Solidification and stabilization of expired chemicals

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Abstract

Expired chemicals are treated to be hazardous waste. Not only are expired chemicals useless for an experiment, but they can also be volatile and dangerous when they exceed their date of expiry and become complicated and difficult to dispose. Once these chemicals get disposed into landfill and if there is any leaching, it leads to pollution of the environment and also affecting human health in the near vicinity. Treatment of hazardous waste is done through solidification and stabilization process designed to encapsulate inorganic hazardous wastes (heavy metals) within cement, thereby creating a non-hazardous product. In this project the expired chemicals are solidified and stabilised before their disposal. One of the main objective of the project is to optimize the mix of binders and to ensure safe disposal of chemicals into landfill in an eco-friendly and an economically viable manner and to study the leaching process of heavy metals, to optimize the process of stabilization of hazardous waste using the conventional materials like fly ash, cement & lime which are used as binders to evaluate the quantity of heavy metals that could possibly release and harm the environment and human beings. Efficiency of the mobilization depends on parameters such as curing time, dosage of stabilizer and combination of stabilizer to reach the criteria of hazardous waste and safe disposal of this waste into the landfill.

Keywords

Solidification, Stabilization, Hazardous waste, Expired chemicals.

1.Introduction

Certain chemicals are unstable and within few years or even few months, tend to turn into dangerous substances. Expired chemicals are treated as to be hazardous wastes [1, 2]. Not only are expired chemicals useless for an experiment, but they can also be volatile and dangerous when they exceed their date of expiry and become complicated and difficult to dispose. Expired chemicals are a real problem in laboratory work. They pose health and safety risks as well as risks to the work being done. There are totally four characteristics in chemical wastes that will make a waste to be hazardous in nature.

Ultimate disposal of the expired chemicals would be into a landfill. Various reasons would lead to the dissolution of harmful chemicals (or materials) from landfills formed from dumping of wastes. The migration of these toxic dissolved chemicals from landfills into the natural resources like river, groundwater, etc. would lead to major environmental problems.

The impact of the toxic agents due to the exposure poses serious health issues in human beings when their concentration increases beyond the acceptable limits. In order to prevent the leaching of chemicals, solidification and stabilization can be done in which materials are added to the waste to produce a solid which is more stable chemically as there would be a chemical bond between these wastes and the additives [3, 4]. By this process, there will be a transformation of toxic component to a new nontoxic substance, which would reduce the risk of affecting the environment adversely [5].

The present study gives an insight about optimization of the stabilizer mixes for the solidification of the expired chemicals and to know which substitute would be better between lime and fly ash to partially replace the conventional binder (cement), for the solidification-stabilization process. This project focuses on treatment/stabilization of hazardous wastes prior to the disposal into a landfill, with addition of cement, fly ash and lime also to know their concentrations discharged into the environment.

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The objectives of this study are:

- Solidification & stabilization of the expired chemicals using lime fly ash & cement.
- Optimization of stabilizer mix for solidification of the chemical waste.
- To arrive at a new unconventional partial substitute, for the conventional binder i.e. cement using waste substances, for the solidification-stabilization process.
- To arrive at the condition, where the heavy metal concentration in the leachate meets the required criteria for disposal when the stabilised waste is disposed into the landfill.
- To study the leaching behaviour of chemicals and also to know their concentrations discharged in the environment.

2. Materials and methodology

This project aims in the safe disposal of expired chemicals into the landfill that it would not cause any leaching into the soil lying under the landfill. Solidification and stabilization technique is adopted which involves the addition of cement [6] and additives which thereby limits the solubility or mobility of the waste constituents [7, 8]. The expired chemicals were collected from the laboratories of BMS College of Engineering, Bangalore. The stabilizing agents chosen for this work are lime and fly ash (*Figure 1*).

Figure 1 Methodology followed

Collection and sampling of expired was done and later arrived at mix proportions by deciding the amount of stabilisers to be added for each of the mix (*Table 1*). Test specimens were casted in the form of

cube of dimension 70.6 mm × 70.6mm × 70.6 mm. Later the specimens were tested for compression strength after 7 and 28 days of curing in the water bath. Digestion of the stabilised samples was done in order to analyse the heavy metals by atomic absorption spectrophotometer.

Table 1 Collected expired chemicals and their quantities

Sl No	Chemicals	Quantity in grams
1	Lead Nitrate	4200
2	Lead II Nitrate	1500
3	Lead Nitrate LR	500
4	Zinc Sulphate	500
5	Copper Nitrate	250
6	Cadmium Sulphate	600
7	Copper II Sulphate	1500
8	Cupric Sulphate	1000
Total quantity of expired chemicals		10,050

All the expired chemicals collected were salts of heavy metals like copper, chromium, zinc and cadmium. The total quantity of expired chemicals collected added to 10 kilograms. Initially pH of the chemicals was checked using pH meter. It was observed that the chemicals were having pH of less than 7 which indicated that it was acidic in nature. The mixture of expired chemicals gave out a very pungent smell. It was observed that this mixture used to easily catch the moisture if it was kept in open air for even few minutes, hence it was preserved in air tight container and thus it was maintained dry all through the course of the experimental work and also until it was casted as a cube using cement, lime and fly ash.

In order to stabilize them, the number of mixes was decided based on the quantity of the collected chemicals and also the stabilizing agents to be used in the process of stabilization was decided to be lime and fly ash [9] as another important objective of this project was to reduce the use of conventional binder which is cement and replace it with a non-conventional material that would serve the purpose as per the required criteria [10]. Proportioning of the stabilizing agents was done for the 15 mix designs in which the cement was kept as least for the first mix which was 20:80 (cement: additives) and the maximum cement quantity was in the ratio 60:40 (cement : additives) and the quantity of expired chemicals was fixed to be constant for every mix i.e. 150 grams. Cement content was kept increasing in each mix. The following *Table 2* shows the quantities of cement, lime, fly ash and the expired chemicals for all the 15 mixes.

Table 2 Proportioning the stabilizing agents

Mix	Cement: additives	Expired chemicals (G)	Quantity (G)		
			Additives +Cement		
			Lime	Fly Ash	Cement
1	20:80	150	1/2	1/2	-
	160g:490g	-	245	245	160
2	20:80	150	1	0	-
	160g:490g	-	490	0	160
3	20:80	150	0	1	-
	160g:490g	-	0	490	160
4	30:70	150	1/2	1/2	-
	240g:410g	-	205	205	240
5	30:70	150	1	0	-
	240g:410g	-	410	0	240
6	30:70	150	0	1	-
	240g:410g	-	0	410	240
7	40:60	150	1/2	1/2	-
	320g:330g	-	165	165	320
8	40:60	150	1	0	-
	320g:330g	-	330	0	320
9	40:60	150	0	1	-
	320g:330g	-	0	330	320
10	50:50	150	1/2	1/2	-
	. 400g:250g	-	125	125	400
11	50:50	150	1	0	-
	400g:250g	-	250	0	400
12	50:50	150	0	1	-
	400g:250g	-	0	250	400
13	60:40	150	1/2	1/2	-
	480g:170g	-	85	85	480
14	60:40	150	1	0	-
	480g:170g	-	170	0	480
15	60:40	150	0	1	-
	480g:170g	-	0	170	480

3.Results and discussions

The experiments were conducted by varying the dosage of the binders at different combinations and also the duration of the curing time. The solidification and stabilization studies were performed at laboratory scale, where the expired chemicals was mixed with various proportions of stabilizing agents like cement, fly ash, and lime in different combinations and duration of curing, so as to solidify it for secure landfill disposal with the reduction in heavy metal concentration [11–13]. To identify which mix would reduce the concentration of heavy metal in the leachate before it has been disposed of into a secured landfill. The collected expired chemicals were checked for the heavy metal content in AAS before the process of stabilization

was started. It was revealed that the sample had a very high content of copper (i.e. 853.87 ppm) as shown in *Table 3*.

Out of the 15 mix proportions casted into cubes, 5 of the mixes after casting into cubes got brittle soon as they were placed into the curing bath and their strength was not reached. The 5 mixes that failed to reach the strength are shown in *Table 4*. After 7 and 28 of the casting of cube samples, the cubes were tested for compressive strength (*Table 5*) in universal testing machine. Expect the cubes of batch 5, rest all gave the compressive strength of greater than 0.35 N/mm², which is the criterion of compressive strength required for the disposal into the landfill. The following *Figures 2 and 3* shows the 7 days and

28 days compressive strength for all the mixes. It was observed that the water prior to the placement of cubes for curing was tested for heavy metals and it showed no presence of Cu, Ni or Cr. Later when the same water was tested for the heavy metal after the cubes were taken out after 28 days then there was presence of Cu, Ni and Cr.

The *Table 8* will give the values of the heavy metals in the water observed before and after the cubes were placed in the water for curing. *Table 6* shows the heavy metal content of the stabilised samples after 7 days curing period. *Table 7* shows the heavy metal content of the stabilised samples after 28 days curing period.

Table 3 Heavy metal concentration in the sample

Heavy metal concentration in expired chemicals	Acid leaching before stabilization (PPM)
Cu	853.87
Cr	0.85
Ni	0.63
Cd	0.078
Fe	0.090
As	0.040
Zn	0.038

Table 4 Failed set of mixes when kept for curing

S. No	Cement: additives	Cement(G)	Lime(G)	Fly ash(G)	Chemicals(G)
1	20:80	160	490	0	150
2	20:80	160	0	490	150
3	30:70	240	410	0	150
4	30:70	240	0	410	150
5	50:50	400	0	250	150

Table 5 Unconfined compressive strength (UCS) of solidified samples

Batch No.	MIX	7 Days compressive strength(N/MM ²)	28Days compressive strength (N/MM ²)
1	20:80 (Cement: Lime, Fly Ash, Chemicals)	0.461	1.906
2	30:70 (Cement: Lime, Fly Ash, Chemicals)	0.682	3.404
3	40:60 (Cement :Lime, Fly Ash, Chemicals)	2.046	8.828
4	40:60 (Cement: Lime, Chemicals)	1.023	2.430
5	40:60 (Cement: Fly Ash, Chemicals)	0.327	0.952
6	50:50 (Cement: Lime, Fly Ash, Chemicals)	3.389	12.372
7	50:50 (Cement: Lime, Chemicals)	0.451	1.976
8	60:40 (Cement: Lime, Fly Ash, Chemicals)	1.775	5.196
9	60:40 (Cement: Fly Ash, Chemicals)	0.962	1.226
10	60:40 (Cement: Lime, Chemicals)	3.213	20.665

Figure 2 UCS of stabilized samples after 7 & 28 days of curing

Table 6 Heavy metal content of the stabilised samples after 7 days curing period

Batch No	Cr (ppm)	Cu (ppm)	Ni (ppm)
1	0.32	64.56	0.54
2	0.33	84.65	0.47
3	0.56	71.45	0.31
4	0.46	157.94	0.35
5	0.52	180.56	0.58
6	0.05	71.56	0.39
7	0.12	77.96	0.25
8	0.44	93.42	0.22
9	0.56	164.34	0.40
10	0.47	103.45	0.18

Table 7 Heavy metal content of the stabilised samples after 28 days curing period

Batch No	Cr (ppm)	Cu (ppm)	Ni (ppm)
1	0.29	41.56	0.41
2	0.31	32.05	0.39
3	0.18	29.34	0.25
4	0.42	28.42	0.32
5	0.38	42.56	0.48
6	0.02	30.2	0.33
7	0.1	31.55	0.18
8	0.32	28.47	0.12
9	0.28	23.09	0.2
10	0.22	25.81	0.11

Table 8 Heavy metal content in the water before and after the curing of the samples

Batch No	Curing water tested for heavy metal content before cubes were placed			Curing water tested for heavy metal content after cubes were placed		
	Cr(ppm)	Cu(ppm)	Ni(ppm)	Cr(ppm)	Cu (ppm)	Ni(ppm)
1	0.0	0.0	0.0	0.02	0.85	0.02
2	0.0	0.0	0.0	0.02	0.64	0.01
3	0.0	0.0	0.0	0.01	0.68	0.03
4	0.0	0.0	0.0	0.03	0.51	0.02
5	0.0	0.0	0.0	0.08	0.71	0.05
6	0.0	0.0	0.0	0.03	0.51	0.01
7	0.0	0.0	0.0	0.00	0.53	0.04
8	0.0	0.0	0.0	0.01	0.24	0.01
9	0.0	0.0	0.0	0.01	0.05	0.01
10	0.0	0.0	0.0	0.02	0.09	0.03

Figure 3 Heavy metal content in the water before and after the curing of the samples

4. Conclusion and future work

Except batch 5 mix, rest of the stabilized mix design samples of expired chemicals proved to be very effective for solidification as their UCS values were much greater than minimum criteria value prescribed for disposal in to secure landfill i.e. 0.35 N/mm².

The best mixes (in terms of UCS), have showed exceptionally high values of compressive strengths (nearly 34 to 57 times the minimum criteria value), indicating the enormous success of the use of the binding material lime, cement, fly ash for solidification. The mixes which had lesser proportion of cement with greater proportion of fly ash with a constant proportion of expired chemicals proved to be very brittle and also showed least compressive strength when tested in UTM. The mixes with a greater proportion of cement, and lesser proportion of binding agents, showed greater stabilization effectiveness, validating the use of the two stabilizing agents as successful stabilizers. It is also noticed that expired chemicals, when used along with cement, fly ash and lime shows a higher rate of reduction in concentration of metals, in the leachate than when applied with only cement and lime or cement and fly ash. For a particular cement: additive ratio, and the same proportion of expired chemicals, the mixes with a greater proportion of cement and equal proportion of lime and fly ash proved to be more effective. It was also observed that the mix with least cement content in it i.e. 20:80 of cement : additives mix showed compressive strength of 0.416 N/mm² for 7 days and 1.906 N/mm² for 28 days, where both the compressive strength of 7 and 28 days were greater than the landfill disposal criteria which is 0.35 N/mm².

In the extraction tests and the determination of heavy metal concentration in AAS has shown that all the three heavy metals present in the expired chemicals which are copper, chromium and nickel are within their permissible levels of disposal into landfill. The heavy metal concentration of Cr = 0.02 ppm, Cu = 30.2 ppm and Ni = 0.33 ppm was seen for the best mix with respect to the compressive strength for 28 days to be 20.665 N/mm².

Further this study can be extended for various other set of expired chemical stabilization also can be used to know the chemical reactions that take place during the process of stabilization and how they would impact the strength of the cube. Heavy metal removal can be investigated by using various other stabilizing agents.

Acknowledgment

None.

Conflicts of interest

The authors have no conflicts of interest to declare.

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