

Preparation Immobilization/Solidification Heavy Metal Waste Cu (II) with Binder Hydration Test

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Abstract:

In this article, by testing the hydration characteristics of the adhesive caused by the addition of Cu(II), the ability of dumping industrial waste containing Cu(II) to be immobilization/solidification (S/S) was studied. Isothermal calorimeter test results show that the addition of Cu (II) will delay the hydration of the early adhesive. Thermo gravimetric analysis and X-ray diffraction showed that the adhesive was hydrated for 3 days and 180 days, and C-(A)-S-H, silicate and Aft were the main products of all adhesive hydration. Characteristic studies have shown that the four binding agents all adopt the immobilization/solidification method, which can immobilize Cu(II) in the mining industrial waste landfill, but the binding agent in the calcined mineral dust has a better immobilization effect as an activator. As more Aft (ettringite) is produced, the addition of CaSO4 can increase fixation. Some slag replaced by metakaolin did not contribute any significant to the formation of hydrated gel, but the best S/S technology was found here. This is due to the presence of lower water permeability and porosity, which is a better physical encapsulation effect.

Keywords —Industry waste of mining, Cu (II) Metal, Binder hydration

I. INTRODUCTION

Huge dumping of mining industrial waste has caused serious damage to the ecological environment. In the last few decades, there have been many studies utilizing mining industry waste as the production of construction materials [1], [2]. However, all these utilization approaches can only dispose of a small part of this mining industry waste. In comparison, cement paste backfill is considered the most effective way to utilize mining industry waste on a large scale today. Mining industry effluents are generally mixed with a binder, such as ordinary portland cement, OPC in a surface backfill plant and then transported to underground pits by pumping [3]. In this way, some metal mines, such as iron mines, can achieve their goals without having to dump industrial waste into the environment. Generally, OPC is a

common binder used during backfilling of cement paste, the total cost of which is more than 70% of the total cost of backfilling cement paste [4]. The high cost of this OPC discourages industrial mining from using it in backfilling cement paste. Not only that, about 5-8% of the total CO2 emissions are due to the production of OPCs, which causes an increase in the greenhouse effect [5]. Therefore, the use of low-carbon and environmentally friendly cement materials as a substitute for OPC is very conducive to reducing carbon emissions. On the other hand, the dumping of mining industrial waste generally contains many toxic elements, such as Cu, Cd, Pb, Cr and As, the leaching of which can have serious consequences [6]. Toxic elements coming out of the sample the backfill of cement paste needs to be ensured that it meets the requirements of the supervision department with a

stabilization/solidification (S/S) process. The immobilization of heavy metals and nuclear elements by the S/S process has been widely used and has been considered a time- and cost-effective technology [7]. OPC is a widely used agent for S/S processes. However, the application of OPC presents a high carbon footprint. Therefore, the use of alternative, low-carbon and high-efficiency cementitious materials for the S/S process has been extensively studied in the last decades [8]. Alkali-activated materials have been extensively studied for OPC alternatives in recent decades [9]. Preparation of alkaline activated materials refers to the mixing of alkaline activator solution and aluminosilicate powder. Commonly used alkaline activators are sodium hydroxide and water glass; calcined clay; blast furnace slag and fly ash, are commonly used as aluminosilicate precursors [10]. Jiang, et al. Have explored the feasibility of using sodium silicate and activated slag sodium hydroxide as alternative binders for backfilling cement pastes. The results showed that the active slag of sodium hydroxide - Backfill cement paste showed a higher compressive strength than OPC- Backfill cement paste. However, given the high energy and cost-intensity production of sodium silicate and sodium hydroxide, these binders do not appear to be suitable for backfilling cement pastes. It is difficult to manipulate sodium hydroxide solution in situ on the other hand, given its highly corrosive nature [2]. Sodium carbonate [11] has also been used as an activator for the preparation of activated slag sodium hydroxide. However, the binding compressive strength is very low make it unsuitable for backfilling cement paste. Basic oxides such as calcium oxide and magnesium oxide appear to be alternative activators in the preparation of activated slag sodium hydroxide for backfilling cement pastes [12]. Zheng, et al [13] found the optimum content of reactive magnesium oxide in sodium hydroxide active slag was around 7.5 wt.%. As a result of this condition, the backfill of cement paste reached the target compressive strength (≥ 1.0 Mpa).

Copper (Cu) is a toxic heavy metal that is

generally produced from various industrial activities. Abundant Cu has been found in industrial waste [13]. Therefore, it is necessary to ensure that Cu can be an effective S/S when disposing of mining industrial waste through backfilling of cement paste. OPC-based S/S has proven to be an effective treatment technique for the isolation of hazardous wastes. However, Cu(II) immobilization using OPC appears to be problematic due to insufficient chemical fixation [14]. Zhang et al [13] and Deja [28] reported effective S/S capacities for Cu(II) using water glass-activated sodium hydroxide and slag, respectively. Meanwhile, sodium hydroxide and water glass are not suitable for the preparation of backfill cement paste, as discussed above. In a previous study [15], calcined mine dust was used as an activator for the production of activated sodium hydroxide slag to explore alternative binders for cement paste backfill. Mine dust is waste from mines and its recycling can lighten the environmental burden. This article is a continuation of previous research.

Therefore, the purpose of the research in this article is to examine the effect of adding Cu(II) to the hydration properties of the binder.

II. RESEARCH METHODE

A. Ingredients

The raw materials used are blast furnace slag and metakaolin, mine dust, CaO, CaSO₄ reagent, K₂CrO₄ analytical reagent.

B. Equipments

Glassware, TGA and XRD instruments, and calorimeter test (Thermometrics TAM).

C. Research Procedure

1. Binder/S/S Preparation

Pasta is prepared by mixing dry ingredients in a saucepan. The mixture was then mixed with water (potassium chromate solution) for 2 minutes and then molded in a polypropylene cylindrical mold (50 mm in diameter and 100 mm in height). Sample closed with plastic film to avoid water loss.

The samples were then transferred to a curing box with a temperature of 20 ± 2 oC and a relative humidity of 90% and preserved for 24 hours before opening. Samples were crushed, wrapped in plastic film and then preserved in a preservation box. Based on previous experiments, the mass ratio of binders in this mining industrial waste heap was 1:6 to meet the required strength for underground support [16]. To begin with, the fastener is made by the same procedure as described above. Then this industrial waste is mixed thoroughly with a binder for 2 minutes to obtain a homogeneous mortar, which is then filled into a cylindrical mold. In this study, the slurry concentration was 70 wt.%. This procedure is the same as the method used in making pasta.

2. Characterization Methode

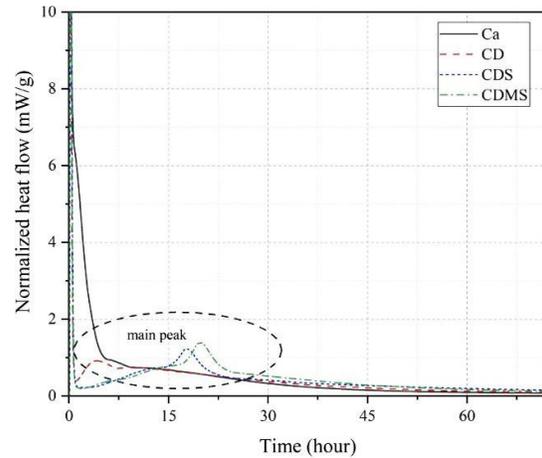
a. Kinetic Hydration

Heat hydration release was monitored by a TAM Thermothermal conduction calorimeter (TA/TAM AIR-8) at 20 oC for 72 hours. The bottle is tightly closed and inserted into the calorimeter and then the heat flow and cumulative heat hydration are recorded continuously.

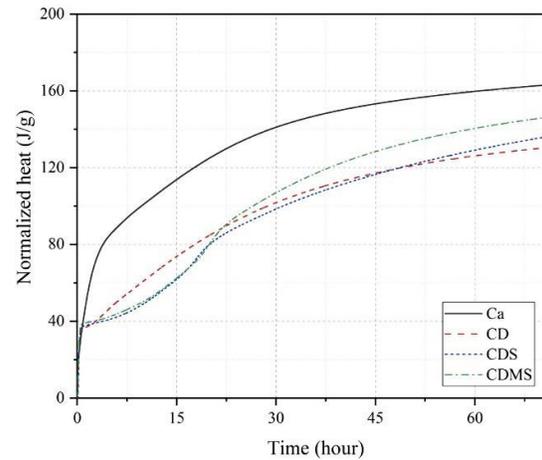
b. Analysis of TGA and XRD

The hardened sample was crushed to a size of < 74 m and immersed in isopropanol (A.R., 99.7%) for 1 hour to stop hydration. After vacuum filtration, the powder was dried in a vacuum drying oven for 24 hours. Dry powder was used for TGA and XRD analysis.

III. RESULTS AND DISCUSSION



(a)



(b)

Figure 1. Test results of isothermal calorimeter: (a) heat flow rate, (b) cumulative heat flow

Figure 1. Shows the results of an isothermal calorimeter test of four hydration binders to illustrate the hydration process. Based on Figure 1, (a) a strong exothermic peak was seen during the first hour of binder hydration in a CaO-activated binder (Ca binder). This sharp peak is caused by the reaction between CaO and water [17], which is an exothermic reaction ($\Delta H = -157.43$ KJ/mol). Another cause is the initial wetting and dissolution of the slag grains [18]. After a strong initial reaction, no significant exothermic peak was seen except for a peak of small intensity around 6-8 h. This indicates that the CaO-activated slag reacts very

slowly, which is in line with previous reports [19]. In calcined mine dust slag (CD binder), a clear exothermic peak was found between 1-7 h after the initial sharp peak. Generally, MgO, which is abundant in calcined mine dust slag (Table 1), does not react with water at room temperature. Even after the reaction between CaO and water, the heat liberated can support the reaction between MgO and water, leading to an exothermic peak of 1-7 h. Thereafter, similar reaction behavior was seen for the Ca and CD binders, at least from the heat flow rate curve. The hydration process in the binder in the presence of CaSO₄ (binding agent from CDS and CDMS) are different again. The located exothermic peak is seen for about 1 hour. This peak has been reported to be due to sulfate depletion, corresponding to the more rapid deposition of ettringite (Aft), as is usually found in OPC hydration [20].

Figure 1, (b) shows the cumulative heat release from the hydration of the binder for 72 hours. In general, the Ca binder presented the highest cumulative heat release, reaching about 163 J/g. However, it cannot show the highest rate of reaction between CaO and slag, considering the high amount of heat released during the reaction between CaO and water.

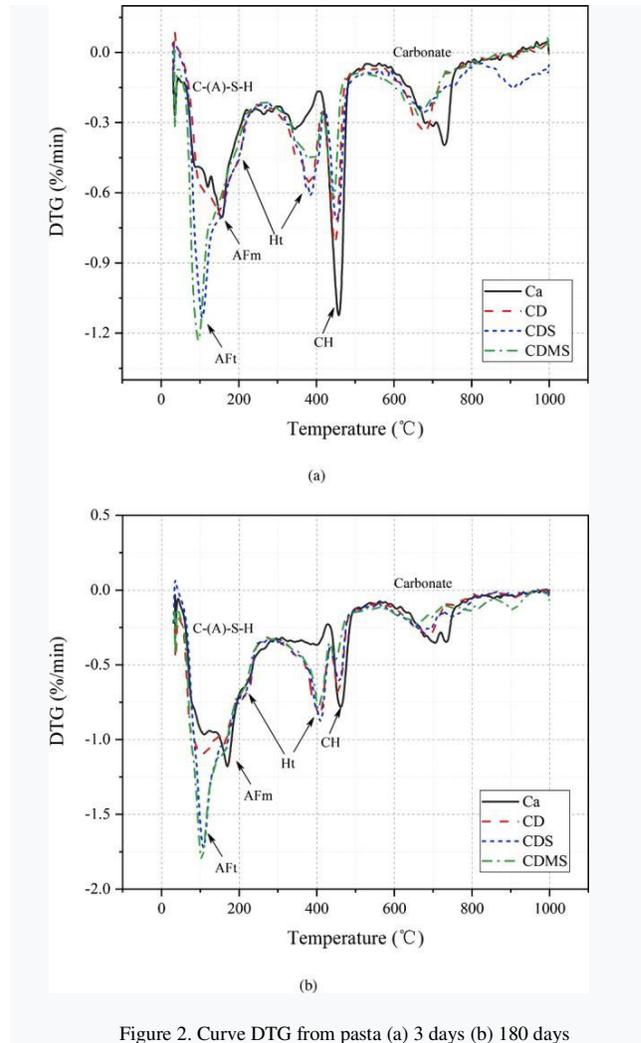
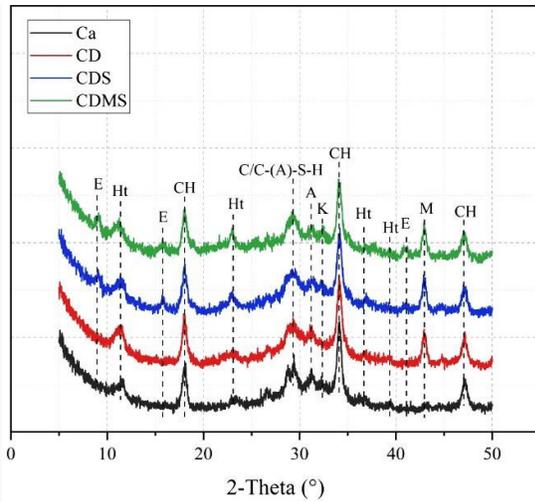
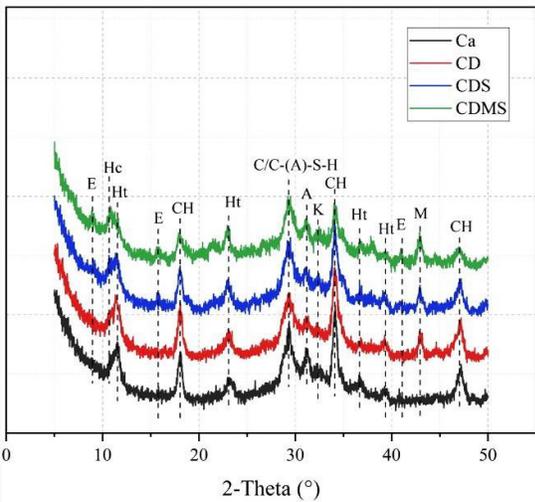


Figure 2. Curve DTG from pasta (a) 3 days (b) 180 days

In other words, the reaction rate of the slag is not necessarily the highest in the Ca binder. This can be confirmed from the TG analysis (Figure 2(a)), which showed that the CDS and CDMS binders exhibited a higher total weight loss. A slightly higher amount of cumulative heat release was seen in the CDS binder, probably because the higher amount of Al favored the formation of a higher Aft content. DTG in Figure 2(b) also shows slightly more Aft formed in the CDMS.



(a)



(b)

Figure 3. Pattern XRD (a) 3 days (b) 180 days: (CH-Portlandite, E- Ettringite, Mc-Monocarbonate, Ht-Hydroalcite, C-Calcite, A-Akermanite, K-Kaolin, M-MgO)

Figure 3 shows XRD patterns of binder hydration for 3 days and 180 days, C-(A)-S-H, Aft and portlandite were the main hydration products in all binders, as shown in Figure 3(a), which is in agreement with previous reports in binders. alkaline activated slag. TG analysis showed more Ht formed in the calcined mine dust slag based binder, and this is in line with the XRD pattern. In addition, After appears to be binding due to the addition of CaSO₄, which confirms the results of the TG analysis. After 180 days of hydration, the C-(A)-S-

H, Ht and Aft intensities were seen to increase, accompanied by a decrease in portlandite content, resulting from the continuous hydration of the slag. Hemihydrate (Hc, about 10.7o2θ) was detected in the CDMS samples after 180 days of hydration. This may be due to the increase in Al provided by

TABLE 1
 CHEMICAL COMPOSITION OF RAW MATERIALS
 (WT. %).

Ingred ien ts	Ca O	Mg O	Si O ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	S O ₃
Mi ne dus t	63,56	31,35	4,46	0,29	0,59	0,02	0,01	0,003
Fro nt sla ves	37,50	9,70	30,3	15,30	0,37	0,19	0,32	0,85
met aka olin	0,17	0,06	50,35	43,28	0,86	0,18	0,55	0,001
Mi ne ind us tr y was te	3,32	0,50	69,64	17,99	2,44	0,06	0,06	0,04

IV. CONCLUSIONS

Incorporation of Cu(II) greatly interferes with binder hydration in terms of reaction dynamic characteristics, spectroscopy/thermogravimetry and mechanical strength. The presence of Cu(II) delays the hydration of the binder at an early stage but promotes the reaction at a later period (about 3 hours later).

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