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Solidification / Stabilisation of Pond Sediments of Union Carbide India Limited, Bhopal

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Abstract: *During the manufacture of carbamate type of pesticides at the Union Carbide India Limited, Bhopal, acidic waste water was generated. This was neutralised and disposed in solar evaporation pond. After evaporation, ponds were left with sediments containing mainly inorganic salts. Due to practical conditions and cost factors, various different treatment alternatives were not considered. Studies were attempted to adopt solidification / stabilisation technique to make blocks with the objective of reuse of blocks and to minimize leaching. Studies were carried out by mixing the sediment with various admixtures namely cement, lime and fly ash. Solidified blocks were subjected to aqueous leaching and compressive strength tests before and after leaching to assess the leaching potential and mechanical strength of the blocks respectively. The studies revealed that solidification / stabilisation technique with commonly available admixtures was not suitable to arrest the leaching and the mechanical strength after leaching was found to be below limits permissible for the blocks to be used as construction material.*
Keywords: *Admixtures, Fly ash, Hazardous, Lime, Sediments, Solar evaporation ponds, Toxic*

I. Introduction

The role of chemical products has improved health and life expectancy, increased agricultural production, enhanced economic opportunities and the quality of life in general. Rapid growth in chemical technology and increasing dependence on chemical products have posed unprecedented risks to human health and environmental quality by the use and overuse of the chemical products as well as by the hazardous wastes generated in their manufacture. Every year, million tonnes of waste are discarded all over the globe and a sizable quantity of this discard is hazardous. The environmentally sound management of hazardous wastes have become one of the major issues of global concern. Thus improper handling of hazardous waste can have more damaging and long term impacts by contaminating the water cycle and the food chain. [1] Irrational dumping of hazardous waste has been responsible for a large number of disasters worldwide. There are reports on hazardous wastes being shipped to under develop / developing countries for dumping. However, the countries of world have now realised the danger and are refusing hazardous waste being dumped under their soil or sea. [2]

II. Hazardous Waste Treatment And Disposal

Recent regulations and growing public concern over the health and environmental implications of hazardous wastes make it mandatory for the industries to undertake the task of effective treatment and environmentally sound disposal of the wastes. The options for hazardous waste management include, on one hand, reactive control measures such as End – of – Pipe (EOP) treatment and disposal, and on the other, anticipative and preventive strategies such as waste minimization through adoption of low and non waste technologies of production. There are many varieties of wastes and they can be subjected to various treatment system. There could be more than one treatment and disposal system for the same waste. [3] Solidification / stabilisation (S/S), employing additives to reduce the mobility of pollutant have gained popularity in recent years following strict regulations on land disposal of hazardous wastes. This is essentially a cost – effective option, prior to landfill disposal of hazardous wastes, involving easily available and inexpensive raw materials and simple techniques. The primary objectives of solidification / stabilisation process is to convert toxic waste streams into an inert, physically stable mass having a very low leachability and with sufficient mechanical strength to allow for land reclamation or land filling. Solidification / stabilisation are treatment technologies designed to either improve waste handling and physical characteristics, decrease surface area across which pollutants can transfer or leach or detoxify the hazardous constituents. Solidification implies that these results are obtained primarily by production of a monolithic block of treated waste with high structural integrity.

Stabilisation describes processes which limit the solubility of or detoxify the contaminant, the physical characteristic, may or may not be improved or changed. [4]

III. Background Information

There are three evaporation ponds covering an area of 14 hectares as shown in Figure 1. The total capacity is 317000 cubic meters with depth varying between 3.3 m and 5.6 m. The wastewater originated during the manufacture of Methyl Iso Cyanate at Union Carbide India Limited (UCIL), Bhopal was neutralised and disposed off in Solar Evaporation Ponds (SEPs). The ponds are not receiving wastewater since December 1984. The earlier studies carried out by NEERI, Nagpur indicated that the pond contents are both water and sediment containing inorganic salts mainly chloride and sulphates of calcium and sodium.[5] The treatment alternatives studied include land farming, soil washing and containment. There is not much report available to evaluate the efficacy of S/S for the salt laden wastes. In view of this, a probing study was initiated to evaluate the application of S/S for the pond sediment as the sediment contains large concentration of chloride. The study is aimed to evaluate the solidification / stabilisation technique for the solar evaporation pond sediments. If the S/S technique is successful for pond sediments, then the sediments could be utilised for product manufacturing such as bricks. Thus the entire area occupied by the ponds could then be utilised. In view of this anticipated utilisation of land, S/S technique is attempted in this study. The plant, spread over an area of 30 hectares is bound by Bhopal Indore railway line on the north Chola nalla on the south, Vidisha road in east and Berasia road on west. The location of plant and the Solar Evaporation Ponds is shown in Figure 2, there are three solar evaporation ponds covering an area of 14 hectares and were built by taking out 20 cm of top soil and constructing bunds using the excavated and fresh soil from nearby area. Special grade low density black polythene sheets as liner was laid on all side and bottom of the pond to prevent any seepage of liquid from the pond. The ends of the sheets were thermally sealed. Clay was spread over the top of the liner to a thickness of 20 cm for effective retention of the liner in position as well as additional barrier for seepage.

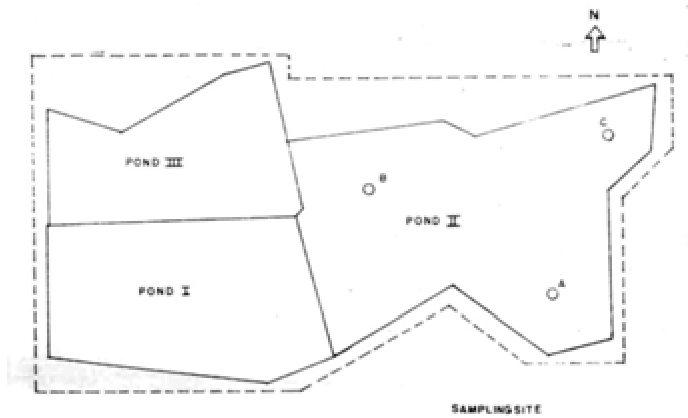

Figure 1: Location of Sediment Sampling Sites In side Solar Evaporation Pond II

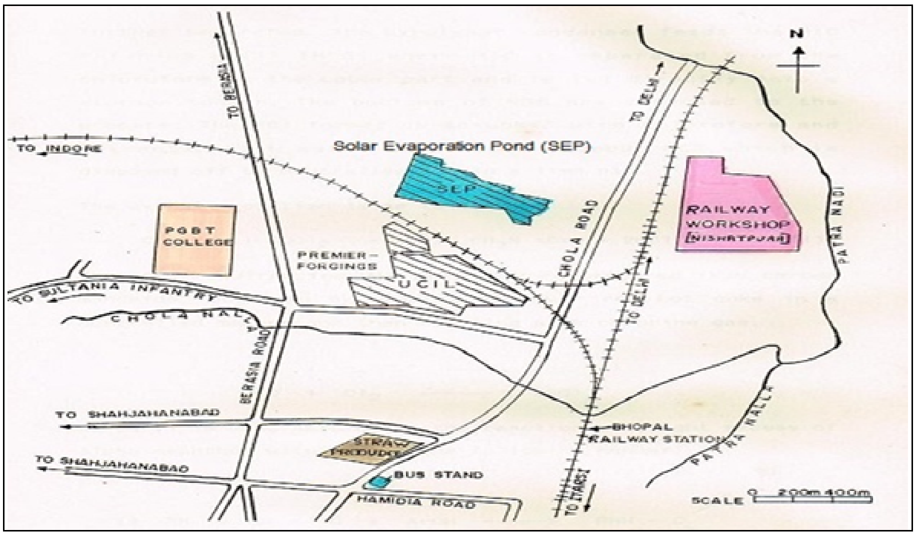

Figure 2: Location of Union Carbide India Ltd., Bhopal

Experimental Setup

In this study, sediment samples from Solar Evaporation Ponds II (SEP) were collected to conduct bench scale experiments on treatment of sediments by the solidification / stabilisation technique. The admixtures considered include Ordinary Portland Cement (OPC), fly ash, and lime. The sediment and the admixtures are mixed in different proportions to form cubes / bricks. In addition to the cubes, bricks are also made both with grab samples collected from three points and from composite sample, denoted as P' and Q' respectively. The difference between P' and Q' lies in the procedure of brick making. Table 1, gives the identification and details of each sample. These cubes and brick samples are then subjected to leachate testing and then for compressive strength test. [6] The cubes and bricks are kept in three litres jars / buckets and 1.5 litres of tap water is added to it and the level is marked. Each jar / bucket is labelled with sample numbers. Additional water is added once in 3 - 4 days to compensate for evaporation losses. All analysis is conducted according to USEPA methods and quality assurance / quality control (QA/QC) procedures, as stated in SW-846. [7][8] The study was carried out with duplicate samples. Each sample is weighed initially and also after the completion of immersion test. The tap water is analysed for pH, EC, chloride, sodium, calcium and magnesium to obtain background level and are shown in Table 2. Water from test jars / buckets is withdrawn at regular intervals for analysis.

Figure 3: Showing Experimental Setup

Figure 4: Finally Kneaded Waste Sample Before Moulding

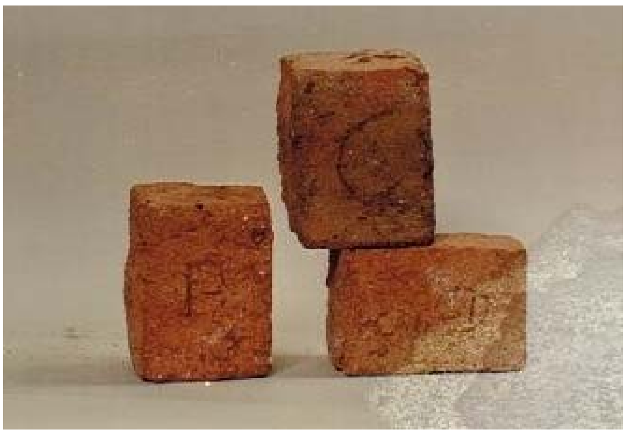

Figure 5: Prepared Brick Samples

IV. Characteristics of Pond Sediment

The sediments samples up to liner depth are collected at three different points (Figure 1). Earlier studies indicated the presence of chloride, calcium and magnesium as the predominant pollutant and the samples are analysed only for these parameters. The data are presented in Table 3. According to table the chloride concentration is varying from 0.50 mg/g at sample location A to 1.766 mg/g at sample location B. The chloride concentration of sample C is 1.22 mg/g. The three samples are mixed to obtain a composite sample. The chloride concentration of composite sample is 1.08 mg/g. The total concentration of calcium and magnesium together ranges from 0.25 mg/g at A to 0.78 mg/g at B. The composite sample has Ca + Mg of 0.5 mg/g at C.

Table 1: Identification and Details of Samples

Type Of Cubes	Symbols	Identification	Ratio
Blank Cubes	BL	Cement + Sand	1:3
Cement Based Cubes	CM	Cement + Waste + Sand + Flyash	1:1:3: 30% of Wt. of Sand
Lime Based Cubes	L	Lime + Waste +Sand + Flyash	1:1:3: 30% of Wt. of Sand
Flyash Based Cubes	F	Flyash + Waste + Sand	1:1:0.5
Bricks	O	Waste + Clay + Flyash + Straw	4:4:1: 2%
Bricks	P	Waste + Flyash + Straw	4:1: 2%
Bricks	A	Waste A + Clay + Flyash + Straw	4:4:1: 2%
Bricks	B	Waste B + Clay + Flyash + Straw	4:4:1: 2%
Bricks	C	Waste C + Clay + Flyash + Straw	4:4:1: 2%

Table 2: Characteristics of Tap Water Used in the Study

Sl. No.	Day	pH	EC*	Na	K	Ca	Mg	Cl
1	0	7.5	98	0	0	76	14	21
2	10	7.1	106	0	0	69	12	26
3	20	7.0	104	0	0	68	17	21
4	30	7.6	103	0	0	74	17	13
5	40	6.9	111	0	0	78	14	17
6	50	7.0	113	0	0	71	15	13
7	60	7.4	114	0	0	79	18	14
8	70	7.7	104	0	0	76	14	13
9	80	7.5	101	0	0	73	14	13

*All values are expressed in mg/l, except for pH and EC. *EC is expressed in μ mhos/cm*

Table 3: Characteristics of Pond Sediments from Solar Evaporation Pond II

Sample	pH*	EC	Chloride	Ca + Mg	Na
		μ mhos/cm @ 25 ^{0}C	%	%	%
A	-	-	0.5	0.25	-
B	-	-	1.766	0.78	-
C	-	-	1.22	0.50	-
Composite (A+B+C)	7.1	18.6	1.08	0.50	0.8

** pH is measured in saturated paste of the sediments.*
All cations, anions and EC are determined in the water extract prepared by taking 1g sediment and 10 g water shaken for 6 hours and filtered through Whatman No. 42 filter.

Table 4: Cement, Lime, Fly-ash, Based Cubes

Parameters	Immersion Period In Days							
	10	20	30	40	50	60	70	80
Cement Based Cubes								
pH	10.8	10.5	9.6	8.7	8.0	7.4	7.3	7.2
Electrical Conductivity	1320	436	420	405	362	320	290	272
Chloride	228	70	62	60	30	28	14	6
Calcium	23	3	6	10	16	22	18	14
Magnesium	1	0	1	2	2	5	2	0
Sodium	142	47	42	38	29	22	14	5
Lime Based Cubes								
pH	11.7	9.6	8.8	8.4	7.9	7.6	7.2	7.1
Electrical Conductivity	1950	394	382	270	258	256	255	250
Chloride	364	221	71	51	51	14	6	6
Calcium	204	6	9	16	19	11	9	6

Magnesium	0	3	3	5	7	2	0	0
Sodium	88	53	60	41	21	16	4	4
Fly-Ash Based Cubes								
pH	8.7	8.5	7.4	7.3	7.3	7.2	7.2	7.1
Electrical Conductivity	3525	4052	4580	2970	1355	1355	356	332
Chloride	1585	1372	1159	458	234	123	11	8
Calcium	524	65	69	76	105	47	33	21
Magnesium	2	16	29	38	60	41	8	6
Sodium	178	218	242	90	66	37	15	5

V. Results And Discussion

Cement Based Cubes: It may be seen from Table 4 that the pH is reduced from 10.8 to 7.2 over a period of 80 days. The decrease of pH is probably due to reduction of Ca and Mg. The conductivity reduced from 1320 µ mho/cm from 10 days to 272 µ mho /cm at the end of 80 days. The decrease of EC could be the absence of dissolved salts such as chloride. The main parameter of concern is chloride which shows a declining trend. The chloride concentration at the end of test period is only 6 mg/l as against 228 mg/l at the end of 10 day. It may be seen from the table that the concentration of chloride is very high and almost absent at the end of test run. This shows that the inorganic compounds present in the cubes have more potential for leaching. It has been computed that the leachate potential of chloride is about 17%. The leaching potential for the next 30 days is only 10% i.e. nearly 27% of chloride present in the cube has leached in 30 days. The leachate potential in the next 50 days is only 9% totalling an aggregate leachate potential as 29.6% over a period of 80 days. Magnesium is also less in water at 29.6% over a period of 80 days. Magnesium is also less in water at the end of test period. Mixing the cement with water triggers numerous reactions. Basically the di$^-$ and tri$^-$ calcium silicates form hydrates releasing calcium hydroxides. The calcium hydroxides and water react with the tri- and tetra calcium aluminates forming hydrates of those compounds. The hydrate then reacts with additional water in the mix to form the crystalline hydrate structure which constitutes the solid matrix. Leaching mechanisms in the pozzolonic based solid matrix are controlled by the free hydrogen ions available in the leachate. Alkalinity leached is the consequence of the penetration of hydrogen ions. Hydrogen ions diffuse into the solid matrix and neutralise the alkalinity provided by the binder in the leach front. pH decreases after the acid neutralisation capacity is consumed.

Lime Based Cubes: In this case also pH has reduced from alkaline pH of 11.7 to near neutral pH of 7.1 at the end of 80 days. It has been observed from Table 4, that the calcium and chloride leaching are very high at the 10th day. The chloride level at the end of 10th day is 364 mg/l as against 6 mg/l at the end of 80 days. The percentage leaching of chloride is about 27.3% at the end of 10 days and the total leaching potential is 34.8%. In view of the decrease in Ca and Mg, the pH has reduced. As the dissolved salt such as chloride is reducing with time the EC has dropped from 1950 µ mhos /cm to 250 µ mhos / cm. Lime based processes behave in a similar manner to cement based ones. Lime does not form solid matrix when mixed with water. It, however tend to precipitate many of the metals. While carbonate formation is important for the long term stability of S/S wastes, lime is often mixed with other materials to produce a binder which sets up more quickly.

Fly-Ash Based Cubes: It is observed from Table 4, that pH is reduced from 8.7 to 7.1 over a lapse of 80 days. This decrease is probably due to reduction in calcium and magnesium. The electrical conductivity reduces from 3525 µ mho/cm at the end of 80 days. This decrease of electrical conductivity could be the absence of dissolved salts such as chloride. The chloride shows a falling trend. The chloride concentration at the end of test period is only 8 mg/l as against 1585 mg/l at 10 day. It has been observed that the concentration of chloride is very high initially and almost nil at the end of test run. This shows that the inorganic compounds present in the cubes have more potential for leaching. It has been computed that the leaching potential of chloride is about 47% for 10 days. The leaching potential for next 40 days is only 10 % totalling an aggregate leachate potential as 92.8% over a period of 80 days.

Brick Variety 'A': From Table: 5, it can be seen that pH has remained constant throughout the test period. It is observed that calcium and chloride leaching are very high for the 10 days. The chloride level at the end of 10th day is 346 mg/l as against 6 mg/l at the end of 80 days. The percentage leaching of chloride is about 51.8 % at the end of 10 days and the total leaching potential is 80% at the end of 80 days period. The dissolved salt such as chloride is reducing with time and the electrical conductivity (EC) has dropped from 1667 µ mhos /cm to 336 µ mhos /cm. The sodium concentration reduces from 12 mg/l to 3 mg/l.

Brick Variety 'B': The pH is more or less constant over a period of 80 days. The conductivity reduces from about 831 µ mhos /cm on the 10th day to 296 µ mhos /cm at the end of 80th day. The decrease of EC could be due to absence of dissolved salts such as chloride. The parameter of concern, chloride is not very high even at 10th day. The falling trend is between 77 mg/l on the 10th day to 7 mg/l on the 80th day. Sodium is not leaching throughout the test period. It has been computed that the leachate potential of chloride is about 2.6% for the 10th

day. The leachate potential for the next 70 days is only 3.3% totalling an aggregate leachate potential at 5.9% over a period of 80 days.

Brick Variety 'C': The pH remains more or less constant throughout the length of study period. The conductivity reduces from 1242 μ mhos /cm to 348 μ mhos /cm. Potassium becomes nil at the end of the test. The chloride concentration shows a declining trend from 177 mg/l on 10th day to 6 mg/l on the 80th day. The percentage leaching of chloride is about 10.8% at the end of 10 days and the leachate potential for the next 70 days is 10.2%. The total leaching potential is 21.0%.

Brick Variety 'O': The pH decreases from 8.5 on the 10th day to 7.8 on the 80th day of the experiment. This decrease of pH may probably be due to reduction of calcium and magnesium. The conductivity reduces from 1026 μ mhos /cm from 10th day to 309 μ mhos /cm at the end of 80th day. The decrease of EC could be the absence of dissolved salts such as chloride. The main parameter of concern is chloride which shows a declining trend. The chloride concentration at the end of test period is only 5 mg/l as against 362 mg/l at 10th day. Sodium has not leached like that in variety 'C'. Calcium decreases from 254 mg/l to 3mg/l. It has been computed that the leachate potential of chloride is 25.1% for initial 10 days. The leaching potential for the next 70 days is only 7.10% totalling an aggregate leachate potential as 32.3% over a period of 80 days.

Brick Variety 'P': The pH reduces from 9.4 on the 10th day to 7.5 on the 80th day. It has been observed that the conductivity reduces from 1330 μ mho /cm to 291 μ mho /cm during the study period. This may probably be due to reduction in chloride concentration from 239 mg/l on 10th day to 9 mg/l on the 80th day. The concentration of sodium also reduces at the end of test period. The percentage leaching of chloride is about 9.94% at the end of 10 days and the leachate potential for the next 70 days is 12% summing to a total leaching potential of 22.1% at the end of 80 days.

Table 5: Immersion Test Values of Clamp Burnt Bricks

Parameters	**Immersion Period In Days**							
	10	**20**	**30**	**40**	**50**	**60**	**70**	**80**
Brick Variety "A"								
pH	7.5	7.7	7.8	7.5	7.3	7.4	7.4	7.3
Electrical Conductivity	1667	1056	945	710	485	421	360	336
Chloride	346	214	146	82	37	21	7	6
Calcium	331	244	158	113	66	48	24	9
Magnesium	19	19	18	13	11	11	11	8
Sodium	13	12	13	16	14	8	3	3
Brick Variety "B"								
pH	8.4	8.2	7.9	7.8	7.8	7.4	7.4	7.5
Electrical Conductivity	831	670	470	491	516	412	308	296
Chloride	77	62	47	34	22	15	7	7
Calcium	156	98	41	39	36	21	2	2
Magnesium	17	15	10	10	11	10	10	9
Sodium	13	14	18	22	18	7	7	3
Brick Variety "C"								
pH	7.4	7.6	7.9	7.8	7.8	7.9	7.9	8.0
Electrical Conductivity	1242	1061	880	698	500	431	362	348
Chloride	117	141	120	58	38	22	8	6
Calcium	238	189	140	101	62	42	22	19
Magnesium	24	29	34	17	15	13	11	10
Sodium	12	13	14	15	15	11	3	3
Brick Variety "O"								
pH	8.5	8.2	7.9	7.9	7.9	7.9	7.9	7.8
Electrical Conductivity	1026	812	600	5.8	420	370	330	309
Chloride	362	220	83	52	16	9	5	5
Calcium	175	129	83	64	46	24	3	1
Magnesium	17	17	15	18	23	15	7	6
Sodium	12	12	14	13	12	9	2	2
Brick Variety "P"								
pH	9.4	8.7	8.2	7.9	7.6	7.6	7.6	7.5
Electrical Conductivity	1330	966	842	727	612	478	303	291
Chloride	239	198	154	111	75	30	10	9
Calcium	262	193	124	102	80	52	25	13
Magnesium	9	18	30	22	10	7	4	3
Sodium	12	13	17	16	16	7	4	3

Brick Made by Control Heating: In addition to bricks made by clamp burning some bricks were also made by control heating in a muffle furnace. The bricks were tested for their leaching potential for 7 days. In general the leaching potential for these bricks were more than the clamp burning by many folds. The weight of bricks has marginal increase and this could be due to water absorption.

Compressive Strength Test: In addition to leaching potential of cubes and bricks, they were subjected to tests for their strength. This is being carried out to evaluate whether the cubes and bricks can be used for construction or otherwise. The data is presented in Table: 6 and Table: 7.The compressive strength of cement based cubes was reduced by 75% at the end of 7 days curing period. However, it is increased considerably after 80 days curing. The compressive strength of lime based cubes was as low as 49 ksi even after 80 days curing. The compressive strength of fly ash based cubes was practically zero as they got deformed as soon as pressure was applied. The compressive strength of bricks is reduced by 30% to 40% compared to the blank bricks. It is interesting to note that the strength of bricks has no direct relationship with the chloride content in the sample. In addition the bricks were immersed for 16 hours to assess the water absorption capacity. The result indicated that the absorption capacity varies from 16% to 20%.

Table 6: Compressive Strength of Various Cubes

Samples	Symbols	Compressive Strength (ksc)		
		7 days	**28 days**	**80 days**
Blank	$B1_1$	171.4	X	X
Cement	$B1_2$	163.3	X	X
Mortar	$B1_3$	X	200	X
Cubes	$B1_4$	X	192	X
Cement Based Cubes	CM_3	40.8	X	X
	CM_4	44.8	X	X
	CM_5	X	61.22	X
	CM_6	X	77.55	X
	CM_1	X	X	138.77
	CM_2	X	X	146.94
Lime Based Cubes	L_3	0	X	X
	L_4	0	X	X
	L_5	X	20.41	X
	L_6	X	16.32	X
	L_1	X	X	40.8
	L_2	X	X	48.98
Fly-Ash Based Cubes	F_3	0	X	X
	F_4	0	X	X
	F_5	X	0	X
	F_6	X	0	X

Table 7: Compressive Strength of Bricks

Samples	Symbols	Dimension in cm			Compressive Strength (ksc)
		Length	**Breadth**	**Height**	
Blank Brick	BB_1	19.8	9.7	8.5	53
	BB_2	19.8	9.5	8.5	52
Grab Samples From Point A (4:4:1:2%)	A_3	19.8	9.5	8.7	31
	A_4	19.5	9.5	8.5	32
Grab Samples From Point B (4: 4: 1: 2%)	B_3	19.7	9.7	8.6	32
	B_4	19.8	9.7	8.6	34
Grab Samples From Point C (4: 4: 1: 2%)	C_3	19.8	9.7	8.3	32.6
	C_4	19.6	9.6	8.3	32.4
Grab Samples From Point O (4: 4: 1: 2%)	O_3	19.8	9.7	8.5	28.6
	O_4	19.8	9.7	8.6	30.7
Grab Samples From Point P (4: 4: 1: 2%)	P_3	19.5	9.5	8.5	29.15
	P_4	19.8	9.5	8.5	27

VI. Conclusion

In this study, cement, lime, fly-ash based cubes and bricks made by clamp burning were studied. The samples are tested for their leaching potential and for strength. The following are concluded from the study:

- The highest leaching potential was recorded with fly-ash based cubes followed by lime and cement. Thus fly-ash is not to be considered for S/S for salt laden wastes.
- The compressive strength of cubes is reduced by 66% in case of cement, 80% for lime and 100% for fly-ash cubes. The fly-ash based cubes broke down as soon pressure was applied and hence not suitable. However, the strength of cement based can be considered after 80 days curing to obtain strength of 140 ksi.
- The compressive strength of bricks with sediment is averaged as 30 ksi as against 53 ksi without sediment.
- It is observed that the burnt bricks also show leaching potential. It is interesting to note that the leaching potential reduces with increased chloride content.

It can be concluded from the study that solidification / stabilization (S/S) technique is not suitable for pond sediment containing high levels of salts. However, the leaching potential may be reduced using urea formaldehyde resins. [9] Polymers have been used successfully in nuclear wastes disposal and in special industrial wastes. Due to their rapid setting, high strength, low permeability and high corrosive resistance, it appears that they have the potential for S/S. Further works are therefore suggested.

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