

Article

Research on the Harmless Treatment of Barium Slag Using Flue Gas Desulfurization Gypsum

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Abstract: This study proposes an innovative method for the harmless treatment of barium slag using the industrial by-product Flue Gas Desulfurization Gypsum. Barium slag is a by-product of the barium carbonate production process, and due to its high content of barium ions and corrosive properties, it poses a significant threat to the environment and human health. It is classified as barium-containing hazardous waste (code HW47) in China. In this study, barium slag was optimally combined with FGD gypsum, utilizing a synergistic precipitation mechanism to solidify the easily leachable barium ions and form stable sulfate minerals. Mechanical and heavy metal leaching tests showed that the harmlessly treated barium slag had a certain compressive strength, and the concentration of barium ions in the leachate was below the national hazardous waste identification standards (100 mg/L) and the drinking water quality standards (0.7 mg/L). Microstructural analysis using X-ray diffraction, Fourier Transform Infrared Spectroscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy indicated that FGD gypsum promotes the solidification of barium slag, and through the synergistic precipitation mechanism, low-solubility barium sulfate minerals are formed. This treatment method also has a low cost and good potential for resource utilization, providing effective technical support for the green treatment of industrial waste.

Keywords: barium slag; Flue Gas Desulfurization Gypsum; harmless treatment; synergistic precipitation; resource utilization



Academic Editors: Eva Chmielewska and Craig Williams

Received: 27 November 2024

Revised: 14 December 2024

Accepted: 18 December 2024

Published: 30 December 2024

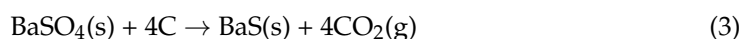
Citation: Wan, Y.; Chen, Z.; Cao, X.; Song, X.; Zhan, Y.; Ma, C.; Zhang, S.; Ni, W. Research on the Harmless Treatment of Barium Slag Using Flue Gas Desulfurization Gypsum. *Processes* **2025**, *13*, 55. <https://doi.org/10.3390/pr13010055>

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1. Introduction

Barium slag refers to the solid waste generated during the production of barium salts from barite through a carbon reduction process [1–3] (Jamshidi and Salem, 2010; Guzmán et al., 2012; Gu et al., 2019). In industry, the most critical reaction is the thermal reduction of barium sulfate, where coal/coke is added to a rotary kiln or a fluidized bed reactor to react with barite at temperatures between 950 and 1100 °C [4] (Salem and Osgouei, 2009). The chemical reaction between the two solid reactants is quite complex, and the overall reaction can be represented by Equation (1). It is generally believed that the true reaction occurs through a gaseous intermediate [5,6] (2)–(4) (Murthy and Reddy, 2012; Zhang et al., 2014). After the reduction reaction, the resulting barium sulfide solution is subjected to water leaching and filtration [7] (Jamshidi and Ebrahim, 2008). The insoluble precipitate mainly consists of unreacted raw materials and some newly formed phases.

The specific reactions are shown in Equations (1)–(4). In the industrial reduction process of barite, carbon is traditionally used as the reducing agent due to its strong reducing properties at high temperatures. However, to improve the efficiency of this reduction process, multiple factors need to be carefully considered: the ratio of mixed materials [8] (Balintova et al., 2017), significant differences in the activation energies of different carbon materials (such as charcoal, coke, graphite, etc.) [9] (Bafghi et al., 2011), and the content of volatile substances [10] (Agarwal, 2014).



To address the issue of carbon dioxide emissions during the reduction process of barite, researchers have actively explored and attempted various alternative reducing agents, including methane [7,11,12] (Alizadeh et al., 2007, 2010; Jamshidi and Ebrahim, 2008), hydrogen [13,14] (Pelovski et al., 1990; Sohn et al., 2006), carbon monoxide [15,16] (Hlabela et al., 2010; Vakilpour and Hamidi, 2016), and elemental sulfur [5,17] (Zhang et al., 2014, 2020). These attempts aim to reduce or avoid the generation of carbon dioxide during the reduction process to meet environmental protection requirements. In addition, innovative processes continue to emerge, such as the method introduced by Gokarn et al. (1999) [18] which produces barium chloride from barite without the need for traditional carbon thermal reduction, and the strategy proposed by Suárez-Orduña et al. (2009) [19], which uses Na under alkaline hydrothermal conditions to convert barite into barium carbonate. Although these new methods show potential application prospects, they are still in the laboratory research stage and have not yet reached the maturity required for commercial application. Currently, China primarily uses the carbon reduction method to produce barium carbonate, with an annual production of approximately 700,000 tons, accounting for about 75% of the world's barium carbonate production [3], making it the leading producer globally. For every ton of barium carbonate produced, approximately 0.9 tons of barium slag are generated. At present, the annual emission of barium slag in China exceeds 1 million tons [20], with a cumulative stockpile of over 10 million tons [21].

The disposal of barium slag has become a significant issue due to its corrosive nature and high levels of barium impurities. In addition to unreacted barite, soluble barium ions exceed national safety limits, posing health risks [22]. Exposure to sunlight and rain can cause leaching of sulfides and alkaline substances, contaminating water sources and surrounding land, leading to soil salinization. As a result, barium slag is classified as hazardous waste (HW47). The varying forms and compositions of barium slag due to different production processes present additional challenges in its treatment [23]. Researchers have extensively studied its treatment, focusing on chemical composition, treatment methods, and toxicity. Current disposal technologies include comprehensive utilization, resource recovery [24], and safe landfilling, but large-scale applications are still in the research stage, with risks of secondary pollution. Harmless disposal methods, such as incineration for toxicity reduction [24], barium ion extraction [25], and barium ion stabilization and solidification [26,27], are primary approaches.

Currently, two main methods for the harmless treatment of barium slag are used in China: the phosphogypsum synergistic treatment method and the sulfate fixation method. The sulfate fixation method solidifies barium ions through chemical reactions, reducing environmental risks [28], but is costly due to the need for large amounts of chemical agents, limiting its industrial application. The phosphogypsum method utilizes two industrial by-products, recycling resources and reducing harmful substances. Phosphogypsum's sulfate, phosphate, and hydrogen ions solidify free barium ions and neutralize hydroxide ions [29]. Several studies have shown that this method effectively reduces barium ion concentrations, with Guo Tengfei (2020) [30] achieving <2 mg/L at a 10:1–20 (BS:PG) ratio, and Li Bo et al. (2024) [31] reducing it from 1490 mg/L to 3.16 mg/L. Dai Yinghui et al. (2024) [32] and Zhou Changping et al. (2024) [33] further optimized the process, improving efficiency and reducing costs while meeting the hazardous waste identification standards. However, the process is still complex and energy-intensive, limiting large-scale application. Overall, most studies provide a theoretical basis for the gypsum-based sulfate solidification of barium slag.

The promotion and application of similar harmless treatment methods are not limited to China. Globally, many countries are also exploring and applying similar technologies for the harmless treatment of barium slag. In the United States, due to strict environmental regulations, particularly regarding barium emissions, many companies in the country have begun using FGD gypsum for the harmless treatment of barium slag. The U.S. Environmental Protection Agency (EPA) and some local governments have promoted the application of and research into this technology, especially in regions rich in gypsum by-products. Through this approach, the effective disposal of barium slag has been achieved, while also reducing environmental costs. In Asia, countries like India and Japan have also started to focus on the harmless treatment of barium slag. Although related research started relatively late, some companies have already conducted pilot applications. Especially in Japan, where high environmental protection standards are required, the treatment of barium slag has become a matter of urgency.

With growing global awareness of environmental protection and the increasing scarcity of resources, the utilization of industrial by-products has become a key pathway to sustainable development. FGD gypsum, a by-product of thermal power plants, has emerged as a significant sustainable resource. Its use not only reduces waste emissions but also decreases the extraction of natural gypsum, preventing ecological damage. Additionally, FGD gypsum helps lower carbon footprints, particularly in cement production, by improving cement strength and durability while reducing energy consumption and carbon emissions. Therefore, FGD gypsum plays a vital role in promoting a green economy and resource recycling.

Given the current challenges of low resource utilization in large volumes of solid waste, synergistically disposing of FGD gypsum and barium slag can achieve waste-to-waste treatment, thereby improving the resource utilization rate of solid waste. Therefore, this paper proposes a new process for the harmless treatment of barium slag using FGD gypsum. The process involves the reaction of sulfate ions in FGD gypsum with soluble barium ions in barium slag to form barium sulfate precipitate, achieving stabilization treatment. Our experimental results show that this method not only significantly reduces the leaching toxicity of barium slag but also has a low cost and good potential for resource utilization. This study provides new technical support for the green treatment and recycling of barium slag.

2. Materials and Methods

2.1. Raw Material

The raw materials used in this experiment were sourced from Hongxing Development Co., Ltd. in Anshun City, Guizhou Province, China, including barium slag and FGD gypsum. The chemical composition of the BS is shown in Table 1. Its chemical composition mainly consists of SiO_2 , BaO , and SO_3 , with the BS containing primarily acid-soluble barium and water-soluble barium. The moisture content of the BS is 18.9%. The barium ion content is relatively high, exhibiting toxicity and strong alkaline corrosion, and is classified as HW47 hazardous waste. The XRD analysis results are shown in Figure 1b, where the main phases in the BS include BaSO_4 , BaSiO_3 , and SiO_2 . Barium sulfate exists in two phases (BaSO_4 and BaSO_4 (VI)), and it is hypothesized that this change may have occurred during the calcination of barite due to temperature fluctuations, leading to a transformation of some of the barium sulfate crystals from BaSO_4 to BaSO_4 (VI). Figure 1c shows the infrared spectrum analysis results of the barium slag raw material, revealing its main chemical composition and structural characteristics. The broad absorption peak at 3400 cm^{-1} indicates the presence of a certain amount of hydrates or moisture in the BS. The peak at 1600 cm^{-1} corresponds to the O-H bending vibration in hydrated silicates, though this peak is weak, suggesting a low degree of hydration in the BS. The peak at 1100 cm^{-1} represents the stretching vibration of the Si-O tetrahedron, indicating that the BS is rich in silicate components, such as quartz (SiO_2). Additionally, the peak at 600 cm^{-1} is associated with calcium aluminate silicates, further confirming the presence of inorganic minerals in the BS. In summary, the BS contains unreacted barium sulfate from barite as well as barium carbonate and barium silicate generated during the calcination process.

Table 1. XRF analysis of BS.

Sample	SiO_2	BaO	SO_3	Fe_2O_3	Na_2O	Al_2O_3	CaO	K_2O	MgO	MnO	TiO_2	P_2O_5
BS	32.7	27.98	19.18	7.83	3.82	3.45	2.35	0.9	0.63	0.63	0.5	0.21

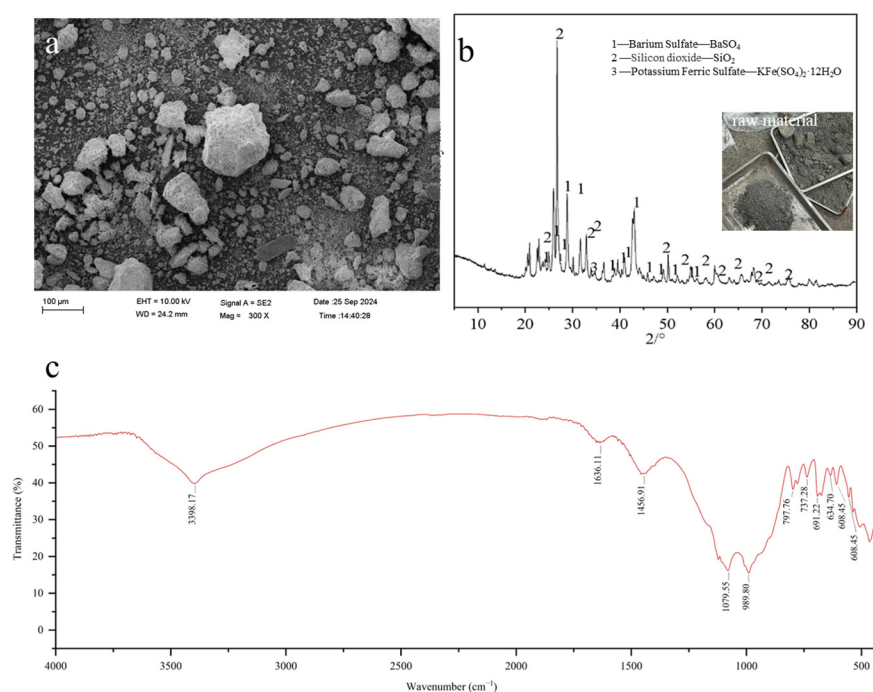


Figure 1. BS test data: (a) scanning electron microscopy (SEM) image of BS; (b) X-ray diffraction (XRD) pattern of BS; (c) infrared (IR) spectrum of BS.

2.2. Method

2.2.1. Experimental Mixture Design

The dried materials were prepared according to the proportions in Table 2, where the labels W, A, B, and C correspond to sample proportions with water-to-binder ratios of 0.18, 0.23, 0.28, and 0.32, respectively. Sampling and fineness analysis were conducted for the experimental materials. First, limit crushing and curing experiments were conducted, using a crusher (Beijing Lide Century Technology Co., Ltd., Beijing, China) to crush the BS. The BS and FGD gypsum were then dried at 50 °C for 12 h and ground for 40 min using a cement laboratory mill. Water-to-binder ratios of 0.18, 0.23, 0.28, and 0.32 were used, and test blocks were prepared with BS-to-FGD gypsum ratios ranging from 1:1 to 10:1. The specific experimental mixture design is shown in Table 2. As shown in Figure 2, (a) is the test block placed into the mold, and (b) is the test block after demolding for 48 h, removed from the mold, with the block appearing as a black square.

Table 2. Proportions of the samples.

Sample	BS/g	FGD Gypsum/g	Water-to-Binder Ratio
W1	1230	410	0.18
W2	1491	149	0.18
A1	406.51	406.51	0.23
A2	482.81	325.2	0.23
A3	569.11	243.9	0.23
A4	650.41	162.6	0.23
B1	390.61	390.61	0.28
B2	487.81	312.5	0.28
B3	569.11	234.38	0.28
B4	650.41	156.25	0.28
C1	378.78	378.78	0.32
C2	454.536	303.024	0.32
C3	530.292	227.268	0.32
C4	606.048	151.512	0.32
C5	681.804	75.756	0.32



Figure 2. Test blocks: (a) prepared test blocks; (b) test blocks after de-molding.

2.2.2. Detection and Analysis Methods

The neat paste samples were prepared according to “Methods for Testing the Strength of Cement Mortar” (GB/T 17671-2021) [34], and their uniaxial compressive strength at 7

and 28 days was tested. Based on this parameter, the effect of FGD gypsum content on the sample's performance and hydration process was discussed.

The moisture content test was conducted according to the relevant standards of the "Soil Test Method Standard" (GB/T 50123-1999) [35] and the drying method was used. The specific procedure was as follows: Ten samples of barium slag were collected from Hongxing Development Co., Ltd. A pre-dried container was weighed, and approximately 500 g of barium slag was divided into ten portions. Each portion was placed into a container, weighed, and numbered. The total weight of each barium slag sample and container (m_2) was recorded. Then, all containers with barium slag samples were placed in a constant-temperature drying oven set at 105 ± 5 °C for drying. After drying was completed, the total weight of the barium slag sample and container was recorded. Finally, the moisture content of the ten barium slag samples was calculated based on the ratio of m_2 and m_3 .

Leaching tests were carried out according to the "Leaching Toxicity of Solid Waste—Horizontal Oscillation Method" (HJ557-2010) [36]. The leaching characteristics of the harmless BS blocks (Ba) with different proportions were studied. A 100 g dried sample (sieved to below 3 mm) was placed in a 2 L leaching bottle, and the liquid-to-solid ratio was adjusted to 10:1. Deionized water was used as the leaching agent, and the bottle was placed on a horizontal shaker for 8 h of oscillation at a frequency of 110 ± 10 oscillations per minute. After 16 h of standing, the supernatant was filtered through a 0.45 µm micropore membrane.

Leaching tests were also performed according to the "Leaching Toxicity of Solid Waste—Sulfuric-Nitric Acid Method" (HJ/T299-2007) [37]. To assess the actual application of the resource products after harmless treatment of the BS, the leaching behavior of the heavy metals under conditions of acid rain or acidic groundwater was investigated. The test steps were as follows: The harmless treated sample was crushed and sieved to below 9.5 mm. A 40 g dried sample was mixed with deionized water and a mixed acid solution ($\text{H}_2\text{SO}_4\text{:HNO}_3$) in a 2:1 volume ratio. The pH of the leaching agent was adjusted to 3.20 ± 0.05 , maintaining a liquid-to-solid ratio of 10 L/kg at room temperature (23 ± 2 °C), with shaking at 30 ± 2 rpm for 18 ± 2 h. The Ba concentration in the leachate was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES).

To explain the harmless treatment mechanism, finely ground BS materials (W1 and W2) were prepared for microscopic testing, including XRD, XRF, FT-IR, and SEM-EDS. XRD analysis was performed using a Rigaku Ultima IV X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with a wavelength of 1.5418, a voltage of 40 kV, and a current of 40 mA. The scan range was 5° to 90° at a scan speed of $10^\circ/\text{min}$ to observe the phases in the powdered samples. XRF was conducted using a Rigaku ZSX Primus III+ (Rigaku Corporation, Tokyo, Japan) X-ray fluorescence spectrometer to measure the types and contents of elements in the powders. FT-IR analysis was performed with a Thermo Fisher Scientific Nicolet iS20 IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) to obtain the FT-IR spectra of the samples. The resolution was set to 4 cm^{-1} , with 32 scans, and the wavenumber range was $400/600\text{--}4000\text{ cm}^{-1}$ to determine the characteristic peaks of the hydration products through the analysis of chemical bonds and functional groups. A JSM-6701F field emission scanning electron microscope (SEM) (JEOL Ltd., Akishima, Japan) was used to observe the microstructure of the hydration products in the samples, with an aperture of 3 and a working voltage of 10 kV at a beam spot size of 6.

3. Results

3.1. Mechanical Property Testing

Figure 3 shows the results of the uniaxial compressive strength tests for each sample cured for 7 and 28 days. It can be observed that as the hydration duration increased from 7 days to 28 days, the compressive strength of the samples with different amounts of FGD gypsum increased. For the A1 sample with a water-to-binder ratio of 0.23 and 50% FGD gypsum content, the compressive strength at 28 days reached 3.33 MPa, indicating that the hydration reaction was continuously ongoing. Regarding the effect of FGD gypsum, its content had a clear influence on the compressive strength of the harmless BS. As shown in Figure 3, for different water-to-binder ratios and varying FGD gypsum contents, the compressive strength of the harmless BS first increased with the gradual addition of FGD gypsum. At a water-to-binder ratio of 0.23, the compressive strength was higher compared to other groups with the same FGD gypsum content. As shown in Table 3, with a water-to-binder ratio of 0.18, the strength of the samples increases with the addition of FGD gypsum, with the average compressive strength rising from 0.79 MPa to 0.23 MPa.

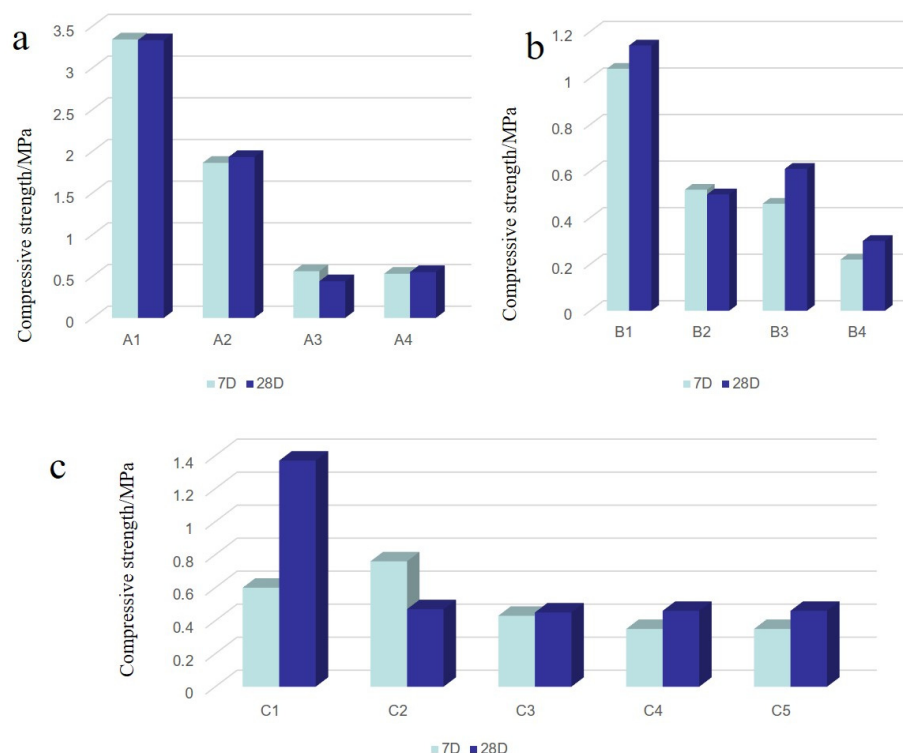


Figure 3. Mechanical performance test results: (a) compressive strength of A1–4; (b) compressive strength of B1–4; (c) compressive strength of C1–5.

Table 3. Seven-day compressive strength of W1–2.

Sample	Compressive Strength/MPa	Average Compressive Strength/MPa
W1	1.26	1.23
	1.27	
	1.16	
W2	0.81	0.79
	0.86	
	0.72	

3.2. Leaching Toxicity Test

3.2.1. Horizontal Oscillation Method

The Ba leaching concentration in the BS raw material was determined using the horizontal oscillation method. As shown in Table 4, the Ba concentration in the BS raw material reached 187.0045 mg/L, exceeding the leaching concentration limit for barium (100 mg/L) specified in the China standards *Hazardous Waste Identification Standard for Leachate Toxicity Identification* (GB5085.3-2007) [38]. The leaching concentration data of the samples at 7d and 28d curing times for different formulations are shown in Figure 4. The leaching concentration significantly decreased at 7d of curing, indicating good curing performance. Among the formulations, A1, B1, and C1 had relatively low Ba leaching concentrations, which were 36.74 $\mu\text{g/L}$, 58.45 $\mu\text{g/L}$, and 83.29 $\mu\text{g/L}$, respectively, representing a reduction in Ba leaching concentration by nearly 20,000 times. After 28d of curing, the Ba leaching concentrations of all samples, except for A1, A2, B3, and B4, showed an increasing trend. The highest Ba leaching concentration was observed in C5, which reached 154 $\mu\text{g/L}$, but it still met the Ba toxicity standard for drinking water as specified in China standards (GB5749-2006) [39]. As shown in Figure 4, the Ba leaching concentration decreased with an increase in FGD gypsum content in the formulations under all water-to-binder ratios. However, when the water-to-binder ratio was higher, the Ba leaching concentration slightly increased. This indicates that desulfurization gypsum has a good solidification effect on Ba ions, but it is necessary to control the water-to-binder ratio within an appropriate range.

Table 4. BS raw material leaching concentration data.

Sample	Ba Concentration ($\mu\text{g/L}$)
BS	1,870,045

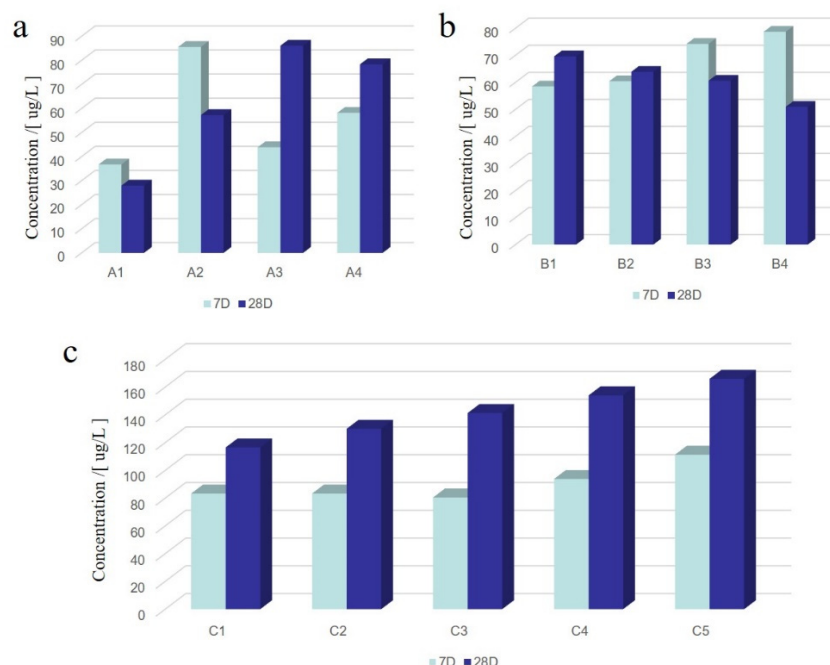


Figure 4. Sample Ba leaching concentration data: (a) A1–4; (b) B1–4; (c) C1–5.

3.2.2. Sulfuric–Nitric Acid Method

Under acidic conditions, the leaching behavior of heavy metals may become more pronounced. The leaching results of the harmless BS obtained according to the method prescribed in the “Leaching Toxicity Testing Method for Solid Waste—Sulfuric-Nitric Acid

Method” (HJ/T299-2007) [37] are shown in Table 5. The Ba leaching concentrations for the C4 and C5 samples were 0.32 mg/L and 0.40 mg/L, respectively, slightly higher than the results from the previous horizontal oscillation method. As shown in Table 5, with the increasing addition of FGD gypsum, the Ba leaching concentrations gradually decreased. The Ba leaching concentration for the W2 sample reached 4.67 mg/L, still well below the leaching limit for barium (100 mg/L), as outlined in the *Leaching Toxicity Identification Standard for Hazardous Waste* (GB5085.3-2007) [38].

Table 5. Leaching concentration data of heavy metals in samples (mg/L).

Sample	Ba	Pb	Zn
W1	0.27	<0.12	<0.04
C4	0.32	<0.12	<0.04
C5	0.40	<0.12	<0.04
W2	4.67	<0.12	<0.04

Further analysis reveals that the leaching concentrations of Pb and Zn in the harmlessly treated samples were both below the detection limit, indicating that the harmlessly treated samples exhibited strong acid resistance stability. Additionally, the treatment effectively controls Ba and other potential heavy metals.

Based on the laboratory formulations, two harmless products were obtained through extreme ratios and used as resource-pretreated materials for further utilization. To assess their safety and environmental impact, leaching tests for target heavy metals, especially barium ions, were conducted. The results showed that the leaching concentration of barium ions was below the hazardous waste identification standards and drinking water quality standards, indicating that the product successfully met the harmless treatment criteria. This provides a solid foundation for subsequent resource utilization.

3.3. Microscopic Analysis

3.3.1. Chemical Elemental Analysis

Table 6 shows the X-ray fluorescence analysis of the W1 and W2 samples at a hydration duration of 7 days. The analysis reveals that in the W1 sample, the BaO content significantly decreased (to 21.04%), while the contents of SO₃ and CaO increased to 23.39% and 15.47%, respectively. This indicates that the sulfate ions in the FGD gypsum fully reacted with the barium ions to form stable barium sulfate (BaSO₄), thus achieving efficient solidification of barium ions.

Table 6. XRF analysis of samples.

Sample	SiO ₂	BaO	SO ₃	CaO	Fe ₂ O ₃	Al ₂ O ₃	MgO	K ₂ O	Na ₂ O	MnO	TiO ₂	P ₂ O ₅
W1	27.27	21.04	23.39	15.47	3.02	2.74	4.19	0.73	0.35	0.05	0.41	0.22
W2	30.52	31.73	18.60	8.19	4.07	3.92	0.64	0.63	0.33	0.07	0.51	0.31

In contrast, the W2 sample showed relatively high BaO content (31.73%) and lower contents of SO₃ and CaO, suggesting that the amount of FGD gypsum was insufficient, resulting in incomplete reactions. As a result, some barium ions remained in a leachable form, leading to poorer solidification.

3.3.2. Phase Composition Analysis

Figure 5 shows the XRD patterns of samples W1, C4, C5, and W2 at a hydration duration of 7 days. Overall, the substances in the samples with distinct crystalline diffraction

peaks can be categorized into three types: (1) reaction products, primarily barium sulfate; (2) unreacted substances, mainly quartz and unreacted FGD gypsum; and (3) generated products, including ettringite. Compared with samples W1, C4, C5, and W2, as the amount of FGD gypsum decreased, the intensity of the diffraction peaks of FGD gypsum gradually diminished, while the intensity of the diffraction peaks of barium sulfate gradually increased. This suggests that the appropriate addition of FGD gypsum promoted the hydration reaction and consumed part of the barium sulfate.

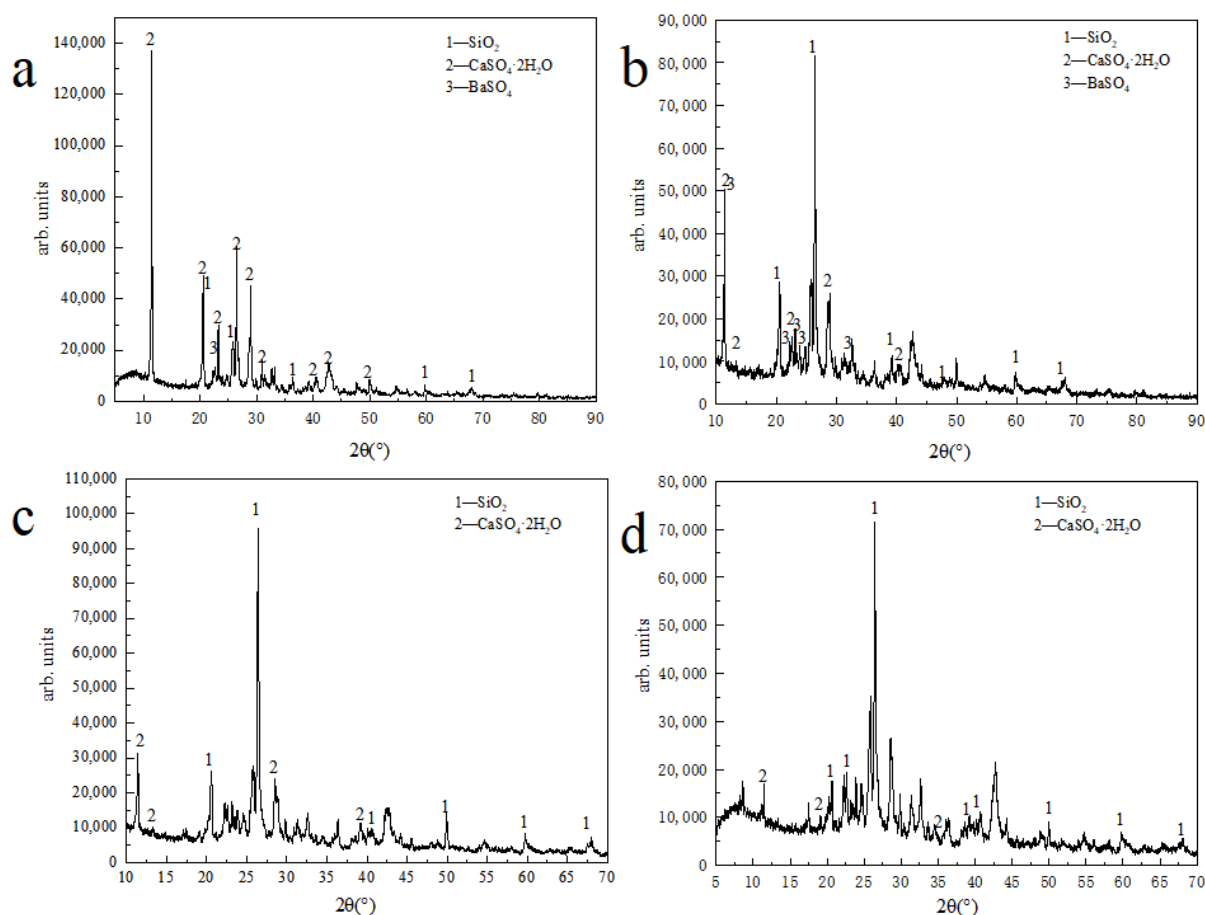


Figure 5. XRD patterns: (a) W1; (b) C4; (c) C5; (d) W2.

3.3.3. Chemical Bond Analysis

Figure 6 shows the FT-IR spectra of samples W1, C4, C5, and W2 at a hydration duration of 7 days. The peaks near 3600 cm^{-1} , 3400 cm^{-1} , and 1600 cm^{-1} correspond to the stretching vibration peaks of gypsum, $\text{Ca}(\text{OH})_2$, and amorphous O-H bonds, respectively, as well as the stretching and bending vibration peaks [40]. The peak near 1400 cm^{-1} corresponds to the asymmetric vibration of the C-O bond in $[\text{CO}_3^{2-}]$, and the peak near 1100 cm^{-1} corresponds to the asymmetric stretching vibration of the S-O bond in $[\text{SO}_4^{2-}]$ of FGD gypsum/barium sulfate. The peaks near 600 cm^{-1} and 460 cm^{-1} correspond to the symmetric stretching vibration bands of Si-O-Al [41]. Overall, the shapes and positions of the major vibration peaks in each sample are largely consistent, but there are differences in peak intensity. Specifically, from W1 to W2, the intensities of the O-H vibration peak near 3400 cm^{-1} , as well as the Si-O-Al vibration peaks near 600 cm^{-1} and 460 cm^{-1} , decrease, while the intensity of the O-H stretching vibration peak near 3600 cm^{-1} (gypsum phase) also decreases. This indicates that as the gypsum content decreases, the crystallinity of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ diminishes, but the hydration products of all three are essentially the same, manifesting as differences in hydration rate and the quantity of products.

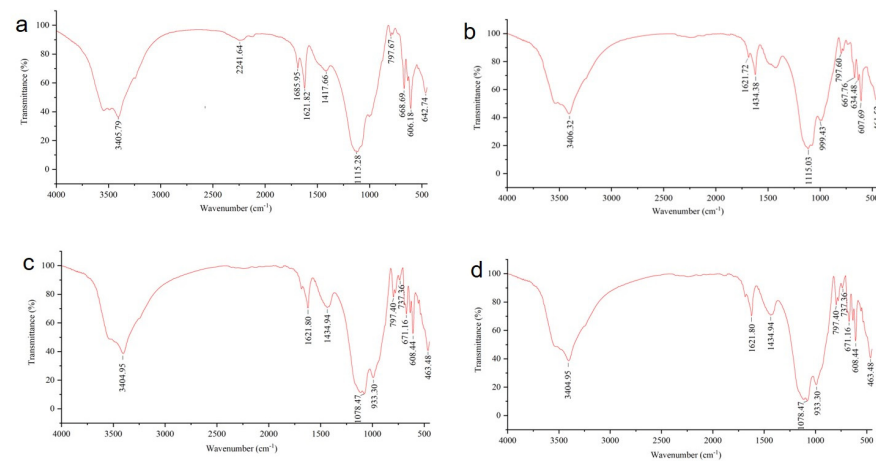


Figure 6. FT-IR spectra of samples: (a) W1; (b) C4; (c) C5; (d) W2.

3.3.4. Microstructural Analysis

Figure 7 shows the electron microscope images of samples W1, C4, C5, and W2 at a hydration duration of 7 days. By observing the microstructures of the samples, a large amount of petal-shaped monosulfate calcium sulfoaluminate hydrate was observed in some samples. Columnar gypsum minerals were present in the samples, and small crystalline particles of BaSO_4 adhered to the unreacted BS. This petal-shaped $\text{Ca}(\text{OH})_2$ provides assurance for the early alkalinity conditions of the samples. When the gypsum content is high, there is a significant amount of unreacted gypsum mineral in the samples. As the amount of FGD gypsum decreases, the gypsum crystals in the samples become smaller. When the ratio of BS to FGD gypsum is less than 10:1, the amount of gypsum produced decreases.

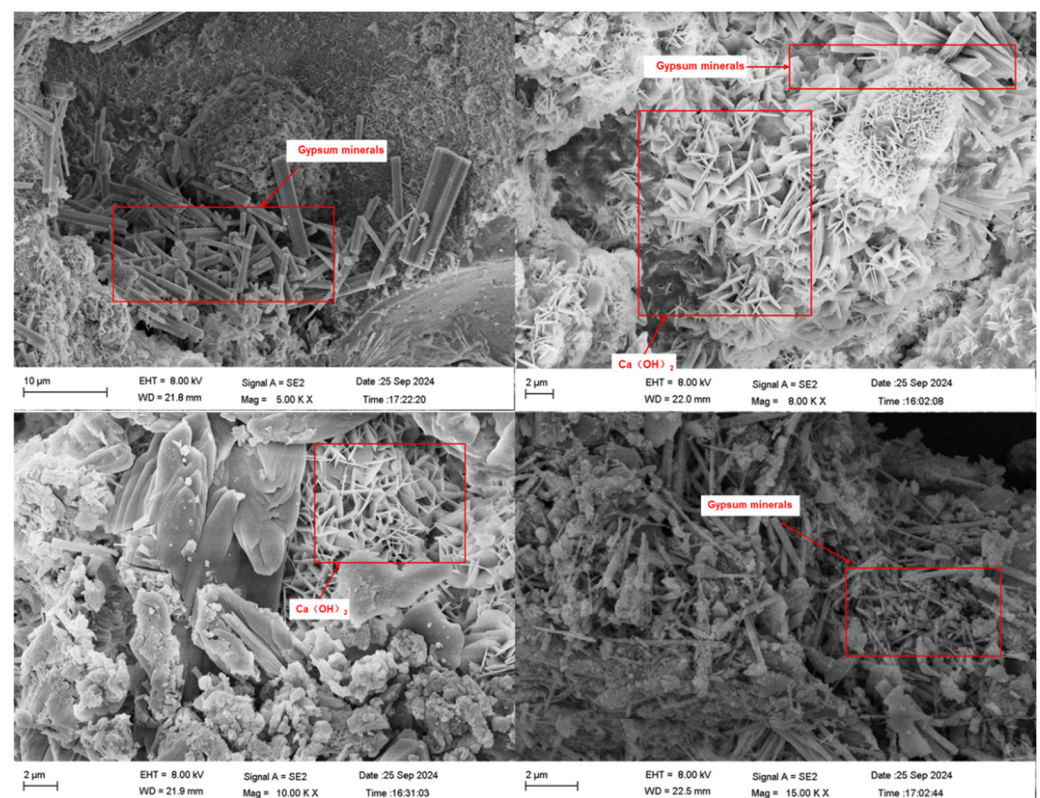


Figure 7. Microscope images of samples: (a) W1; (b) C4; (c) C5; (d) W2.

3.4. Analysis of Harmless Treatment Mechanism of FGD Gypsum on BS

The mechanism of the harmless treatment of BS by FGD gypsum relies on the synergistic effects of chemical precipitation, phase transformation, and microstructural optimization. The experimental analysis clearly shows that FGD gypsum mainly consists of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with small amounts of impurities. Since CaSO_4 is slightly soluble in water, the soluble sulfate provided by FGD gypsum can be used to precipitate and fix the free barium ions in the BS. The sulfate ions (SO_4^{2-}) in the FGD gypsum react with the free barium ions (Ba^{2+}) in the BS to form stable barium sulfate (BaSO_4), as shown in reaction (5). At the same time, the soluble calcium ions can react with sulfides or with hydroxide ions, providing an alkaline environment that stimulates the continuation of the reaction, as shown in Equations (6) and (7). The X-ray diffraction (XRD) results indicate that the characteristic peak of barium sulfate significantly increases in the treated samples, while the BaO content significantly decreases, suggesting that a large number of barium ions are transformed into insoluble minerals through chemical reactions. Additionally, the gypsum phase fills the pores of the hardened matrix, enhancing the structural strength.



Infrared spectroscopy (FTIR) further confirmed the formation of barium sulfate. A S-O stretching vibration absorption peak appeared near 1100 cm^{-1} in the treated samples, indicating the formation of barium sulfate crystals. Meanwhile, the intensity of the O-H stretching vibration peak at 3600 cm^{-1} , corresponding to the crystallization water in gypsum, weakened as the gypsum content decreased. The appearance of these characteristic peaks indicates that FGD gypsum was consumed in the reaction, and barium sulfate was generated, effectively enhancing the curing stability of Ba^{2+} in the BS.

Scanning electron microscopy (SEM) observations showed that the microstructure of the treated samples underwent significant changes. Large rod-shaped gypsum crystals filled the pores, forming a dense microstructure. This structural optimization effectively hindered the invasion of external liquids into the interior of the hardened body, further restricting the migration of barium ions. The energy-dispersive spectroscopy (EDS) results revealed the presence of Ba, S, and Ca elements both on the surface and inside the pores of the samples, further confirming that the formation of barium sulfate is the main mechanism for the stabilization of Ba^{2+} .

4. Significance, Applicability, and Future Research Prospects of Using FGD Gypsum for Harmless Treatment of BS

Harmless treatment, also known as safe treatment, refers to the use of advanced technologies and processes to reduce the toxicity of harmful biological or chemical substances in toxic and hazardous waste, thus minimizing their environmental impact and reducing waste emissions. As a type of hazardous solid waste, research into harmless treatment technologies for BS not only offers a potential solution to the environmental hazards it causes but also lays the foundation for its safe disposal and even resource utilization. At the same time, FGD gypsum is abundant and inexpensive, making it an ideal material for large-scale industrial waste treatment. Therefore, this study, based on the concepts of 'waste-to-waste' and 'turning waste into treasure', utilizes the effective components in FGD gypsum through a synergistic precipitation mechanism to fix the soluble barium ions in the BS while addressing other industrial solid waste issues. Our experiments show that after optimizing the proportion of FGD gypsum and BS, the leaching concentration of barium

ions in the treated samples is far below the national drinking water standard (0.7 mg/L). Moreover, the chemical properties of the treated hardened products are stable, and they can be used as building materials, road base materials, etc., achieving a win-win situation in terms of both economic value and environmental benefits. Therefore, this method has good prospects for widespread application, especially in regions with significant BS stockpiles.

It is worth noting that the method proposed in this study is significantly more cost-effective for the harmless treatment of barium slag compared to traditional chemical solidification methods. According to the latest industry average pricing data, the cost of treating barium slag with FGD gypsum is approximately six to eight times lower than that of chemical solidification methods. The raw material cost of FGD gypsum is CNY 15 per ton of barium slag, and with equipment and operational costs included, the total treatment cost is about CNY 63.5 per ton of barium slag. In contrast, the reagent cost for chemical solidification ranges from CNY 80 to 160 per ton of barium slag, with a total treatment cost of CNY 400 to 500 per ton, highlighting the significant economic advantage of the FGD gypsum method.

FGD gypsum not only reduces direct costs but also decreases leaching toxicity by generating stable barium sulfate and ettringite, and it facilitates the resource utilization of the treatment products, further reducing the environmental burden. Therefore, the FGD gypsum treatment method demonstrates substantial advantages over chemical solidification in terms of economic viability, environmental benefits, and resource potential, making it highly promising for industrial application.

In addition to the direct cost savings, the FGD gypsum treatment method offers environmental benefits as well. Chemical solidification requires the use of large quantities of chemical reagents, which may lead to secondary pollution. In contrast, FGD gypsum generates stable barium sulfate and ettringite, which not only reduces the leaching risks of heavy metals but can also be used as building materials, offering higher resource utilization potential and aligning with sustainable development principles. Overall, the FGD gypsum treatment method presents a more cost-effective and environmentally friendly approach for the harmless treatment of barium slag, with strong prospects for industrial-scale application.

Although the harmless treatment method proposed in this study performs well in laboratory conditions, there are several challenges to its industrial application, given the large annual production of BS. The main obstacles include raw material supply and cost control, process stability and adaptability, equipment investment, and potential secondary pollution risks. Due to the huge production volume of BS, ensuring a stable supply of sufficient raw materials while controlling costs—especially when large quantities of chemical reagents or auxiliary materials are required—may create pressure for large-scale application. Moreover, the good results obtained under laboratory conditions do not necessarily mean that they can be directly replicated in industrial production. During large-scale applications, the stability and adaptability of the process may be affected by factors such as raw material batch variations and fluctuations in production conditions, which, in turn, could influence reaction efficiency. Equipment and technology investment is also a key challenge, particularly when large-scale reactors and complex waste gas and wastewater treatment facilities are needed, which involve high construction and maintenance costs.

In addition, secondary pollution risks associated with industrial-scale applications, especially in managing by-products such as waste gas and wastewater generated during the treatment process, need to be addressed in future research. Large-scale applications also require strict environmental compliance to prevent secondary pollution from causing harm to the environment.

Therefore, future research should focus on the feasibility of this harmless treatment technology for large-scale industrial applications, conduct detailed cost–benefit analyses, evaluate the technology’s economic viability at different production scales, and perform long-term stability tests to ensure the technology can be successfully transitioned into industrial use and achieve its intended environmental protection benefits.

5. Conclusions

This study used Flue Gas Desulfurization Gypsum for the harmless treatment of barium slag, verifying the effectiveness of this method in reducing the toxicity leaching of barium slag and improving its environmental friendliness. Through comprehensive analysis of chemical reactions, microstructure, and environmental characteristics, the following conclusions were drawn:

Adding an appropriate amount of Flue Gas Desulfurization Gypsum can effectively stabilize the free barium ions in the barium slag. Considering the performance of the samples at 7 and 28 days, and also aiming to maximize the utilization of barium slag, it was determined that a barium slag-to-Flue Gas Desulfurization Gypsum ratio ranging from 1:1 to 9:1 meets the national hazardous waste standard (100 mg/L) and drinking water standard (0.7 mg/L). When the water-to-binder ratio is 0.23, the samples exhibit higher strength, with the average strength of group A1 at 7 days being 3.34 MPa and at 28 days being 3.33 MPa.

The mechanism of the harmless treatment of barium slag with Flue Gas Desulfurization Gypsum can be summarized in three aspects: the formation of barium sulfate, phase transformation into stable minerals, and microstructural optimization. The formation of barium sulfate fundamentally reduces the mobility of heavy metals in the barium slag, while the filling effect of barium sulfate and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ on the matrix forms a dense hardened structure, which not only enhances the compressive strength but also significantly reduces the leaching risk of heavy metals.

This study not only effectively achieved the harmless treatment of barium slag but also provided a feasible approach for the resource utilization of Flue Gas Desulfurization. The treated hardened bodies exhibited good mechanical properties and environmental stability, making them suitable for use as road base materials or other building materials, demonstrating strong resource potential. At the same time, the process is cost-effective and aligns with the environmental concepts of ‘waste-to-waste’ and sustainable development.

Author Contributions: Conceptualization, C.M. and Y.Z.; methodology, Y.W.; software, X.S.; validation, Y.W., X.C. and Z.C.; formal analysis, Y.W.; investigation, Z.C.; resources, X.C.; data curation, X.S.; writing—original draft preparation, Y.W.; writing—review and editing, X.S.; visualization, S.Z.; supervision, Z.C.; project administration, S.Z.; funding acquisition, W.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data are available on request due to privacy restrictions. The data presented in this study were derived from a confidential project and can be obtained upon request to the corresponding author.

Conflicts of Interest: Author Yang Wan, Zhou Chen and Xiaohui Cao were employed by the company Guizhou Redstar Developing CO., LTD. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The [company Guizhou Redstar Developing CO., LTD-companies in affiliation and funding] had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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