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Effects of Lead and Chromium Hydroxides on Cement-Based Solidified Waste Properties

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Abstract

Experiments were completed to investigate the effects of synthetic lead and chromium hydroxides on the properties of cement-based solidified wastes. Synthetic lead and chromium hydroxides have been mixed with Ordinary Portland Cement at 10, 20 and 30 % by weight and a water-to-solid ratio of 0.45 has been used throughout the experiments. The final setting, strength development and metal leachability of the solidified wastes were determined using vicat needle, unconfined compressive strength and a modified ANSI/ANS-16.1 respectively. It was found that the addition of lead and chromium hydroxides interferes with the normal hydration reaction of OPC by prolonging the final setting time from 4 hours to 78 and 100 hours at 10 and 20% by wt. addition of lead hydroxide and setting was not observed up to 150 hours when a 30 % by wt. was added. Chromium hydroxide also causes similar interference but the effect is significantly less than that of lead hydroxide. The hydration retardation caused by the addition of lead and chromium hydroxide results in the microstructural development of the solidified wastes to be different from that of normal cement hydration and therefore the compressive strength of the solidified wastes has been reduced. Leaching of lead and chromium from the solidified wastes is determined primarily by leachate pH. The ingression of acidic leachant through connected porosity of the solidified wastes causes desorption and resolubilization of lead and chromium.

Keyworks: Stabilization/Solidification, lead, chromium, Portland cement, setting, strength, leachability

1. Introduction

There has been increasing concern in recent years associated with the management and disposal of hazardous industrial wastes and the control of their potential impact on both public health and the environment. This has led to the introduction of waste related laws and regulations in many countries which have controlled the disposal options available for hazardous wastes and made waste producers and waste management companies develop more environmentally safe disposal methods. Consequently there will be significant emphasis on the elimination of hazardous wastes from manufacturing processes and increased reliance on reuse and recycling

Stabilization/solidification (S/S) processes are potential treatments for the hazardous wastes produced by a range of different industries. Wastes suitable for this form of treatment include many types of industrial sludges and treatment residues which contain high levels of inorganic components but relatively low levels of organics. The technology aims to prevent the release of hazardous components from the solidified wastes after disposal in a landfill by limiting the solubility and mobility of the contaminants. This results from the transformation of the waste into a monolithic solid material and the chemical interactions between the waste and the solidification binders or additives. The chemical changes that take place as a result of the interaction between waste components and Portland cement play an important role in controlling the quality of cement-based solidified waste products [1-6].

Current solidification processing normally involves simply mixing wastes with binders, and this generally produces relatively poor materials. They are mechanically very weak in comparison with structural concretes and their microstructures normally contain high levels of porosity [7]. Slight variations in process formulation or waste composition could induce undesirable effects and produce products with reduced mechanical stability and increased leachability [8].

The leachability of waste constituents from cement-based S/S products after landfilling is the most important factor determining the effectiveness of the treatment process. Leaching of contaminants may occur when cement-based S/S products are in contact with landfill leachate. Several leach testing procedures have been developed to simulate the landfill environment and take into account the monolithic nature of S/S wastes [9]. These tests assess both the short and long-term environmental impact due to leaching of hazardous constituents from S/S treated wastes. In this work, the interfering effects on setting times, strength development and leachability of cement-based solidified waste forms caused by the addition of lead and chromium hydroxide were investigated.

2. Materials and methods

2.1 Synthetic Lead and Chromium Hydroxides

Lead and chromium hydroxides were prepared by precipitation from 1M lead nitrate and chromium nitrate solution by adding 10M sodium hydroxide to control the pH of the solution. The slurries of lead and chromium hydroxides were thoroughly mixed to achieve a pH of 9.5 ± 0.1 and 7.5 ± 0.1. The slurry was vacuum filtered through Whatman No.1 filter paper and the filter cake dried overnight at 105°C before being ground to a particle size of < 500 μm.

2.2 Sample Preparation

Solidified waste samples were prepared by mixing synthetic lead and chromium hydroxides with OPC at 10, 20 and 30% by weight. A water to solid ratio of 0.45 was used to maintain good workability when transferring the sample into a cylindrical plastic mould. The slurry was mixed following the standard test method ASTM C 305-94 to achieve a uniform distribution of metal waste before being transferred to the plastic mould. The cement solidified metal wastes were allowed to solidify in the sealed plastic moulds to avoid carbonation prior to testing.

2.3 Time of Setting of Hydraulic Cement by Vicat Needle

The standard test method ASTM C 191-92 has been modified to determine the time of setting of cement metal waste mixes. The cement metal waste mixes were prepared at w/s ratio of 0.45. The mix was then transferred into the ring and the excess mix was removed. The penetration of the needle was determined every 15 minutes for the control cement paste and every 30 minutes for the cement metal waste mix. The final setting time is obtained when the needle does not sink visibly into the mix.

2.4 Unconfined Compressive Strength

The unconfined compressive strength of the solidified wastes was done following ASTM D 1633-96. The size of the cylindrical sample was modified to a diameter of 50 mm. and height of 100 mm. The compressive strength of the solidified waste samples was determined after curing for 1, 3, 8, 15, 29, 57 and 91 days.

2.5 Dynamic Leach Test

Metal leaching from the solidified wastes has been assessed using a modified ANSI/ANS 16.1 leach test on the samples cured for 28 days. Cylindrical samples (25 mm. diameter and 25 mm. height) were suspended in a plastic net in 0.2N acetic acid solution, at a leachant volume to surface area ratio of 20:1. The leachates were removed to determine the pH and metal concentration and the leachant was replaced periodically after intervals of static leaching. The leachants were renewed at 1, 8, 15, 29 and 57 days. This produces severe leaching conditions and allows assessment of leaching performance over longer time periods.

3. Results and Discussion

3.1 Time of Setting of the Solidified Wastes

Time of setting of ordinary Portland cement (OPC) in the presence of 10, 20 and 30% by weight of synthetic lead and chromium hydroxides are presented in Figure 1 and 2. The final setting time of mixes with 10 and 20% by wt. additions of lead hydroxide were 78 and 100 hours compared to 4 hours for control OPC whereas those mixes with 10, 20 and 30% by wt. addition of chromium hydroxide were 5, 6.5 and 7.5 hours respectively. It is noticed that the final setting time of the lead doped OPC is much longer than that of the chromium doped OPC and the final setting had not occurred up to 150 hours of observation when a 30% by wt. of lead hydroxide was added. This suggests that lead hydroxide causes more interference on normal hydration of OPC than chromium hydroxide.

Both lead and chromium hydroxides are amphoteric metals which were extensively resolubilized under highly alkali environment of cement and adsorbed onto the hydrating surfaces of cement clinker particles causing hydration retardation [1, 10]. It is possible that the adsorption of hydroxy lead ion onto the hydrating surfaces of cement clinker particles leads to the formation of less permeable coatings which cause more severe retardation of normal cement hydration than that of chromium.

3.2 Unconfined Compressive Strength of the Solidified Wastes

Figure 3 and 4 show the compressive strength of the solidified wastes doped with 10, 20 and 30% by weight of lead and chromium hydroxides as a function of curing time. The interfering effect of lead and chromium hydroxides on OPC hydration results in a lower rate of strength development of the solidified waste forms compared to control hardened cement. It was found that strength has not been developed during the first day of curing when lead hydroxide was added at 10 and 20% by weight, and up to 3 days of curing with 30% by weight addition.

It was also noticed that there is a decrease in compressive strength of the solidified waste forms with an increase in the concentration of lead and chromium hydroxides addition. It is possible that lead and chromium hydroxides which were adsorbed onto the hydrating surface of cement clinker particles were incoporated into the CSH gels. It was reported that hydration of clinkers in the presence of 16% by weight of lead nitrate induced an increased gel formation [11]. This increased gel formation is associated with volume change in the solidified waste forms which leads to micocraking and as a result, a decrease in compressive strength was observed.

3.2 Leachability of Metals from the Solidified Wastes

Leachate pH of the solidified wastes after each interval of exposure is shown in Table 1. The cumulative amount of lead and chromium leached from the solidified wastes as a function of exposure duration is presented in Figure 5 and 6.

The pH of leachants from control OPC samples changed from an initial pH of 2.9 to approximately between 4.2 and 4.7 at different exposure duration. Similar variations in leachate pH were observed for both lead and chromium doped OPC samples. An increase of leachant pH is a result of dissolution of calcium hydroxide which is produced in large quantities during the hydration reactions of OPC. Calcium hydroxide and the high pH of the pore water provide a buffering capacity to the solidified waste forms against acid attack [12].

The cumulative amounts of lead and chromium leached from the solidified wastes in the presence of 10, 20 and 30% by weight of lead and chromium hydroxides after leaching for 57 days were 688, 1,438, 3,548 and 21, 48, 151 mg/l respectively. Metal hydroxides are amphoteric metals and their solubilities are strongly dependent on leachate pHs [13]. Lead and chromium hydroxides have minimum solubility around pH 9.5 and 7.5 whereas leachate pHs of the solidified wastes were between 4.4 and 4.8. The difference between minimum solubility of lead hydroxide and leachate pH is large compared to that of chromium hydroxide. As a result, lead was released from the solidified wastes at a higher rate than chromium.

It is also possible that lead hydroxide causes more severe hydration retardation than chromium hydroxide and this results in poor microstructural development of the solidified wastes which contain a high level of porosity. During leaching tests of monolithic samples the ingress of the acetic acid leachant through the open and connected porosity leads to a reduction in the pH of the internal pore water causing desorption and resolubilisation of heavy metals.

4. Conclusions

The following conclusions can be drawn from this work:

- Lead hydroxide causes more severe hydration retardation than chromium hydroxide as is indicated by the longer final setting time and lower rate of strength development of the solidified wastes.
- The interfering effects caused by the addition of lead and chromium hydroxides increase with the increasing addition of heavy metals.
- Lead and chromium hydroxides interfere with the normal cement hydration by adsorption onto the hydrating surface of cement clinker particles and thus reducing the inward diffusion of water to the cement grains.
- Compressive strength of the solidified wastes decreased with increasing waste loading. Although strength requirements for solidified wastes are not as important as those for structural concretes, failure to obtain adequate strength is an indicator of a poor microsturcture and may be expected to lead to increase leaching.
- Leaching of the amphoteric lead and chromium from the solidified wastes is strongly dependent on leachate pH.

5. Acknowledgements

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6. References

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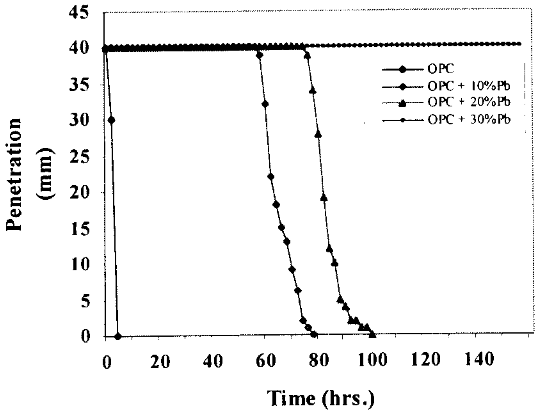

Figure 1. Time of setting of OPC in the presence of lead hydroxide

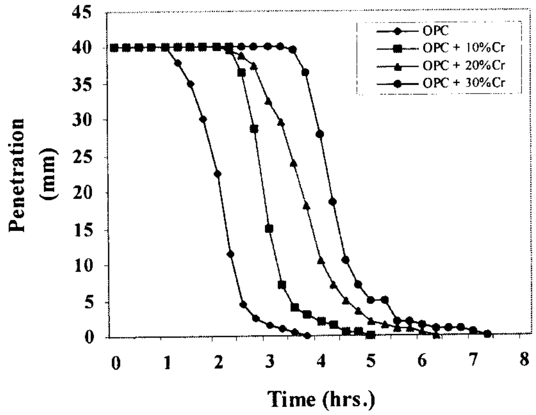

Figure 2. Time of setting of OPC in the presence of chromium hydroxide

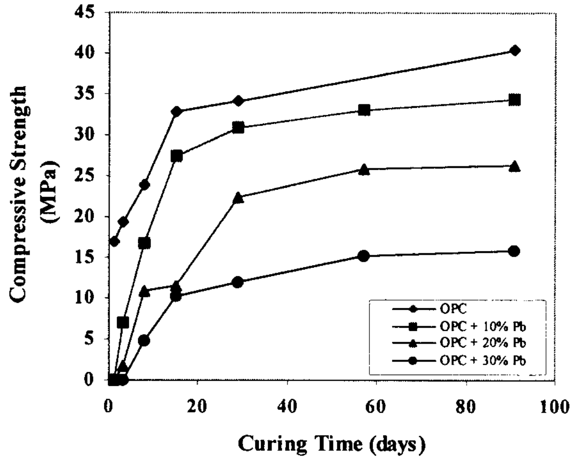

Figure 3 Compressive strength of the OPC/Pb waste mixes as a function of curing time.

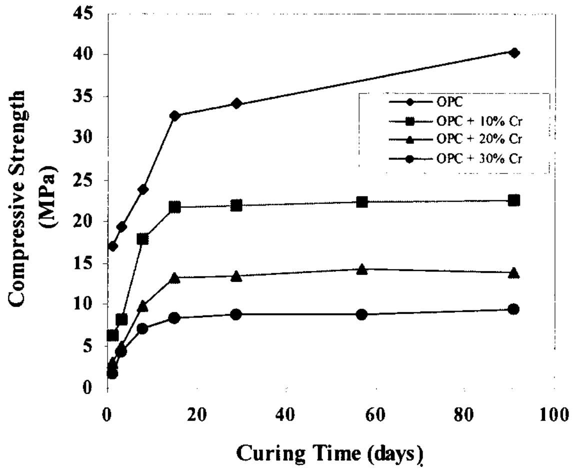

Figure 4 Compressive strength of the OPC/Cr waste mixes as a function of curing time.

Table 1 Leachate pHs of the solidified wastes at each interval of exposure.

Sample	Leachate pHs					
	initial	Day 1	Day 8	Day 15	Day 29	Day 57
OPC	2.9	4.2	4.7	4.6	4.6	4.6
OPC + 10% $Pb(OH)_2$	2.9	4.3	4.7	4.6	4.4	4.5
OPC + 20% $Pb(OH)_2$	2.9	4.3	4.7	4.3	4.3	4.4
OPC + 30% $Pb(OH)_2$	2.9	4.3	4.6	4.2	4.3	4.3
OPC + 10% $Cr(OH)_3$	2.9	4.4	4.8	4.4	4.4	4.5
OPC + 20% $Cr(OH)_3$	2.9	4.4	4.8	4.5	4.5	4.5
OPC + 30% $Cr(OH)_3$	2.9	4.4	4.6	4.4	4.4	4.5

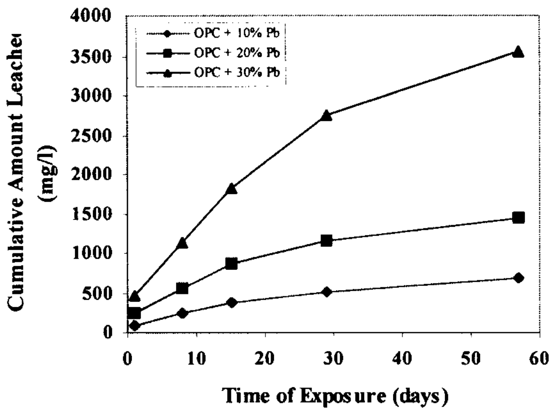

Figure 5 Cumulative amount of Pb leached after exposure to 0.2 N acetic acid leachant

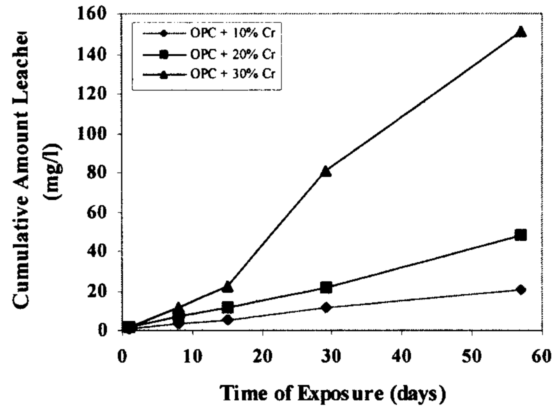

Figure 6 Cumulative amount of Cr leached after exposure to 0.2 N acetic acid leachant