

# Heavy Metals Immobilization Property and Mechanisms of LDHs-modified Cementitious Materials

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**Abstract.** Layered double hydroxide (LDH) has a positive effect on the adsorption and immobilization of heavy metals. The compressive strength and the heavy metal ions  $Pb^{2+}$  immobilization of CaAl-LDH modified cement paste were studied in this paper. Through research, it was found that compared with the cement paste sample with a  $Pb^{2+}$  content of 1% after curing for 7d and 28d, the addition of CaAl-LDH to the cement paste sample increased the compressive strength by 6.1% and 1.6%, respectively, demonstrating the enhancing effect of CaAl-LDH on the strength of cement paste. Compared with the sample containing only  $Pb^{2+}$ , the addition of CaAl-LDH to the cement increased the immobilization rate by 0.3% after 12 hours of leaching time and showed varying degrees of improvement at different leaching times. The immobilization mechanism of heavy metals in LDH blended cement paste was revealed by microstructure characterization. It was founded that  $Pb^{2+}$  can replace  $Ca^{2+}$  in AFt, AFm, and LDH, and can co-precipitate with  $OH^-$ .

**Keywords:** LDH, compressive strength, heavy metals immobilization, cement paste

## 1 Introduction

With the continuous development of mineral resources, a massive accumulation of tailings has become a major obstacle to ecological restoration efforts in mining areas. This is due to the presence of low-stability heavy metals such as lead, zinc, copper, cadmium, etc., which are commonly found in tailings. During the stacking process, rainfall can cause leaching and soaking effects that allow these heavy metals to enter surrounding soil, surface water, and groundwater, leading to heavy metal pollution. As the concentration of harmful heavy metals in the environment rises, they can eventually accumulate in living organisms and pose a threat to human health. Therefore, reducing, rendering harmless, and recycling Heavy metals in tailings treatment has become a crucial research topic. There are many types of methods for treating heavy metals today, such as precipitation, ion exchange, immobilization, and biological treatment, which are commonly used in wastewater treatment.

In the concrete industry, cement is the main binding material, and its production not only consumes a large amount of resources but also causes serious environmental pollution. Tailings, after being crushed and ground as mineral admixtures, can be used to replace all or part of cement in concrete construction, which is one of the main ways of tailings recycling(Thomas, Damare, & Gupta, 2013), cement curing technology is just one application of this recycling method, which can reduce the release of heavy metals while utilizing tailings to replace cement and reduce cement consumption.

The curing mechanism of heavy metals by cementitious materials mainly includes chemical immobilization, physical encapsulation, formation of insoluble compounds, and ion or ion group substitution(B., 2006;F., 1997;Q., M., C., X., & P., 2008;Qian, Cao, Chui, & Tay, 2006).

The C-S-H gel generated by cement hydration has a large specific surface area and can physically and chemically adsorb and encapsulate heavy metals (Sung-Yoon & F., 2002). Under the alkaline conditions of cement-based materials, hydrates such as Aft and AFm can react with most heavy metals to form composite hydroxides with calcium, and Heavy metals can also exist in the form of carbonate, sulfate, silicate, and oxide precipitation (Jr. Conner & Hoeffner, 1998). Heavy metal ion or ion group substitution mainly occurs in C-S-H gel and AFt. Research on the properties of heavy metal ion-solidified immobilization by cementitious materials, such as strength, setting time, volume stability, and curing effectiveness of heavy metals, is limited, and how to enhance the curing performance of cementitious materials while ensuring their own properties will be the focus of future research.

Layered double hydroxides (LDHs), also known as hydrotalcites, are a new type of composites with a layered structure. LDHs have good interlayer anion exchange capacity, memory effect, and immobilization capacity, and they have a larger specific surface area and better pore structure. Generally, there are four ways to remove Heavy metals from LDHs, including the formation of metal hydroxide precipitates, surface complexation with hydroxyl groups on LDHs, and isomorphic substitution.

This study investigates the flowability, setting time, flexural strength, compressive strength of CaAl-LDH cement mortar, as well as the compressive strength of cement paste after adding  $Pb^{2+}$  at a macro level. The immobilization rate of  $Pb^{2+}$  by cement paste was tested using inductively coupled plasma (ICP) at a micro level, and the mechanism of heavy metals immobilization in CaAl-LDH cement-based materials was analyzed using X-ray diffraction (XRD).

## 2 Materials and methods

### 2.1 Materials

The cement is the benchmark cement (P-I 42.5) for concrete admixture testing produced by China United Cement Group Co., Ltd., and its chemical composition is shown in Table 1.

**Table 1.** The main chemical composition of cement Composition

Composition	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	f-CaO
Mass fraction/%	64.66	22.04	4.51	3.30	2.90	0.46	0.60	0.95

The CaAl-LDH used in this study was provided by Shandong Yusuo Chemical Technology Co., Ltd., and its chemical composition is shown in Table 2.

**Table 2.** The main chemical composition of CaAl-LDH

Inspection item	Appearance	Al <sub>2</sub> O <sub>3</sub>	Fe	CaO	Pb	Moisture	Whiteness	pH
Result or Mass fraction/%	White powder	18.8	0.5	30.2	0	0.3	94	8.5

The concentrated nitric acid (HNO<sub>3</sub>, 70%) was provided by Sinopharm Chemical Reagent Co., Ltd. Shenyang; anhydrous ethanol was provided by Jiangsu Qiangsheng Functional Chemical Co., Ltd. All reagents mentioned above are of analytical grade.

## 2.2 Heavy metals immobilization properties

### 2.2.1 Cement paste preparation

CaAl-LDH was mixed in cement with a ratio of 4% by weight. The heavy metals were added in the form of an aqueous solution during the preparation of the cement paste. The content of  $Pb^{2+}$  was set to 0.5%, 1%, and 2%, respectively (calculated according to molar mass ratio of  $Pb(NO_3)_2$  and mixed with the proportion of cement by weight percentage). The mix ratios are shown in Table 3. According to the standard ASTM C 305-99, the cement containing heavy metals was stirred before slowly pouring the cement paste into a mold with a dimension of 20mm×20mm×20mm. The excess paste on the surface was scraped flat, and the mold was vibrated and covered with plastic film. After one day, the mold was demolded and placed in a standard curing room with a temperature of  $(20\pm 2)^\circ C$  and humidity of 65% .

**Table 3.** The proportion of  $Pb^{2+}$  cement composite materials

Constituencies	Water-cement ratio	Raw material (g)			
		Cement	$Pb(NO_3)_2$	Water	LDH
Ref.	0.45	200	0	90	0
Pb0.5	0.45	200	1.6	90	0
Pb1	0.45	200	3.2	90	0
Pb2	0.45	200	6.4	90	0
LPb0.5	0.45	192	1.6	90	8
LPb1	0.45	192	3.2	90	8
LPb2	0.45	192	6.4	90	8

### 2.2.2 Compressive strength

The compressive strength of CaAl-LDH cement paste is measured according to Standard ASTM C 109/109M-21. The compressive strength was tested at curing ages of 3 days, 7 days, and 28 days, respectively.

### 2.2.3 Cement paste heavy metals immobilization properties

Samples are taken from the center of the test piece, dried at  $40^\circ C$  for 24h, and sieved through a 0.99 mm sieve to select samples with a solid-liquid ratio of 20:1. Weigh 10g powders into a 250mL volumetric flask, add 200mL of diluted hydrochloric acid solution ( $pH=2.88\pm 0.05$ ), and place the volumetric flask on a HY-5A variable speed shaker for shaking experiments. Using a pipette, take the upper clear liquid at 6h, 12h, 24h, 48h, 72h, and 96h, and test the content of heavy metals in the leachate using an inductively coupled plasma optical emission spectrometer (ICP-OES).

## 2.3 XRD

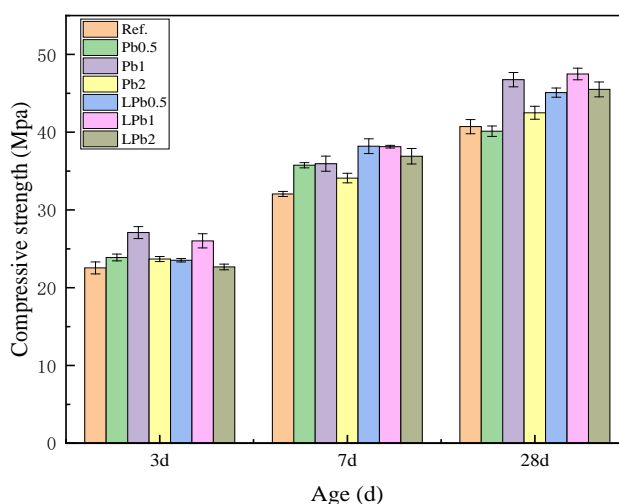
Samples were crushed and soaked in anhydrous ethanol to stop hydration reactions. After 24h of soaking, the samples were ground into powder in a mortar, sieved through a 200-mesh sieve, and dried at  $40^\circ C$  or above in a vacuum drying oven for more than 48h before being sent for XRD testing. The Bruker D8 Advance X-ray diffractometer produced by Brook (Beijing) Technology Co. Ltd. was used to test the crystal parameters of the cement matrix before and

after the addition of LDH and immobilization of  $Pb^{2+}$  ions. Test conditions: wide-angle diffraction-Cu target, diffraction angle of  $5-85^\circ$ , and a scan rate of  $8^\circ/\text{min}$ .

### 3 Results and Discussions

#### 3.1 Compressive strength

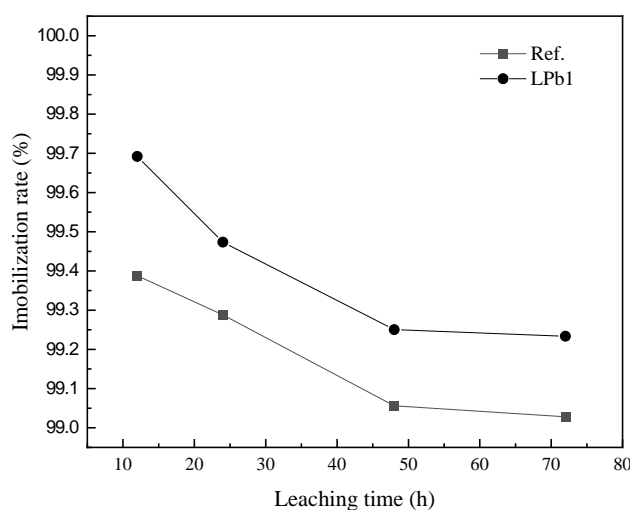
Fig.1 shows the compressive strength of cement paste with different  $Pb^{2+}$  concentrations. It can be observed that the compressive strength increases with the increase of  $Pb^{2+}$  concentration, reaching its highest value when  $Pb^{2+}$  concentration is 1%. Compared to the blank group, the addition of 1%  $Pb^{2+}$  increased the compressive strength by 20.1%, 12.1%, and 14.8% at 3 d, 7 d, and 28 d of hydration, respectively. The reason for this increase in strength could be that  $Pb^{2+}$  can replace calcium ions in C-S-H, which plays a major role in the strength of the material, and then form chemical bond with calcium and silicon elements in C-S-H, thus being solidified and stabilized in the setting and hardening of cement-based materials. This makes the microstructure of C-S-H gel more compact, leading to an increase in compressive strength (Gineys, Aouad, & Damidot, 2010). Compared to the strength of the blank group, the addition of 2%  $Pb^{2+}$  increased the compressive strength of paste by 5.1%, 6.4%, and 4.4% at 3 d, 7 d, and 28 d of hydration, respectively. However, compared to the strength of 1%  $Pb^{2+}$ , the strength decreased, possibly because excessive  $Pb^{2+}$  easily combines with  $OH^-$  to form amorphous lead hydroxide precipitates, which adhere to the surface of already hydrated cement particles, hindering further hydration of cement and causing a decrease in compressive strength. This indicates that 1%  $Pb^{2+}$  is the optimal concentration. Compared to the cement paste samples with 1%  $Pb^{2+}$ , adding CaAl-LDH to the cement paste with 1%  $Pb^{2+}$  reduced the strength by 3.9% at 3d, but increased the strength by 6.1% and 1.6% at 7 d and 28 d, respectively. It can be seen that the addition of CaAl-LDH generally increases the compressive strength of  $Pb^{2+}$  mixed cement paste, possibly because 4% of CaAl-LDH have a strength-enhancing effect on the cement paste itself.



**Figure 1.** Compressive strength of cement paste with different  $Pb^{2+}$  concentrations

### 3.2 Heavy metals immobilization property

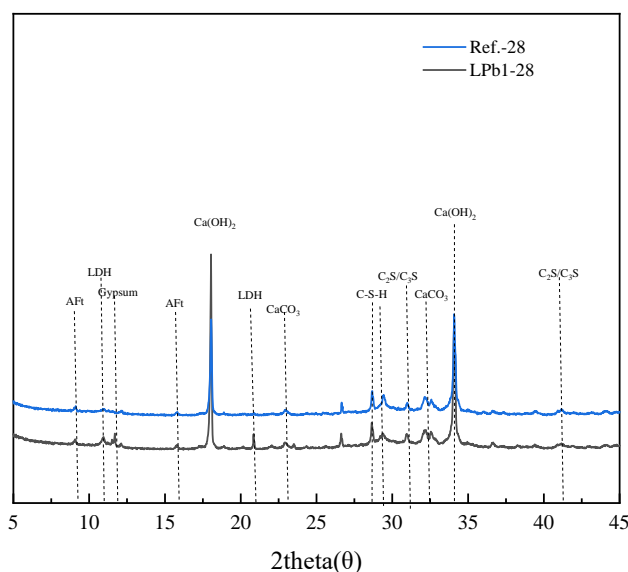
Fig.2 shows the immobilization rate of cement paste mixed with  $Pb^{2+}$ , respectively, under different leaching times. It can be observed that the immobilization rate of heavy metal ion-mixed cement paste decreases as the leaching time increases. The immobilization rate of cement paste mixed with  $Pb^{2+}$  is 99.39% at 12h. When the leaching time is 24h, 48h, and 72h, the immobilization rate of cement paste decreased by 0.1%, 0.33%, and 0.36%, respectively. The reason for this is that the concentration difference of heavy metals between the leaching particles and the leaching solution gradually decreases over time in the limited solution assumption. That is, the leaching amount of heavy metals first increases and then remains unchanged with the extension of leaching time, leading to a downward trend in the immobilization rate. Compared with the cement sample containing only  $Pb^{2+}$ , the addition of CaAl-LDH to the cement sample increased the immobilization rate by 0.3% after 12h of leaching time and showed varying degrees of improvement at different leaching times.



**Figure 2.** Immobilization rate of cement paste mixed with  $Pb^{2+}$  under different leaching times

### 3.3 Immobilization mechanisms

Using XRD analysis to investigate the hydration products of cement specimens mixed with  $Pb^{2+}$  and LDH at different groups, as shown in Fig.3 According to the XRD patterns, the main hydration products are AFt,  $Ca(OH)_2$ , and C-S-H gel. Compared with cement pastes of the same age, the  $Ca(OH)_2$  peak value of pastes mixed with LDH at  $2\theta = 18.1^\circ$  is higher. This may be due to the leaching of  $CO_3^{2-}$  from LDH, which can promote the release of  $OH^-$  in cementitious materials during the diffusion and transport of  $CO_3^{2-}$  (Ping, Wei, Juntao, & Zhonghe, 2013).



**Figure 3.** XRD pattern of cement paste with  $\text{Pb}^{2+}$  content

## 4 Conclusions

This paper mainly focuses on the effect of layered double hydroxide (LDH) of the adsorption and immobilization of heavy metals. The compressive strength and the heavy metal ions  $\text{Pb}^{2+}$  immobilization of CaAl-LDH modified cement paste were studied in this paper. And the immobilization mechanism of heavy metals in LDH blended cement paste was revealed by microstructure characterization. The main conclusions of this study are as follows:

(1) Compared with the cement paste with 1%  $\text{Pb}^{2+}$ , the addition of CaAl-LDH to the cement paste sample increased the compressive strength by 6.1% and 1.6% after curing for 7d and 28d, respectively.

(2) According to the immobilization rate, the immobilization rate of cement paste containing heavy metal ions decreases with increasing leaching time. The immobilization rate of cement paste containing  $\text{Pb}^{2+}$  at 12h is 99.39%, and it decreases by 0.36% when the leaching time is 72h respectively. Compared with the cement sample containing only  $\text{Pb}^{2+}$ , the addition of CaAl-LDH to the cement sample increased the immobilization rate by 0.3% after 12h of leaching time and showed varying degrees of improvement at different leaching times.

(3) Hydration products AFt and AFm have ion exchangeability, in which  $\text{Ca}^{2+}$  can exchange with  $\text{Pb}^{2+}$ .  $\text{Pb}^{2+}$  can undergo coprecipitation with  $\text{OH}^-$ , and  $\text{Pb}^{2+}$  can react with CaAl-LDH to generate similar hydrotalcite products ( $(\text{Pb}_3\text{Al}_2(\text{OH})\text{SO}_4)_{12} \cdot n\text{H}_2\text{O}$ ), ultimately leading to the immobilization of  $\text{Pb}^{2+}$ .

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