the use of fly ash in solidification of metal-bearing sludges had been conducted. Studies were conducted to investigate the feasibility and effectiveness of solidification/stabilisation of hazardous heavy metal-laden sludges with portland cement. The results indicated that the sludge properties had a significant effect on the compressive strength of the solidified samples. The study further reported additives, such as lime, sodium silicate, calcium chloride, and fly ash could enhance the compressive strength and reduce the leachability of heavy metal. Leaching studies conducted by them indicated that stabilisation minimised or prevented the release of heavy metals and created a non-hazardous product [5-10].

Based on the review of previous work, a study is taken to utilize Treated Pickling Sludge (Treated Spent Liquor Sludge) commercially to avoid its disposal problem.

III. EXPERIMENTAL PROCEDURE

The pickling waste and sludge were collected from a company in Wazirpur Industrial Area, Delhi, India. In this industry stainless steel components and sheets are pickled by using sulphuric acid. Sludge is collected before treatment and after treatment (Figs. 1, 2).

Fig. 1 Pickling sludge before treatment

Fig. 2 Pickling sludge after treatment (treated spent liquor sludge)

XRD- Analysis of untreated sludge and treated sludge has been carried out (Figs. 3, 4).

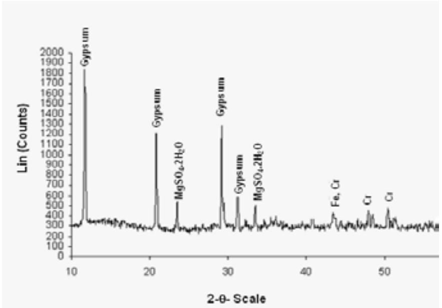

Fig. 3 XRD analysis of treated spent liquor sludge

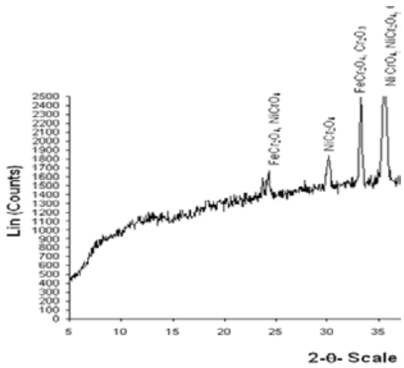

Fig. 4 XRD analysis of sulphuric acid pickling bath sludge

A. *Characterization of Sludge*

Sludge is being characterized on Atomic Absorption Spectrometer (AAS) [11] and Fly Ash is being characterized by XRF (Tables II, III).

TABLE II CHARACTERISATION OF TREATED SPENT LIQUOR SLUDGE

S. No.	Element	Mass %
1	Mg	0.65
2	Al	23.79
3	Si	49.13
4	S	1.74
5	Cl	0.03
6	K	3.92
7	Ca	2.45
8	Ti	4.37
9	Fe	13.92

TABLE III XRF SPECTROSCOPY RESULTS FOR FLY ASH ANALYSIS

S. No	Parameters	Value
1	pH	9.26
2	Calcium Oxide (CaO)	62.62 %
3	Silica (SiO2)	3.13%
4	Iron (Fe)	0.57 %
5	Total Chromium (Cr)	0.038 %
6	Nickel(Ni)	0.002 %
7	Loss on Ignition (LOI) at 1050°C	9.21 %
8	Bulk Density	2020 kg/m^3
9	Moisture content of the sludge	11.23%

IV. PREPARATION OF CEMENT-CONCRETE HOLLOW CAVITY BRICKS

An attempt has been made to make cement concrete hollow closed cavity brick with a mixture of cement, fly ash and sludge. For a comparison purpose, an industry called "Shilpi" situated in Beldi village, Roorkee, India supported by Khadi Gram Organisation has been contacted. This industry makes hollow bricks with cement, fine aggregate and coarse aggregate using a ratio of 1:3:6. The compressive strength of the cement-sludge-fly ash brick prepared in this study has been compared with cement concrete hollow bricks prepared by the industry.

This industry makes cement concrete hollow closed cavity bricks in two sizes: 400 mm x 200 mm x 200 mm & 400 mm x100 mm x 200 mm as substitute of clay bricks. In the study, brick size 400 mm x100 mm x 200 mm is used. (Fig. 5)

Fig. 5 Cement concrete hollow cavity brick

Chemical and physical properties of cement are as per Table IV and sieve analysis of fine aggregate (sand) is as per Table V. Sieve analysis of coarse aggregate used in the study is shown in Table VI.

TABLE III CHEMICAL AND PHYSICAL PROPERTIES OF CEMENT

Chemical Analysis		
S. No.	**Parameter**	**Value**
1	Lime (CaO)	63.5%
2	Silica (SiO_2)	19.05 %
3	Alumina (Al_2O_3)	4.2%
4	Iron Oxide (Fe_2O_3)	3.1%
5	Magnesia (MgO)	2.9 %
6	Sulphur Tri Oxide (SO_3)	2.5%
7	Soda and/or Potash ($Na_2O + K_2O$)	0.9%
8	Loss on Ignition	2.1%
Physical Tests		
1	Consistency of standard cement paste	28%
2	Soundness of cement	3.5 mm
3	Initial setting time of cement	125 min
4	Final setting time of cement	182 min
5	Fineness by air permeability	2698 cm^2/g

Compressive Strength of 50 cm^2 (7.06 cm x 7.06 cm x 7.06 cm) Cubes, MPa with Variation of Curing Time		
1	3 days compressive strength	24.8 MPa
2	7 days compressive strength	34.4 MPa
3	28 days compressive strength	45.9 MPa

TABLE V SIEVE ANALYSIS RESULTS OF FINE AGGREGATE

IS Sieve Size	Fine Aggregate (Percent Passing)	Remarks
4.75 mm	100	Conforming to grading zone(3) of Table 4 of IS: 383-1970. [14]
2.36 mm	100	
1.18 mm	93	
600 µm	62	
300 µm	13	
150 µm	3	

TABLE VI SIEVE ANALYSIS OF COARSE AGGREGATE

IS Sieve Size	Coarse Aggregate (Percent Passing)	Remarks
20 mm	100	Special type of coarse aggregate is used for the production of cement concrete hollow closed cavity bricks. Commercial name of the gravel is zero grade gravel.
10 mm	100	

To utilize the sludge, different ratio of sludge is mixed with 15% Fly Ash [13] to get the optimum strength (Tables VII, VIII).

TABLE VII SLUDGE CEMENT RATIO IN PREPARATION OF CEMENT CONCRETE HOLLOW CAVITY BRICKS

Brick No.	Tsls wt % as the Partial Replacement of Cement	Fly Ash wt % as the Partial Replacement of Cement
M1	2.5%	15
M2	5%	15
M3	7.5%	15
M4	10%	15
M5	15%	15
M6	20%	15
M7	25%	15
M8	30%	15

TABLE IVI COMPRESSIVE STRENGTH OF CEMENT CONCRETE HOLLOW CAVITY BRICKS WITH DIFFERENT % OF SLUDGE IN CEMENT

S. No.	Cement Concrete Hollow Cavity Bricks Strength at 28 Days		
	TSLS wt % as the Partial	Fly Ash wt % as the Partial	Compressive Strength

	Replacement of Cement	Replacement of Cement	(kg/cm^2)
M0	0 %	15	124.3
M1	2.5%	15	128.2
M2	5.0 %	15	130.4
M3	7.5 %	15	134.6
M4	10 %	15	120.9
M5	15 %	15	118.4
M6	20 %	15	105.6
M7	25 %	15	95.7
M8	30 %	15	80.1

V. TREATMENT OF SPENT LIQUOR

By treatment with sodium bi-sulphite, hexavalent chromium is reduced to trivalent chromium, and this is checked by solution of diluted sulphuric acid and diphenylcarbazide [11]. If no colour is indicated, hexavalent chromium is taken as absent, and if red-violet colour appears, hexavalent chromium is present.

Further, the lime solution is added to spent liquor to raise the pH to 11-12, then alum solution is introduced to bring the pH of the solution in the range of 7.5-8.5, and finally it is allowed to settle. Following reactions take place during the reduction of hexavalent chromium to trivalent chromium and its precipitation in the form of chromium hydroxide and calcium sulphate.

$$4\,CrO_3 + 6\,NaHSO_3 + 3H_2SO_4 \longrightarrow 2\,Cr_2(SO_4)_3 + 3\,Na_2SO_4 + 6\,H_2O \quad (4.1)$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad (4.2)$$

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Cr(OH)_3 + 3\,CaSO_4 \quad (4.3)$$

VI. SUB-AQUEOUS BATCH LEACHING TEST (24 WEEKS) AT 28 DAYS OF CURING

As the cement concrete hollow closed cavity brick will be exposed to atmospheric conditions, to assess the leachability of the trace elements from the concrete under submerged, or predominantly anaerobic, conditions, testing is carried out by submerging the test samples of 200 g concrete in 1 litre of synthetic acid leachant in a barrel for a period of 24 weeks. The liquid-solid ratio is kept 5:1, without crushing the test materials. Two halves of concrete, approximately 20 mm thick and weighing 200 g (+ 2%) cut from the mid height of cement concrete hollow closed cavity brick are used. The synthetic acid rain water is an unbuffered mixture of sulphuric and nitric acids, diluted to pH 4.5. This test is carried out as per Zhang et. al. [12].

Synthetic acid-rain water is prepared in the laboratory by adding conc. H2SO4 (0.1 ml), conc. HNO3 (0.1 ml) diluted by distilled water to make pH 4.5.

VII. DISCUSSIONS

With incorporation of fly ash, average compressive strength of cement concrete hollow closed concrete bricks has found to increase, which can be attributed to C-S-H gel formation. Sub-aqueous batch leaching test (24 weeks) results on cement concrete hollow closed concrete bricks show that Cr and Ni are below detection limits in the leachate. Cr and Ni may be adsorbed by adsorption ability of fly ash. pH of the leachate as per sub-aqueous batch leaching test (24 weeks) conducted on cement concrete hollow closed cavity brick is increased from 4.5 to 10.6. It may be contributed by alkaline nature of cement concrete hollow closed cavity bricks(Table IX).

TABLE IX CONCENTRATION OF METALS IN LEACHING TEST

Brick No.	Cr(Chromium) mg/l	Ni(Nickel) mg/l
M1	ND	ND
M2	ND	ND
M3	ND	ND
M4	ND	ND
M5	ND	ND
M6	ND	ND
M7	0.002	ND
M8	0.09	ND

It is therefore safe to recommend use of TSLS (Treated Spent Liquor Sludge) and fly ash in the production of cement concrete hollow closed cavity bricks.

VIII. CONCLUSIONS

a) Compressive strength of cement concrete hollow cavity brick is found to increase with addition of 7.5% TSLS and 15% fly ash as a partial replacement of cement. Formation of C-S-H gel may be contributing to increase in compressive strength.

b) Cr & Ni are found absent in sub-aqueous batch leaching test (24 weeks) carried on cement concrete hollow cavity brick, thereby indicating effective encapsulation of treated spent liquor sludge.

c) Development of cement concrete hollow cavity bricks with treated spent liquor sludge and fly ash is expected to save about Rs. 800 per 1000 bricks.

Note: Salient Features of Cement Concrete Hollow Closed Cavity Bricks:

- Higher degree of automation, thus needs less labour force;
- Good durability, strength, impact resistance and low maintenance cement concrete hollow closed cavity bricks wall under a variety of exposures;
- Used for thermal insulation;
- Earthquake resistant structures;
- Needs lower maintenance, has longer life, resistance to insects and moisture, non combustible and environmentally safe;

- Materials reduction 20-30% with comparison to clay bricks depending upon the configuration of cement concrete hollow closed cavity bricks;
- Reduction in plaster due to uniform size;
- Faster construction by using of cement concrete hollow closed cavity bricks.

All the tests were carried out at IIT Roorkee during the Ph.D. work of author.

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