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Solidification/stabilization of lead with the aid of bagasse as an additive to Portland cement

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Received 28 April 2000; received in revised form 19 May 2000; accepted 19 June 2000

Abstract

Solidification/stabilization (S/S) of hazardous waste is a widely used technology; therefore, it is crucial to evaluate its effectiveness and make attempts to improve the technique. A better matrix for S/S of hazardous waste was designed that is effective and economically feasible. This was accomplished by adding bagasse (byproduct of milling or diffusing sugar cane) to the waste/cement matrix. Lead nitrate was used as the model heavy metal waste with a 10 or 15% lead by weight to cement loading. Samples were cured for 7, 14, and 28 days at 24°C. Samples containing bagasse typically resulted in TCLP (modified) extract lead concentrations of approximately 0.5 mg/l of lead for all samples, while samples containing no bagasse had lead extract concentrations of approximately 5 mg/l for 10% samples and 45 mg/l for 15%. Results indicate that using bagasse as an additive to cement effectively improved the S/S of lead. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Bagasse; Heavy metal waste; Lead; Portland cement; Solidification/stabilization

1. Introduction

Solidification/stabilization (S/S) of hazardous wastes is a widely used technology; therefore, it is crucial that its effectiveness be evaluated and attempts made to improve the technique. There has been a large interest in studies dealing with leaching of stabilized metals such as arsenic,

cadmium, chromium, and lead from cement waste forms [1]. Immobilization by cement is effective for some metals and for some wastes, but not others. Since cement alone is not always effective, new and cheaper stabilizing agents are always sought for tailoring formulations when the need arises.

Heavy metals have been successfully bound to insoluble substrates [2]. Organic byproducts have proven to bind heavy metals. Insoluble starch xanthates are an example of such a substrate [1]. Xanthates are produced by reacting an organic hydroxyl-containing substrate, such as starch, cel-

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lulose, or alcohol with carbon disulfide in the presence of a strong base such as NaOH [3,4]. Metals are bound by exchanging the base metal sodium in xanthates for generally heavier metals [5]. Insensitivity to pH is important in stabilizing RCRA metals by binding to insoluble substrates, such as, xanthates. When combined with cement, the substrate must prove stable at a pH range of up to 13 (for neat cement pastes, cement-pozzolans typically has a pH of approx. 11) and remain stable when exposed to acidic mediums in regulatory testing (e.g. pH of 3–5 in TCLP) or the environment (e.g. acid rain).

Although detailed research on heavy metal adsorption for xanthated starches, straws, and sawdusts have been reported [3–7], all involve xanthates prepared by using CS_2 , which is extremely flammable and highly toxic. Our efforts are aimed at designing a matrix for solidification/stabilization of hazardous waste that will be effective while being economically feasible and safe to produce. The adsorbent used with cement to enhance the effectiveness of the cementitious system to contain heavy metal waste was lignin. The heavy metals will be stabilized by complexing it with a large lignin molecule, significantly reducing leach rates from wastes. To make the process economically feasible, the source of lignin came from the large excess of bagasse (≈ 1.8 million tons annually in Louisiana) produced each year from sugar cane processors. Bagasse is the byproduct or residue of milling or diffusing sugar cane. One of the components of bagasse is lignin, approximately 22% by weight [8]. Developing a better matrix to bind heavy metal waste was examined by using bagasse as an adsorbent for lead prior to solidification with cement. Even though lead is usually stabilized by cement-pozzolan processes at low lead concentrations, it was chosen as the model waste to determine if using bagasse as an adsorbent improves performance even at high lead concentrations.

2. Materials and methods

2.1. Bagasse treatment

The bagasse was treated under two different

conditions: (1) acid, (2) base. The purpose of these treatments is to eliminate cellulose fibers as much as possible and to liberate the lignin. All soluble sugars within the bagasse must be eliminated before the bagasse is added to the cement. Sugars in concentrations as low as 0.03–0.15 wt.% in cement will retard the setting time and the strength of the cement [9]. The bagasse was boiled with 0.1 M HCl or 0.1 M NaOH for approximately 45 min, with the residue washed free of sugars and hydrolysis products. This procedure was repeated 3–4 times until the filtrate was virtually colorless. The residual product was oven dried at 110°C overnight and ground to a fineness of 200 μ . The main difference between the acid/base treatments was the texture of the final product, the residual product formed from the base treatment was sticky and harder to grind.

2.2. Sample preparation

Each set of solidified samples was prepared from a bulk batch to eliminate homogeneity problems within any particular set of samples. Bulk batches typically contained 294 g of ordinary Portland cement type I, 10 or 15% lead [source of lead: 47 g or 70 g $\text{Pb}(\text{NO}_3)_2$] by weight to cement, no bagasse (control) or up to 5% treated bagasse by weight to cement, and 162 g deionized water (water/cement ratio of 0.55). The batch was mixed in the following manner (with the exception that control samples which contained no bagasse): $\text{Pb}(\text{NO}_3)_2$ was dissolved in 120 ml of water by vigorously shaking the solution. The bagasse and lead nitrate solution was placed in a normal household blender and blended on low speed for 1–2 min making sure that all the bagasse was saturated. The solution beaker was rinsed with the remaining water and placed in the blender. This bagasse/lead nitrate mixture soaked for approximately 1 h before proceeding. The cement was added to the blender and mixed with a stirring rod until all cement was moist. The mixture was blended on high speed for 5 min with periodic scraping of the sides of the blender. Approximately 20 g of the bulk batch was scooped into 20 ml borosilicate screw-cap vials. Four samples were made for each set of cure times (7, 14, 28 days) from a bulk batch. Care was taken to ensure that

representative bulk samples from the top, middle, and bottom were obtained for each set of cure times. Once a set of samples was made, the borosilicate vials were capped, and samples were stored in a standard laboratory oven at 24°C until the appropriate time for the experiment.

2.3. Crushing

After the appropriate cure time, the samples were crushed in the following manner: a vial was placed into a wide-mouth plastic bottle, and the vial broken by striking it with a steel rod. The whole sample slug was removed from the glass and crushed with a steel rod, with particles between 8.0 and 9.5 mm being retained. All particles smaller than 8.0 mm were eliminated to ensure reproducibility of the method [10]. The mass of the entire sample was recorded (typical sample mass: 10 g of the original 20 g bulk batch) and placed into a 250-ml Nalgene wide-mouth HDPE bottle.

2.4. Modified TCLP procedure

To each sample, a volume of TCLP leachant No. 2 (5.7 ml/l glacial acetic acid aqueous solution at pH 2.88) was added at a volume of 20 times the weight of the sample. The extraction period for the sample was 18 h under rotary agitation at 30 rev./min. Subsequently, the sample was filtered using Grade GF/F 0.7- μ m glass-fiber filter paper. The sample was filtered within 2 h of the 18-h extraction period to ensure method reproducibility [10]. The filtrate was acidified using 0.5 ml concentrated nitric acid and analyzed for lead using a Perkin-Elmer Model 5000 atomic absorption spectrometer at 283.3 nm. This procedure differs from the EPA TCLP [11,12] experiment in that one-tenth of the amount of sample was used (10 g instead of 100 g) and only particles between 8.0 and 9.5 mm were used.

3. Results and discussion

Since the model waste used in this study was

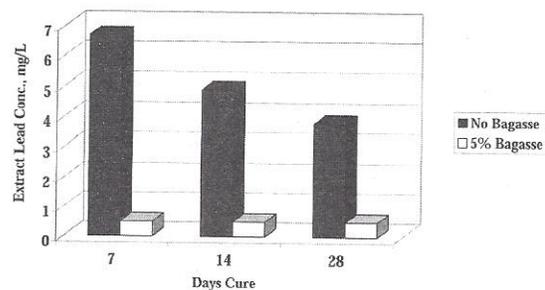


Fig. 1. Comparison of matrix composition on TCLP extract lead concentration for 10% lead loading.

ACS reagent grade lead nitrate, the pretreatment extract concentration (approx. 5000 mg/l) can be safely calculated based on a 10% lead loading. Fig. 1 compares the average TCLP extract lead concentrations for samples containing 10% lead and cured for 7, 14, and 28 days at 24°C. Samples containing bagasse typically had extract concentrations of less than 0.5 mg/l of lead (limit of sensitivity) for all cure times, while samples containing no bagasse had extract concentrations of approximately 7 mg/l (7 days cure), 5 mg/l (14 days cure), and 4 mg/l (28 days cure) of lead. There is a significant decrease in the amount of lead leached with those samples containing bagasse, compared to those that did not, for all cure times studied. All bagasse samples are well below the EPA leaching standard for lead of 5 mg/l [12] while the control samples (no bagasse) fail at 7 days cure and are borderline at 14 and 28 days cure.

It has been reported in literature that lignosulfonic acid derivatives strongly adsorb onto tricalcium aluminate [13]. The strong adsorption and thick layering of lignosulfonates onto tricalcium aluminate is indicative of a chemical reaction involving the organic and tricalcium aluminate hydration product [14]. A similar reaction is believed to be occurring between the lignin in the bagasse and the tricalcium aluminate component of the cement. It is suspected that the lead was stabilized by complexing with the large lignin molecule, and the resulting product was strongly adsorbed onto the tricalcium aluminate component of the cement preventing the lead from

leaching. Bagasse used with cement enhanced the effectiveness of the cementitious system, to complex lead to the matrix.

Fig. 2 shows the average TCLP extract lead concentrations for samples containing 15% lead. Samples containing 15% lead by weight to cement and no bagasse had extremely high TCLP lead extract concentrations (~ 45 mg/l) compared to 10% lead samples and no bagasse (~ 5 mg/l). Bagasse samples were able to stabilize the increased amount of lead added in the 15% lead samples (~ 1 mg/l) which is comparable to 10% lead samples with bagasse (< 0.5 mg/l). Samples containing 20% lead by weight to cement were also analyzed. Lead extract concentrations for all samples (no bagasse and 5% bagasse) were extremely high. The small amount of water used in comparison to the large amount of lead nitrate yielded a saturated solution. It is suspected that the high concentration of lead nitrate affected the cement hydration process, which may have saturated the chelating sites on the bagasse and left much of the lead in its ionic form causing higher lead extract concentrations.

The question arises as to the quantity of bagasse needed to effectively stabilize the lead metal waste. Experiments were conducted varying the amount of bagasse added. Results in Fig. 3 indicate that the amount of bagasse affects the rate of stabilizing lead. Samples containing 1.25 and 2.50% bagasse by weight to cement required longer cure times (14–28 days and 7–14 days, respectively) to obtain TCLP lead extract concentrations similar to 5% bagasse samples. However, all samples containing bagasse decreased the

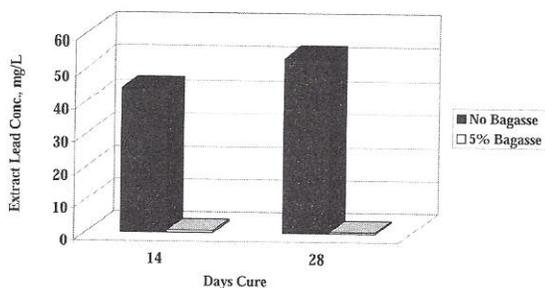


Fig. 2. Comparison of matrix composition on TCLP extract lead concentration for 15% lead loading.

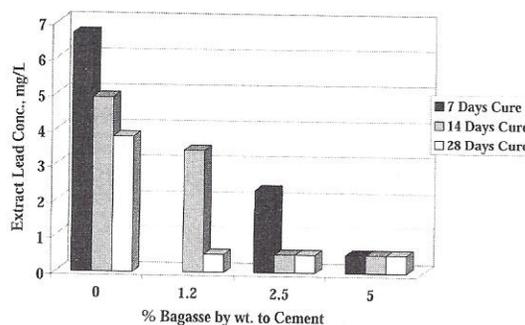


Fig. 3. Effects of percent bagasse on TCLP extract lead concentrations for 10% lead loading.

amount lead leached as compared to bagasseless samples.

As for the comparison of acid and base pretreatment of bagasse, it was found that similar results could be obtained with either treatment. The main advantage of the acid treatment is the texture of residual product because the bagasse treated in this manner is easier to grind. Under acid conditions, the softening point of the lignin is lowered by plasticizers derived from the decomposition of the pentosans present in the bagasse while under basic conditions the pentosans are liberated without decomposition [8], leaving a sticky residual product that is difficult to grind.

4. Conclusions

Our efforts were aimed at designing a better matrix for solidification/stabilization of hazardous waste that would be effective while being economically feasible and safe to produce. This was accomplished with the use of bagasse. The advantages of bagasse are the cost and a relatively safe treatment process. Bagasse is a byproduct or residue of milling or diffusing sugar cane, and there is approximately 1.8 million tons produced annually in Louisiana. As for the treatment process, it is simple and does not require careful control. There are no toxic or flammable chemicals involved in the treatment process as compared to the xanthates.

Solidification of lead with the aid of bagasse as an adsorbent reduces the leachability of lead al-

lowing cement matrices formed to easily pass the EPA TCLP test, often by a considerable margin. Results indicate that using bagasse as an additive to cement is effectively improving the solidification/stabilization of lead even at higher lead concentrations. Other metals (Cd, Cr, Hg, Ni) have been effectively immobilized by xanthates [3–7], and it is expected that the same will occur for bagasse; however, the answer will come from future studies.

Acknowledgements

This research was funded by the Louisiana Education Quality Support Fund (Contract# LEQSF(1997-99)-RD-B-11) and the American Sugar Cane League. This research has not been subjected to the funding Agencies' review and may not necessarily reflect the views of the Agencies.

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