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Solidification and Release Characteristics of Heavy Metals in Gypsum from Coal-Fired Power Plants

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Abstract: Heavy metals in flue gas desulfurization (FGD) gypsum from coal-fired power plants are at risk of releaching during the processes of stockpiling and resource utilization. In this study, the effects of organosulfur chelators dithiocarbamate (DTC) and trisodium trithiocyanate-15 (TMT-15) on the solidification characteristics of heavy metals in desulphurized gypsum under different mass fractions, pH values, water contents and reaction times were investigated. The chemical composition and morphology were analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES) and scanning electron microscope (SEM). The experiments showed that both DTC and TMT-15 were effective at stabilizing the heavy metals in the FGD gypsum, with more than a 50% curing effect for all the heavy metals except Pb. DTC showed a better stabilization for Pb, Hg, Cu, Zn, and Cr, and TMT-15 showed a better curing effect for Cd. The solidified gypsum had good heavy metal stability in low-water-content environments. Increasing the mass fraction, reaction time, and pH decreased the heavy metal leaching, and the mass fraction had the greatest effect on the total heavy metal leaching concentration, followed by the reaction time and pH value.

Keywords: coal-fired power plants; desulfurization gypsum; heavy metals; chelating agent; solidification

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1. Introduction

The limestone–gypsum wet desulfurization process is currently the most mature and widely used flue gas desulfurization technology for coal-fired power plants around the world. Desulfurization gypsum is the product of the reaction of limestone with SO_2 in the flue gas desulfurization process. The main component is $CaSO_4 \cdot 2H_2O$ [1], which can be used as a raw material for resource utilization, construction material, and so on [2,3].

Volatiles, potentially hazardous trace elements (e.g., As, Hg, and Pb) from coal-fired power plants, migrate into FGD gypsum during combustion and the subsequent flue gas treatment. During the disposal, storage, and resource utilization of flue gas desulfurization gypsum, rainwater and surface water leaching, the release behavior of mobile elements, personnel handling, and wind erosion disturbance during ground stacking can have impacts on groundwater, the atmospheric environment, and human health, for instance, in order to enhance the value of industrial gypsum, and desulfurization gypsum needs to undergo drying and calcination processes to eliminate residual moisture. The thermal treatment involved in gypsum production can lead to the release of mercury into the atmosphere, resulting in pollution and posing potential risks to human health. Therefore, it is imperative to investigate the migration behavior of heavy metals within desulfurization gypsum [4–8].

In a study on the heavy metal stability in desulfurization gypsum, Zhao et al. [9] investigated the thermal stability, chemical speciation, and leaching characteristics of seven heavy metals (Hg, As, Cr, Cd, Ba, Mn, and Pb) in the desulfurization gypsum from three coal-fired power plants in China. The results show that the contents of Hg, As, Cd, Pb, Cr, Ba, and Mn in FGD gypsum are 0.20–3.85, 1.04–2.87, 0.02–0.69, 3.50–7.01, 9.19–21.32, 14.84–55.94, and 45.95–69.85 mg/kg, respectively. With the increase of heat treatment temperature, the evaporation rate of heavy metals in FGD gypsum increases. Gypsum in the heat treatment process should pay more attention to Hg, because the evaporation rate of gypsum at temperatures above 350 °C is higher than 94%, which is its worst thermal stability. Hg and Ba in FGD gypsum mainly exist in the residual form. The proportions are 73.11–86.69% and 72.97–82.46%, respectively. The minimum percentage of soluble As in the three FGD gypsums is 2.75–4.78%. The sum of Cr in water-soluble exchangeable fraction (F1), reduced fraction (F2) and oxidized fraction (F3) in FGD gypsum is 37.88–53.84%. Compared with those of other heavy metals in FGD gypsum, the easily soluble form of Mn accounts for the largest share, 40.64–55.43%, and under typical environmental conditions, Mn is leached from gypsum and bioavailable to the environment. The high-temperature compounds of FGD gypsum are at different risk levels, namely low risk (including Hg, As, Cr, and Ba), medium risk (including Cd and Pb (except FGD-G1)), high risk or very high risk (Mn), and Mn should be carefully considered. The leaching characteristics test shows that FGD gypsum is a non-hazardous waste, but considering the mass production of gypsum and complex landfill conditions, several appropriate disposal measures need to be taken to minimize the risk of heavy metal release into the environment. Fu et al. [10] studied the distributions of the Cr, Pb, Cd, Cu, Zn, and As elements and their chemical forms in fly ash and flue gas desulfurization gypsum (FGD gypsum) from a large coal-fired power plant in Anhui Province, China. The partitioning behavior of the heavy metals indicates that they are mainly retained in the coal combustion ash (88.9–98.7%) and FGD gypsum (1.26–4.33%). The risk assessment indicates that the heavy metals in FGD gypsum pose a moderate–high risk to the environment. The environmental heavy metal stability in gypsum is weak, and the reuse of FGD gypsum should be carefully assessed. Hao et al. [11] analyzed FGD gypsum from 12 power plants, and the risks of the heavy metals according to their average values in descending order were as follows: Zn > Cr > Mn > Ni > Pb > Cd, with all the samples posing a risk to the environment, especially Zn and Mn.

Previous research has focused on the solidification of heavy metals in fly ash and desulfurization wastewater from coal-fired power plants, with chemical solidification being the more common method recently [7,8,12–16]. Chelating agents are gradually being used to chelate heavy metals in wastewater due to their better effectiveness at solidifying them. Dithiocarbamates (DTCs) have an extremely strong complexing ability with metals and are now used in the treatment of heavy metal wastewater [17,18]. The main component of the chelating agent TMT is trisodium trithiocyanate, which can form stable compounds with heavy metal ions and has been widely used in areas such as fly ash solidification and the heavy metal treatment of coal-fired power plant wastewater [19–22].

In wastewater, the removal of heavy metals mainly involves precipitation reactions with additives to reduce their release [23]. The research on the solidification of heavy metals in solid waste mainly focuses on the solidification of heavy metals in fly ash. By adding stabilizers, the heavy metals in fly ash become more stable and transform into forms that are difficult to leach. Research has shown significant differences in the behaviors of heavy metals between fly ash and gypsum. Fu et al. [10] studied the behavior of heavy metals in fly ash and desulfurization gypsum from a large power plant in Anhui and found that the content of heavy metal enrichment is much higher in the fly ash than in the desulfurization gypsum, but the heavy metals in the fly ash mainly exist in the residual form. However, the majority of the heavy metals in desulfurization gypsum exist in their available form, with lower environmental stability and a greater leaching risk. There is currently no relevant research on the chelation solidification of heavy metals in gypsum, and coal-fired power plants are therefore in need of research on this topic. In this study, we used the organic sulfur-chelating agents DTC and TMT-15 to solidify the heavy metals in desulfurization gypsum, and we investigated their solidification and release characteristics.

2. Experimental Section

2.1. Experimental Methods

2.1.1. Solidification Experiment

A sample of 20 g was weighed. A chelating agent (DTC (purity: 90%) or TMT-15 (purity: 15%)) was weighed at different mass percentages of 4%, 6%, and 8% and dissolved in 100 mL of deionized water. Then, the dissolved liquid was mixed with the gypsum sample (liquid-to-solid ratio of 3:1; the liquid-to-solid ratio is the ratio of the amount of leaching agent in contact with the test sample for a given period to the amount of the test sample) and mixed well. The samples were allowed to stand in a fume hood for 24 h. The samples were then dried in an oven at 70 °C and bagged.

2.1.2. Leaching Experiment

In this experiment, the HJ/T300–2007 solid waste-extraction procedure for the leaching toxicity-acetic acid buffer solution method was used [24]. Leaching agent #1 was prepared by adding 5.7 mL of glacial acetic acid to 500 mL of deionized water, followed by 64.3 mL of 1 mol/L sodium hydroxide, and the mixture was finally diluted to 1 L. The pH of the prepared solution was 4.95 ± 0.05. Leaching agent #2 was prepared by diluting 17.25 mL of glacial acetic acid with deionized water to 1 L. The pH of the prepared solution was 2.64 ± 0.05. To determine the leaching agent to be used, 5.0 g of the sample was put into a 500 mL beaker or conical flask, 96.5 mL of deionized water was added, the surface dish was covered, and the mixture was stirred vigorously with a magnetic stirrer for 5 min. The solution was cooled to room temperature, and the pH was determined. If the pH was <5.0, leaching agent #1 was used, and if the pH was >5.0, leaching agent #2 was used. After these experiments, the leaching agent chosen for use in the gypsum samples in this experiment was leaching agent #1. A cured and dried sample of 1 g was taken, and 20 mL of the leaching agent was added according to the liquid-to-solid ratio of 20:1 (L/Kg). The sample was shaken in a shaking device for 18 ± 2 h. The shaken sample was filtered to obtain a final sample for the measurement.

2.1.3. Environmental Release Experiment

After curing the FGD gypsum via chelation, the group with the best curing effect was selected for the experiment on the environmental release characteristics. The release of the heavy metals was measured after the cured gypsum samples were placed in different pH and water-content environments for different times to investigate the effects of different pH values (pH values of 6, 8, 10, and 12; the pH was adjusted using a NaOH solution and a HNO_3 solution), water contents (0%, 5%, and 15%), and reaction times (12 h, 24 h, and 36 h) on the release of the heavy metals.

2.2. Analysis Methods

The samples were measured for As using a PSA10.055 Excalibur AFS atomic fluorescence spectrometer from the UK; the Hg was measured using Teledyne Hydra II AA from Leeman, Houston, TX, USA; the Pb, Zn, Ni, Cr, Cd, and Cu were measured using a Leeman Prodigy inductively coupled plasma emission spectrometer (ICP-AES) from the USA. The micromorphology of the gypsum was characterized using an FEI Quanta 250 FEG scanning electron microscope (USA). The detection limit of the instruments was ppb (μg/L).

Principal component analysis (PCA) is an algorithm that is used to reduce the dimensionality of the data to two or three dimensions based on the original multidimensional features, which is convenient for analysis and visualization [25]. The experimental data were first imported into SPSS for Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity tests, and if they passed, PCA analysis was performed.

3. Results and Discussion

3.1. Effects of Curing Agents on Heavy Metal Leaching

The leaching concentrations of each element in the original gypsum are shown in Table 1, among which the leaching concentration of Zn was the highest (64.18 ppb) and that of Hg was the lowest (0.07 ppb).

Table 1. Leaching concentrations of elements in original gypsum.

Element	Leaching Concentration (ppb)
Cu	10.02
Zn	64.18
Ni	11.01
Cr	6.34
Pb	44.38
Cd	1.89
As	0.84
Hg	0.07

Figure 1 shows the leaching concentrations of various heavy metals from the FGD gypsum after treatment with the two chelating agents and the comparison with the heavy metal leaching from the original gypsum sample. Overall, there was a significant reduction in the heavy metal leaching from the two chelating-agent-cured desulfurization gypsum samples, which decreased with the increase in the chelating agent addition ratio.

As shown in Figure 1, for most heavy metals, the optimal addition ratio of DTC-solidified gypsum was 8%. Compared with the original gypsum, the Cu, Zn, Ni, Cr, and Cd leaching concentrations were reduced by 72.55%, 52.83%, 55.85%, 69.86%, and 74.07%, respectively. The best Pb-curing effect under the DTC treatment was 6%, which was 18.68% lower than that of the original gypsum leaching.

The optimal proportion of the curing agent TMT-15 for curing gypsum was also 8%. The Cu, Zn, Cd, and Pb leaching concentrations were reduced by 24.96%, 56.80%, 45.27%, and 32.56%, respectively. The best curing effect of the Ni and Cr elements under the TMT-15 condition was 6%, and those of the Ni and Cr were reduced by 54.31% and 11.85%, respectively, compared with that of the original gypsum leaching. For the Hg element, due to the low Hg leaching concentration in the raw desulfurization gypsum, the chelating agent was not as effective at curing it as the other massive elements. However, the Hg leaching concentration after the gypsum was cured with DTC was lower than that of the original gypsum sample, and the leaching concentration with the best effect was 0.05 ppb, which was 72.22% lower compared with that of the raw gypsum.

The leaching of elemental As was below the detection limit after curing the gypsum with either chelating agent, which may be related to the already low content of elemental As in the gypsum.

In conclusion, the chelating agents DTC and TMT-15 were effective at curing most of the heavy metal elements in the desulfurization gypsum. Follow-up experiments were conducted with a chelating agent mass fraction of 8%. The different results of adding different levels of curing agents to treat the heavy metals may be due to a number of factors. Firstly, the curing effects of the different heavy metals showed different trends in the DTC-cured heavy metal experiments. Pan et al. [26] showed that DTC is more effective than Cu^{2+} and Zn^{2+} for the removal of Ni^{2+} in electroplating heavy metal wastewater. DTC binds most easily to Ni^{2+}, followed by Cu^{2+} and Zn^{2+}; thus, DTC also has a reaction sequence for heavy metals in gypsum, and after adding a chelating agent, it preferentially bind to certain ions. From the experimental results, the order of the DTC curing of Pb and Hg in the gypsum was also better than for Cu, Cr, and Cd. If more of the chelating agent is added, the cured copper, Cr, and Cd tend to decrease with the increase in the curing agent content. Similarly, TMT-15 may give priority to the treatment of Cu, Zn, Cd, and Pb in gypsum, and the addition of more curing agents for other heavy metal elements should also show a trend of content reduction.

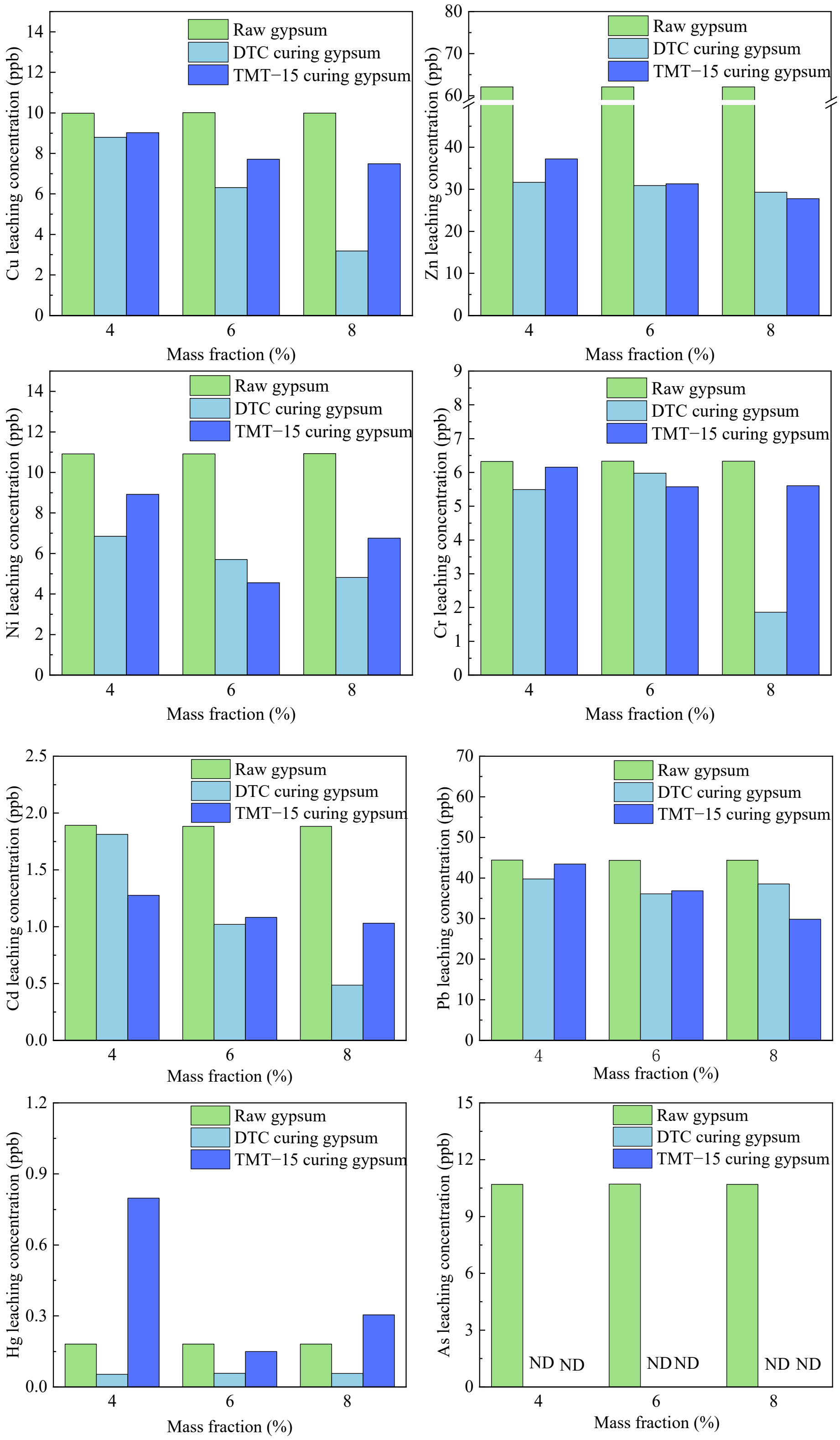

Figure 1. Leaching concentrations of heavy metals before and after curing gypsum.

After curing the desulfurized gypsum from coal-fired power plants via the chelation method, the group with the best curing effect (i.e., the group with an 8% mass fraction) was selected for the experiment on the environmental release characteristics. The effects of the water contents (0%, 5%, and 15%), initial pH values (pH = 6, 8, 10, and 12), and reaction times (12 h, 24 h, and 36 h) on the release of the heavy metals were considered.

3.2. Effect of pH on Environmental Release of Heavy Metals from Gypsum

Figure 2 shows the heavy metal release contents of the raw gypsum, as well as those of the two chelator-treated gypsums, in different pH environments. The chelating-agent-treated gypsum had better heavy metal stability in an acid-base environment than the raw gypsum, and the overall heavy metal leaching concentration had a tendency to decrease with the increasing pH value.

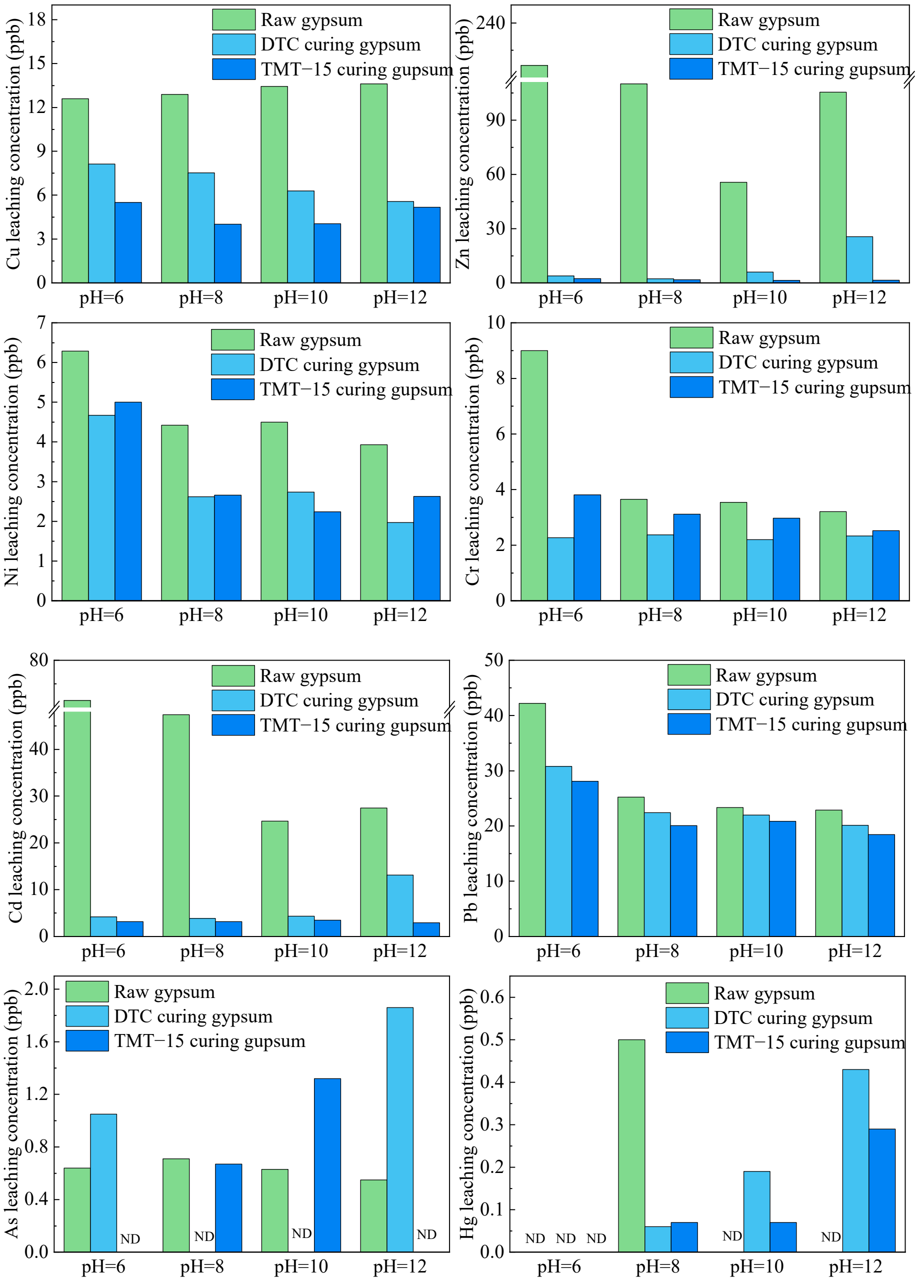

Figure 2. Environmental release contents of heavy metals at different pH values.

For the raw gypsum, the Cu leaching concentration kept increasing with the increasing pH; the Zn, Ni, Cr, Cd, and Pb leaching concentrations showed a decreasing trend, while the As and Hg leaching concentrations were not affected much. In a related study, Liu et al. The authors of [27] investigated the environmental stability of trace elements in desulfurization gypsum via TCLP leaching experiments and the BCR step-by-step extraction method, and the six trace elements studied included As, Se, Cd, Cr, Pb, and Hg. The leaching experiments showed that the leaching rates of the trace elements in the FGD gypsum increased with the decreasing pH value in the studied range, and they were more easily leached into an acidic environment. This finding is consistent with that of our experiment, in which most of the heavy elements leached at a pH of 6.

For the DTC-cured gypsum, the Cu, Ni, and Pb leaching concentrations showed a decreasing trend with the increasing pH, and the Zn, Cd, and Cr leaching concentrations did not change significantly. The As leaching concentrations decreased and then increased, and the lowest leaching concentrations were at pH values of 8 and 10, at which As was below the detection limit. The Hg leaching concentrations increased continuously, and the lowest leaching concentrations were at a pH of 6, at which Hg was below the detection limit. In different acid-base environments, the leaching concentrations of most heavy metals in DTC-cured gypsum decrease with the increase of pH value. DTC, also known as dithio-carbamate, is considered to be a kind of chelating agent that can effectively stabilize heavy metals. By pairing S atoms with metal ions, the C-N bond length is shortened, sulfur atoms can form coordination bonds with metal ions, and bond energy tends to show certain double bond characteristics. At the same time, DTC salts dissociate S^{2-}, which can be combined with Pb^{2+}, Cd^{2+}, and other heavy metal ions to form precipitation. However, under different pH values, the heavy metal leaching concentration of DTC-cured gypsum decreases with the increase of pH value, and the H^+ concentration is higher in acidic environments. Relevant studies have shown that in acidic media, the protonation of hydrogen ions reduces the electron-donating ability of S atoms, thus weakening the chelating performance of DTC-like chelating agents [28].

For the TMT-15-cured gypsum, the Cu, Zn, and Cd leaching concentrations did not change significantly with the increasing pH, and the Ni, Cr, and Pb leaching concentrations gradually decreased. The As leaching concentrations increased and then decreased, and the lowest leaching concentrations were at pH values of 6 and 12, at which As was below the detection limit. The Hg leaching concentrations kept increasing, and the lowest leaching concentrations were at a pH of 6, at which Hg was below the detection limit. Relevant studies have shown [29] that the group ions involved in the reaction of the chelated products of TMT-15 are different at different pH values. The group ion involved in the reaction is $(C_3N_3S_3)^{3-}$ in alkaline environments, and the group ion involved in the reaction is $(HC_3N_3S_3)^{-}$ in acidic environments. The reactive group ion in a relatively neutral environment is $(HC_3N_3S_3)^{2-}$. Therefore, from a structural point of view, TMT-15 is mainly chelated with heavy metal ions by coordination bonds dominated by –S–. When pH value decreases, the number of H^+ increases under the action of dissociation equilibrium, and it is easy to connect with S atoms to form an atomic group, forming sulfhydryl -SH. However, –SH is not easy to chelate with heavy metal ions. At the same time, the formation of sulfhydryl group reduces the number of group ions involved in chelation reaction, which is not easy to remove heavy metals. In addition, if the pH value is too low, excessive H^+ changes the standard electric potential of heavy metal ions, oxidize heavy metal ions and hinder the chelation reaction.

In conclusion, under different pH environments, the stabilities of the heavy metals in the cured gypsum were better than those in the raw gypsum, and most of the leached heavy metal concentrations were lower than those of the original gypsum. Moreover, the different heavy metals showed different patterns at different pH values, probably due to the different mutual reactions between the chelating agents and different heavy metals, resulting in different chelate precipitation structures. The chelating-agent-cured gypsum leached less in an alkaline environment. Because the chelating agents DTC and TMT-15 are both organosulfur chelating agents, the combination of S and divalent heavy metals in them does not strictly follow the theoretically calculated value of 4:1 under the same chelating agent dosage [30]. On the basis of the theoretical reaction equation, external conditions, coexisting ions, the solution pH, and other factors can affect the chelation reaction. Nevertheless, each heavy metal has a different complexing ability with the chelating group. Furthermore, the leaching properties of heavy metals are closely related to the compounds they form; metals that leach easily in acidic environments may be due to the formation of alkaline-precipitating substances, while the easy leaching of some metals in alkaline environments may be related to their binding to hydroxyl groups or their ability to form oxyacid anions [30,31].

Heavy metals in cured and original gypsum are more leached in acidic environments. Under the condition of a certain pH value, the maximum H^+ mole number in the solution is certain, and the acid neutralization capacity of gypsum is relatively strong. When the acid neutralization capacity is consumed, even if heavy metals are dissolved, secondary precipitation is formed in the alkaline environment and enriched on the surface of gypsum. Once the acid neutralization capacity is completely consumed and the environmental medium becomes acidic, it is possible to cause the concentrated release of heavy metals, and there is a risk of a large amount of heavy metals dissolving. Therefore, in actual engineering applications of gypsum solidification and stabilization, resource utilization in the acidic environment should be avoided as far as possible.

3.3. Effect of Water Content on Environmental Release of Heavy Metals from Gypsum

Figure 3 shows the effect of the water content on the environmental release of the heavy metals from the gypsum. Overall, the chelator treatments resulted in the good heavy metal stability of the FGD gypsum in environments with different water contents, with a better heavy metal stability in the cured gypsum in low-water-content environments.

For the raw gypsum, the Cu, Zn, Cd, and Hg leaching concentrations decreased continuously with the increase in the water content, and the lowest leaching concentrations were 4.45 ppb, 2.42 ppb, and 3.39 ppb at a 15% water content, respectively. No Hg leaching was detected at 5% and 15% water contents. The Ni, Cr, and Pb leaching concentrations decreased with the increase in the water content and then increased, and the lowest leaching concentrations were at a 5% water content. The Ni, Cr, and Pb leaching concentrations were 6.34 ppb, 11.07 ppb, and 43.17 ppb, respectively. The As leaching concentration increased with the increase in the water content and then decreased, and the lowest leaching concentrations were at a 0% water content, at which As was below the detection limit.

For the DTC-cured gypsum, the Cu and Cr leaching concentrations increased and then decreased with the increasing water content; the Zu leaching concentration kept increasing; the Ni and Pb leaching concentrations decreased and then increased; the Cd leaching concentrations kept decreasing. The lowest leaching concentrations were all at a 15% water content, at which Cd, As, or Hg leaching was below the detection limit.

For the TMT-15-cured gypsum, the Cu, Ni, and Pb leaching concentrations increased continuously with the increase in the water content; the Zn leaching concentration increased and then decreased; the Cr leaching concentration decreased continuously; the Cd leaching concentration decreased and then increased; As and Hg leaching were below the detection limit after curing.

Both TMT-15 and DTC can form stable compounds with heavy metals, and their solubility is much lower than that of hydroxide precipitation, so the moisture content has less influence on them. In conclusion, the environmental stabilities of the heavy metals in the cured gypsum were better than those of the heavy metals in the original gypsum sample under different water contents, and the leaching contents of most of the heavy metals were lower than those of the original gypsum sample. The different heavy metals had different release patterns under different water contents, which may be related to the formation of chelated precipitation and the adsorption of heavy metals. The authors of [32] conducted experiments for the water content of fly ash from 10% to 100%. The heavy metal leaching concentration changed relatively little with the increase in the water content, and a small amount of water was not enough to change the alkaline environment. According to our experiment, due to the relatively low water content, the experiment was conducted in an open system, and the water easily evaporated during the static process. Thus, the water content had little influence on the heavy metal leaching in the desulfurized gypsum. However, the presence of water inevitably weakened the stabilities of some of the heavy metals after they reacted with the chelating agent. Therefore, the heavy metal stability in the gypsum after chelation was better under the low-water-content condition.

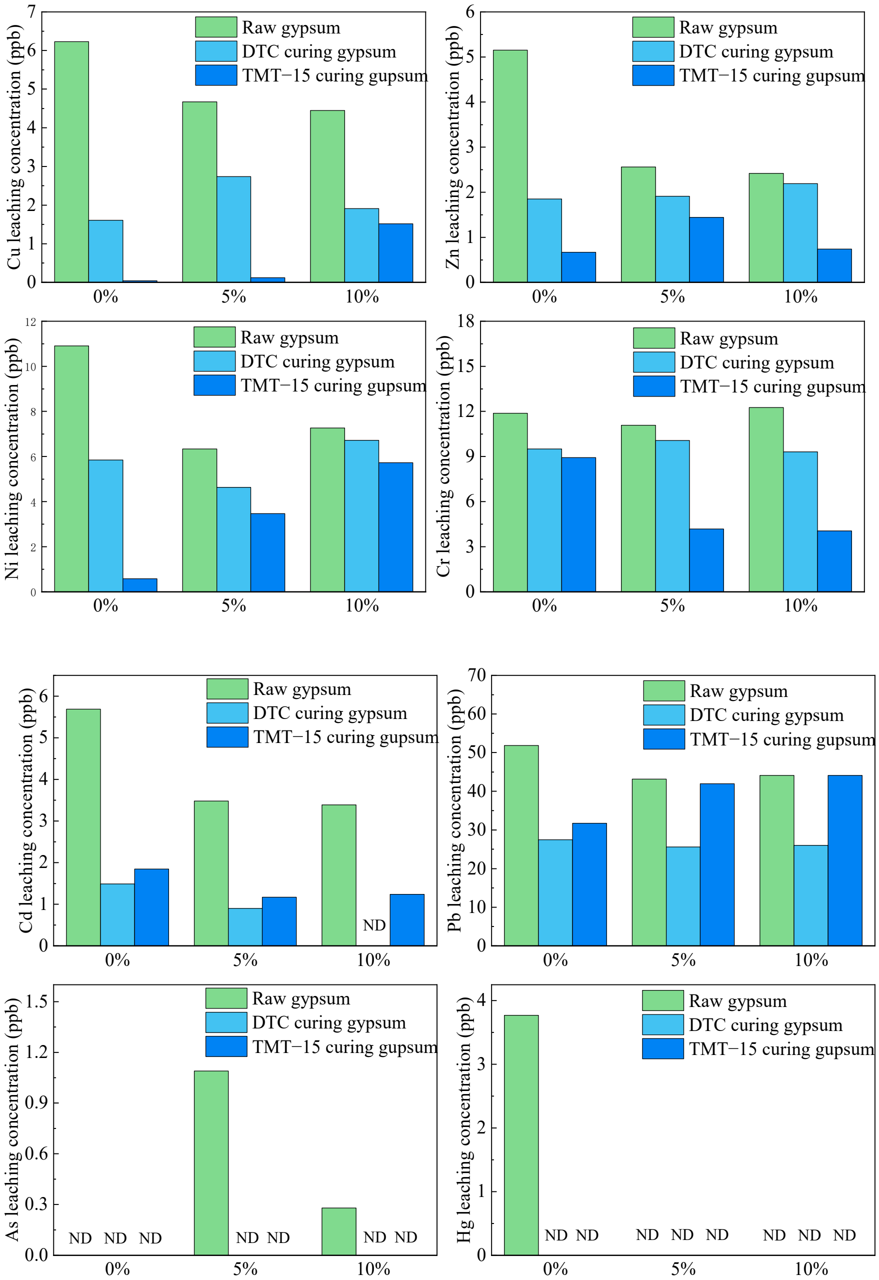

Figure 3. Environmental release contents of heavy metals at different water contents.

3.4. Effect of Reaction Time on Environmental Release of Heavy Metals from Gypsum

Figure 4 shows the effect of the reaction time on the environmental release of the heavy metals. Overall, there was no significant change in the heavy metal leaching concentrations with the increasing reaction time, and only a slight decrease in the trend was observed. There was no significant difference in the curing effects of the two chelating agents at different disposal times.

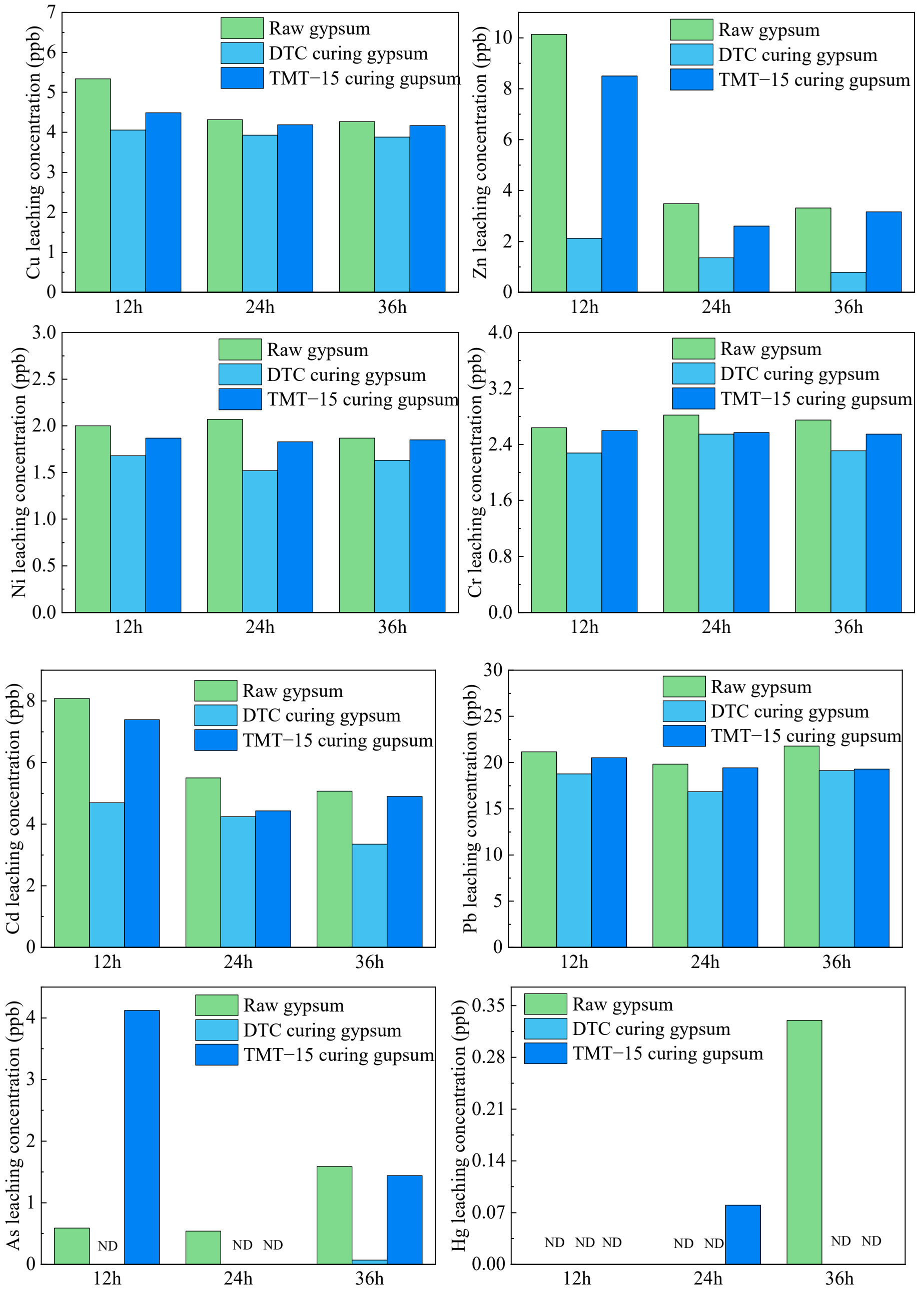

Figure 4. Environmental release levels of heavy metals at different reaction times.

For the raw gypsum, the Cu, Ni, Cr, and Pb leaching concentrations remained basically unchanged with the increasing reaction time, the Zn and Cd leaching concentrations gradually decreased, and the As and Hg leaching concentrations increased.

After the additions of DTC and TMT-15, the Cu, Ni, Cr, and Pb leaching concentrations remained basically unchanged with the increase in the reaction time, the Zn and Cd leaching concentrations gradually decreased, and the As and Hg leaching concentrations were lower and did not change significantly.

To sum up, the heavy metal leaching concentrations in the cured gypsum at different reaction times were lower than those of the raw gypsum, and it can be concluded that the heavy metal stability in the cured gypsum was better. Wu et al. [33] studied the loss of mercury in desulfurization gypsum under natural stacking conditions for a time interval of 6–12 months, during which its maximum mercury loss rate was 21.35% at 9 months and was influenced by environmental conditions such as temperature and precipitation. The change of reaction time is to simulate the stability of heavy metals in the stacked environment of desulphurized gypsum. According to the experimental results, the desulphurized gypsum treated by two kinds of chelating agents maintained good stability when stacked. The reason is that the chelating agents changed the form of heavy metals in the holes of desulphurized gypsum into a form that was not easy to leachable. Stable heavy metal ions can effectively resist changes in the external environment.

3.5. Principal Component Analysis

Because the abovementioned experiments were carried out to study the effects of multiple curing agents and parameters, in order to comprehensively evaluate which parameters were more effective for curing, the data were analyzed using principal component analysis, and the sum of the Cu, Zn, Ni, Cr, Cd, Pb, As, and Hg leaching concentrations was defined as the heavy metal leaching concentration. The results are shown in Figure 5.

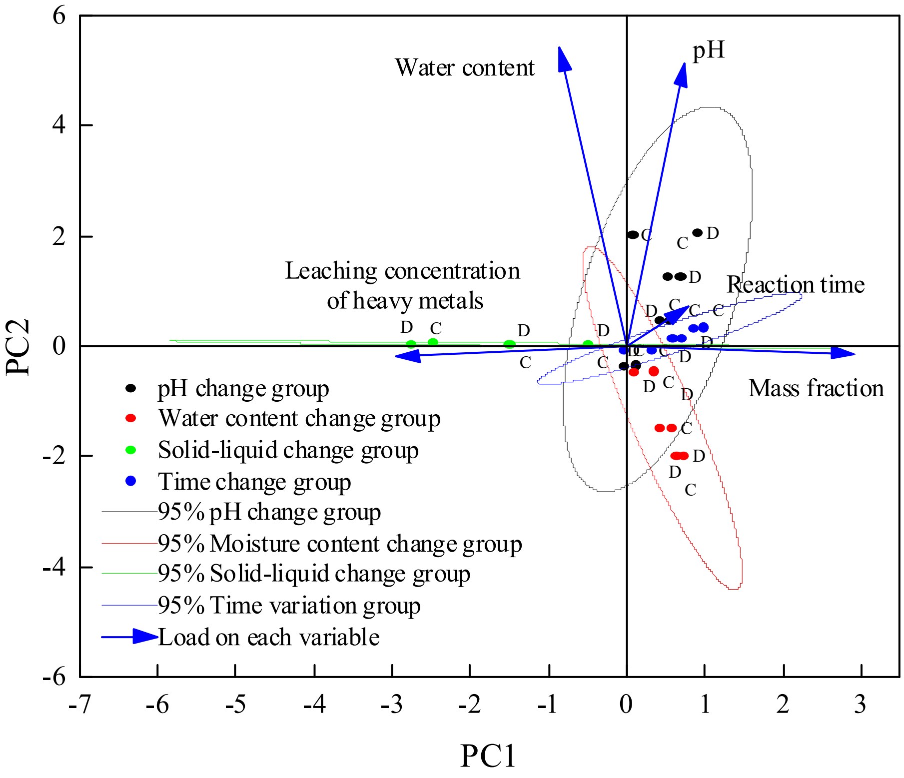

Figure 5. Effects of different parameters on heavy metal curing.

The group C represents the use of DTC-cured gypsum, the group D represents the use of TMT-15-cured gypsum, and the blue vector arrows represent the vector loadings of each data variable. The angle between the vectors is less than 90°, representing a positive correlation (the smaller the angle, the stronger the positive correlation). On the contrary, an angle greater than 90° represents a negative correlation (the larger the angle, the stronger the negative correlation), while an angle equal to 90° indicates that the vectors are not correlated. The distribution of each group (C and D) was uniform, indicating that the difference between using DTC-cured gypsum and TMT-15-cured gypsum was not obvious. The water content was positively correlated with the heavy metal leaching concentration, and parameters such as the mass fraction, reaction time, and pH were negatively correlated with the heavy metal leaching concentration, which is consistent with the analysis of the experimental results presented above. The angle between the vectors can be judged from the angle between the mass fraction and the heavy metal leaching concentration, which shows that the mass fraction had the greatest influence on the heavy metal leaching concentration, followed by the reaction time and pH value.

Figure 6 shows the SEM scanning images of the gypsum sample before and after solidification. The main component of the original gypsum was calcium sulfate. It can be seen from the SEM scanning images that calcium sulfate crystals mainly existed in the gypsum in the shape of needles [34], which made the gypsum full of various crevices, and heavy metals were easily leachable in the environment with water. The solidified gypsum flocculation precipitated the gypsum, filled the crevices and made it difficult to leach heavy metals.

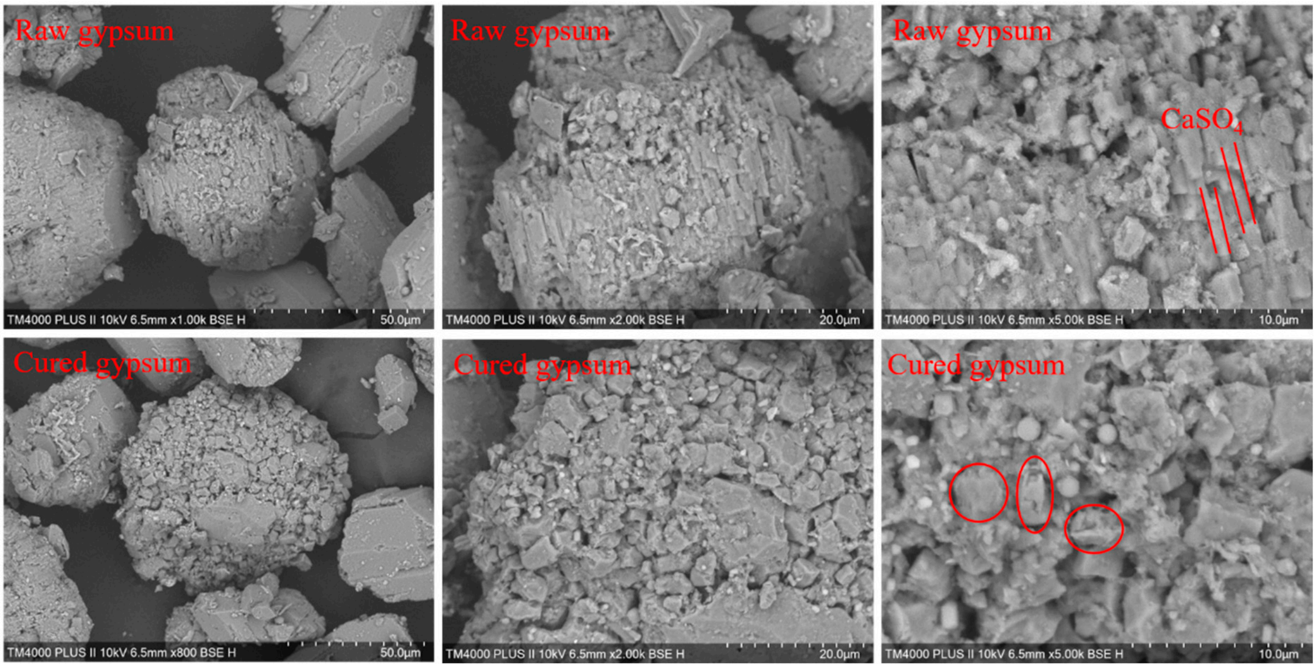

Figure 6. SEM images of gypsum before and after curing.

4. Conclusions

DTC and TMT-15 had different curing effects on different heavy metals. By ICP-AES heavy metal detection of the gypsum leaching solution before and after solidification, DTC had better curing effects on Pb, Hg, Cu, Zn, and Cr in FGD gypsum, while TMT-15 only showed better curing effects on Cd in FGD gypsum. Therefore, DTC can be used as a curing agent for the curing of most heavy metals in gypsum.

The leaching concentrations of most of the heavy metals in the cured gypsum were lower than those of the original samples under different pH values, water contents, and reaction times, and the heavy metal stability in the cured gypsum was better than that of the original samples. Changing the pH value may lead to changes in the reactants of the chelating agents and heavy metals and affect the leaching. The effects of the water content and reaction time were not obvious, but both tended to reduce the heavy metal leaching concentration.

The results of the principal component analysis showed that the water content was positively correlated with the heavy metal leaching concentration, and the mass fraction, reaction time, and pH parameters were negatively correlated with the heavy metal leaching concentration. The mass fraction had the greatest effect on the total heavy metal leaching concentration, followed by the reaction time and pH value. SEM characterization of gypsum before and after curing showed that the surface of gypsum after curing was wrapped by flocculent chelation precipitation, which inhibited heavy metal leaching.

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