

Article

A Novel Process Strategy for Efflorescence Control of Ceramsites Sintered from High-Sulfur Kiln Slag

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Abstract: The high sulfur content in kiln slag ceramsites leads to pronounced efflorescence, significantly limiting the application of such solid-waste-derived products in construction engineering. In this study, a sintering experiment of 50 kg ceramsites with 60% kiln slag content was conducted at 1150 °C on small-scale ceramsites sintering equipment. The research focused on discussing the mechanisms of efflorescence and putting forward the process strategy to control efflorescence in kiln slag ceramsites. The results revealed that the sulfur content (4.53%) and water absorption rate of ceramsites (8.5%) were the primary causes of efflorescence. During the sintering process, sulfur evolved on the pathway of “pyrite in raw materials → partial oxidation to SO₂ and partial fixation in CaSO₄ → decomposition of CaSO₄”. In order to reduce content of sulfur, it was proposed that not only was sulfur in pyrite oxidized enough to be removed in the low-temperature stage but, also, residual CaSO₄ decomposed more to eliminate S in the high-temperature stage. This optimizing sintering process reduced the sulfur content from 2.0% to 0.72%. Furthermore, enhancing its densification contributed to avoiding efflorescence. By controlling its sintering temperature and increasing the formation of Fe₂O₃, the densification of ceramsites was improved by decreasing its water absorption rate from 8.5% to 1.2%, and its efflorescence was thereby enhanced. This provides both a theoretical foundation and technological support for the high-value utilization of high-sulfur solid waste.

Keywords: kiln slag ceramsites (KSCs); efflorescence mechanism; sintering process; solid waste valorization



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1. Introduction

The steel industry clusters generate massive amounts of solid waste dust, most of which is processed through high-temperature zinc reduction recovery in rotary kilns. However, this treatment produces secondary solid waste amounting to 30–50% of the kiln's input materials, termed zinc-recovery kiln slag [1]. In 2022, China's accumulated stockpile of such slag reached 30–40 million metric tons [2]. After magnetic separation, the processed slag generates new tailings characterized by high sulfur content, large storage footprint, and low valorization rates. These tailings pose significant environmental pollution risks and safety hazards, urgently requiring valorization solutions.

Current valorization approaches for kiln slag primarily include recovering valuable metals (e.g., iron and silver) and solid carbon powder, as well as utilizing it as raw material for building products like cement and ceramsites [3–6]. Among these, ceramic materials

such as ceramsites have garnered significant research attention due to their dual capability of incorporating diverse oxide components from slag and immobilizing heavy metal ions, demonstrating broad market potential. Meng et al. [7] developed high-strength, low-water-absorption glass-ceramics using zinc-recovery kiln slag through a one-step synthesis process. Wang et al. [8] fabricated high-performance ceramsites with a bending strength of 85 MPa by combining zinc-recovery slag with dredged sediment. Cenrui [9] produced ceramsites exhibiting cylindrical compressive strength of 24.1 MPa using 60% slag content. Under low sintering temperatures (typically 950–1100 °C) with short processing durations, the resulting ceramsites exhibit a rough surface texture, abundant micro-pores, high specific surface area, low expansion coefficient, elevated density, and moderate hardness. These characteristics endow it with superior adsorption capacity, making it ideal for use as wall filler material [10–13]. Conversely, high-temperature sintering (>1100 °C) with extended durations produces ceramsites encapsulated by a vitreous glaze layer. This variant demonstrates high hardness, a porous honeycomb internal structure, significant expansion coefficient, low density, and stable physicochemical properties. Its exceptional insulation performance qualifies it as an advanced lightweight aggregate, primarily employed in roadbed construction materials [14].

Due to the presence of sulfur in the kiln slag, during the reduction process, most of the sulfur forms sulfides, primarily in the form of FeS, and remains in the kiln slag. Under high-temperature sintering conditions, the oxidation process of pyrite would release heat and produce SO₂ volatilizing in gas or/and sulfates kept in ceramsites, which affected the sintering process and final performance of the kiln slag ceramsites [15]. Research [16] on the sintering of pyrite showed that the oxidation and combustion products varied under different atmospheres, temperatures, and particle sizes. When heated in an inert gas, pyrite decomposes and releases SO₂, forming iron sulfide with lower sulfur content—pyrrhotite FeS_x ($1 \leq x < 2$) [17]. Under conditions of lower-reaction-temperature regions (400–600 °C) and higher oxygen concentration, pyrite (FeS₂) is directly oxidized to oxides and sulfates [18,19]. At higher reaction temperatures and lower oxygen concentrations, pyrite (FeS₂) is first desulfurized to pyrrhotite FeS_x ($1 \leq x < 2$) and then oxidized to iron oxides (Fe₂O₃, Fe₃O₄, and FeO) [20,21]. When the concentrations of SO₂ or SO₃ gas are high, pyrite is first oxidized to sulfates (FeSO₄ and Fe₂(SO₄)₃) and then decomposed into iron oxides (Fe₂O₃ and FeO) and SO₂ [22,23].

However, field applications have revealed that KSC develops numerous fine white crystalline deposits on its surface after prolonged use. These water-soluble substances, appearing as powdery or flocculent coatings, are collectively termed “efflorescence”. This phenomenon not only compromises the aesthetic integrity of ceramsites but also significantly degrades its mechanical strength due to environmental factors like dehydration or carbonation, leading to structural defects such as cracking and disintegration. Consequently, elucidating the root causes of efflorescence and developing source-control strategies have emerged as critical challenges in the production and application of KSCs.

Efflorescence predominantly occurs in permeable bricks and concrete [24]. Research indicates that this phenomenon results from the migration and surface crystallization of soluble salts, a process closely correlated with ambient temperature and humidity [25,26]. Compositional analysis identifies calcium sulfate (CaSO₄) as the primary component of these white deposits, with potassium sulfate (K₂SO₄) as a secondary constituent [27,28]. Further investigations reveal that efflorescence formation requires essential conditions [29–31]: soluble salt components in the material composition, porous matrix providing ion migration pathways through capillary pores, water as a transport medium for soluble ions under environmental exposure, and low-temperature, shaded, and continuously cooling conditions that reduce salt solubility and accelerate crystallization.

Efflorescent salts originate from both intrinsic material components and external environmental sources. Internal sources: cement-based materials generate substantial $\text{Ca}(\text{OH})_2$ through hydration reactions, which serves as the main alkaline source for carbonate efflorescence. Aggregates containing soluble alkaline ions such as Na^+ and K^+ , as well as unreacted free CaO in admixtures (e.g., fly ash), can act as “salt reservoirs” [32]. External sources: groundwater, rainwater, or meltwater infiltrate the material via capillary action, carrying erosive ions like Cl^- and SO_4^{2-} . Acidic gases such as SO_2 and NO_x in industrial atmospheres react with $\text{Ca}(\text{OH})_2$ on the material surface, forming $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Ca}(\text{NO}_3)_2$, further increasing salt diversity and concentration [33]. Additionally, the porous structure of these materials provides ion migration channels, known as capillary pores. In porous media, moisture moves upward through capillary forces, transporting dissolved salts to the evaporation surface where they accumulate [34,35].

Agrawal V et al. [36] studied the phenomenon of alkali efflorescence in red mud ceramics, where solid-state reactions form Na_2SO_4 between BaSO_4 , $\text{Na}_2\text{Fe}_2\text{Ti}_6\text{O}_{16}$, and NaAlSiO_4 above 1000 °C. The addition of KOH to the mixture reduces Na_2SO_4 generation by reacting with red mud and BaSO_4 to form stable phases of $\text{K}_3\text{NaS}_2\text{O}_8$ and KAlSiO_4 , thereby mitigating efflorescence. Zou S et al. [37] investigated the effects of steam curing on high-strength slag-based alkali-activated materials. They found that, after 24 h of steam curing, the compressive strength of the alkali-activated materials significantly improved, efflorescence was markedly reduced, and steam curing proved to be an economical, practical, and effective method. Zhang et al. [38] summarized efflorescence prevention measures for permeable bricks: using low-alkali cement or incorporating pozzolanic materials (e.g., silica fume) to immobilize free Ca^{2+} and reduce alkali content; refining pore structures to inhibit salt migration; and applying silicone-based materials to lower surface water absorption via hydrophobic coatings, though durability concerns require attention.

During the fabrication of KSCs, surface efflorescence occasionally occurs under specific environmental conditions, significantly hindering its engineering applications. To address this challenge, a systematic investigation into the causes of efflorescence and preventive strategies during production is imperative for advancing the practical implementation of this material. This study employed a multi-method analytical framework—including X-ray diffraction (XRD), scanning electron microscope (SEM), element analysis (EA), and thermogravimetric-mass spectrometry (TG-MS)—to conduct targeted experiments, evaluating efflorescence susceptibility of ceramsites sintered at 1150 °C, identifying critical environmental triggers for efflorescence during storage, and elucidating the influence of key sintering parameters on efflorescence development. Through this integrated approach, we aim to unravel the fundamental mechanisms of efflorescence in KSCs and establish optimized process control protocols.

2. Materials and Methods

2.1. Preparation of Raw Materials

The raw materials used in this experiment were sourced from Botai Environmental Protection Technology Co. Ltd. in Tangshan, China. The chemical composition and mineral phases of the raw materials were analyzed at room temperature (25 °C) using X-ray fluorescence (XRF, Rigaku ZSX Primus, Tokyo, Japan) and X-ray diffraction (XRD, Rigaku SmartLab 9 kW, Tokyo, Japan).

2.2. Preparation of Basic Experimental Samples

The raw materials were dried and then a ball mill was used to finely grind the mixed raw materials to a powder state. Next, the kiln slag, fly ash, and clay were accurately mixed in a ratio of 60:35:5 by mass. The homogenized mixture was pulverized using a ball mill

(DH488-2Z, Beijing, China) and sieved through a 200-mesh screen. The resulting powder was then processed through an extrusion pelletizer (SKJ-320, Jinan, Shandong, China) to form green KSCs pellets with diameters of 10–15 mm and moisture content of 11–13%. These pellets were subsequently dried at 105 °C for 2 h.

The extrusion pelletization mechanism comprises four sequential stages: feeding, extrusion, profiling, and cutting. First, the ball-milled raw material was loaded into the hopper, where spiral blades conveyed it toward the extruder. Next, the extruder compacted and pressurized the material through the rotation of a screw. Subsequently, the material was forced through a die orifice to form continuous strands of the desired shape. Finally, a cutting device segmented the extruded strands into ceramsites pellets with lengths of 10–15 mm.

The dried green KSCs were sintered in a gradient crystallization furnace (GR1300/13, Lilienthal, Berlin, Germany) under controlled thermal conditions. The sintering protocol involved heating at a rate of 300 °C/h to target temperatures (1090 °C, 1110 °C, 1130 °C, 1150 °C, 1170 °C, and 1190 °C), followed by a 15 min holding time at each target temperature. After sintering, the samples were furnace-cooled to room temperature. Water absorption rate measurements were subsequently conducted on the cooled KSCs samples.

The dried green KSCs were loaded into a small-scale sintering kiln (50 kg capacity) and sintered with a heating rate of 10 °C/min. Upon reaching the target sintering temperature of 1150 °C, the samples were held for 15 min, followed by furnace cooling to room temperature. The sintered KSCs samples were then subjected to XRD and carbon–sulfur analysis.

2.3. Efflorescence Test Protocol

To simulate efflorescence under accelerated humid conditions, half of the KSCs samples were partially immersed in water for 72 h to observe surface alterations. Subsequently, the samples underwent forced-air drying under a ventilation fan. Post-drying visual inspections were conducted to detect efflorescence. The efflorescent deposits (white crystalline substances) on the ceramsites surface were meticulously collected for chemical composition analysis and mineral phase identification via XRD.

2.4. Introduction to Small-Scale Verification Experiment

The experiment was carried out in a small-scale sintering kiln system at Botai Environmental Protection Technology Co. Ltd. Tangshan, China. The sintering furnace system is shown in Figure 1, which mainly consists of three parts: sintering furnace, dust removal device, and desulfurization device. The dried green KSCs were placed in a beaker inside the sintering furnace B. The detailed structure of the sintering furnace is shown Figure 1, where 50 kg of KSCs was placed in the beaker inside the sintering furnace, with a beaker height of 300 mm. The bottom was pre-laid with a base material, namely sintered KSCs, to avoid overheating of the perforated grate at the bottom. The upper part of the sintering furnace was a natural gas combustion chamber A, where natural gas entered the combustion chamber for combustion, forming a gas of the set temperature. The gas passed through KSCs in the beaker and was discharged from the bottom of the sintering furnace. It then passed through the dust removal device C and was drawn by an induced draft fan before entering the desulfurization device G for desulfurization and subsequent emission. The concentration of SO₂ and O₂ in the flue gas was measured in the pipeline after the fan outlet and before the flue gas treatment (at point L in Figure 1).

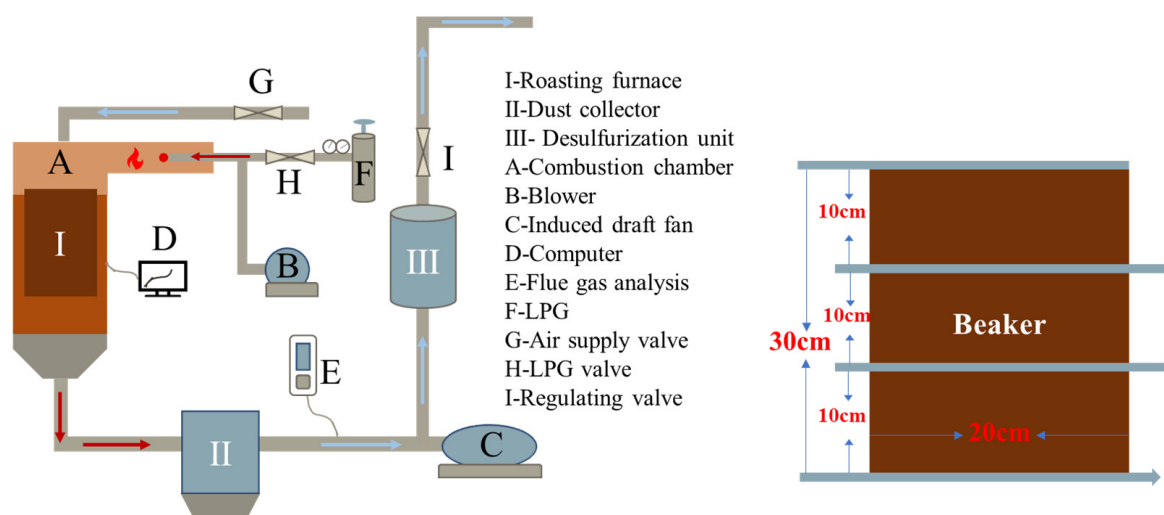


Figure 1. Small-scale KSCs sintering equipment and detailed diagram of a roasting furnace.

2.5. Characterization Methods

The thermal behavior and gas emissions of KSCs during the sintering process were analyzed using thermogravimetric–mass spectrometry (TG-MS, Netzsch QMS4range03, Selb, Germany). The thermal analysis was conducted under stable airflow conditions, with a linear heating rate of 10 °C/min. The measurements were performed within a temperature from room temperature (25 °C) to 1000 °C.

A carbon and sulfur analyzer (LECO, CS844, St. Joseph, MI, USA) was used to determine the change in carbon and sulfur content in KSCs at different temperatures. X-ray diffraction analysis (XRD, Rigaku Smartlab 9kw, Tokyo, Japan) was conducted to observe the phase transition of KSCs before and after sintering. The XRD test mode was continuous scanning with a step length of 0.02°, Cu target, scanning rate of 10 (°)/min and 2θ range of 10°~90°. Field emission scanning electron microscopy (FESEM, Zeiss GeminiSEM 300, Oberkochen, Germany) was utilized to analyze the microstructure. The thermodynamic data associated with the reaction equation were calculated using the thermodynamic analysis software Outokumpu HSC Chemistry 6.0: $\Delta_r G_m^\theta$ (298.15 K), $\Delta_r H_m^\theta$ (298.15 K), and $\Delta_r S_m^\theta$ (298.15 K).

3. Results

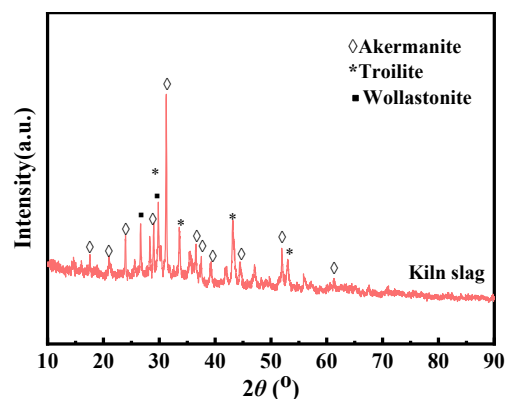
3.1. Composition and Properties of KSCs

The chemical compositions of raw materials and green KSCs are shown in Table 1, and the XRD pattern of kiln slag is shown in Figure 2. The kiln slag contained as high as 22.11% calcium oxide and 22.05% iron oxide, making it a type of high-calcium and high-iron smelting slag. The fly ash and clay contained relatively high proportions of silicon dioxide and aluminum oxide. Both the kiln slag and clay had significant loss on ignition at 6.67% and 17.41%, respectively. The kiln slag had a sulfur content of 7.34%, which is shown in Figure 2 to be mainly present in pyrite (FeS). The sulfur contents in the fly ash and clay were both less than 0.5%, indicating that the sulfur content in the kiln slag mainly came from FeS in the kiln slag.

Table 1. Chemical composition of raw materials and green KSCs (wt%).

Raw Material Composition	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	ZnO	MgO	Na ₂ O	TiO ₂	Cl	LOI
Kiln slag	20.97	22.11	10.30	22.05	7.34	2.28	3.22	1.04	0.85	0.52	6.67
Fly ash	48.8	2.73	41.1	3.37	0.48	0.05	0.36	0.18	1.54	0.11	1.28
Clay	50.11	3.62	14.74	4.54	0.10	0.01	2.60	3.81	0.66	0.08	17.41
Green KSCs	32.16	14.40	21.30	14.63	4.57	1.38	2.18	0.87	1.08	0.35	5.32

LOI: loss on ignition.

**Figure 2.** XRD patterns of kiln slag.

The KSCs in the small-scale furnace exhibited distinct black and brown coloration, as shown in Figure 3. Black KSCs predominantly formed in the central zone of the furnace. The XRD profile is shown in Figure 4; analysis revealed dominant mineral phases in KSCs: anorthite, mullite, and hematite (Fe₂O₃). Notably, pyrite (FeS) underwent complete conversion to anhydrite (CaSO₄). During the sintering process, the state of sulfur could be divided into two stages: low-temperature FeS combustion and sulfation and high-temperature CaSO₄ decomposition. The diffraction peak of the FeS phase (33.6°) gradually decreased as the temperature rose and disappeared. The diffraction peak of the Fe₂O₃ phase (33.166°) began to appear and gradually increased with temperature. It was speculated that FeS reacted with oxygen to produce Fe₂O₃ through oxidative combustion. A new diffraction peak of CaSO₄ (anhydrite) appeared at 25.442°, and its intensity gradually increased with temperature, reaching its peak within the temperature region of 800–1000 °C. The high-temperature calcium sulfate decomposition stage occurred between 1000 and 1150 °C.

**Figure 3.** Picture of sintered KSCs at 1150 °C.

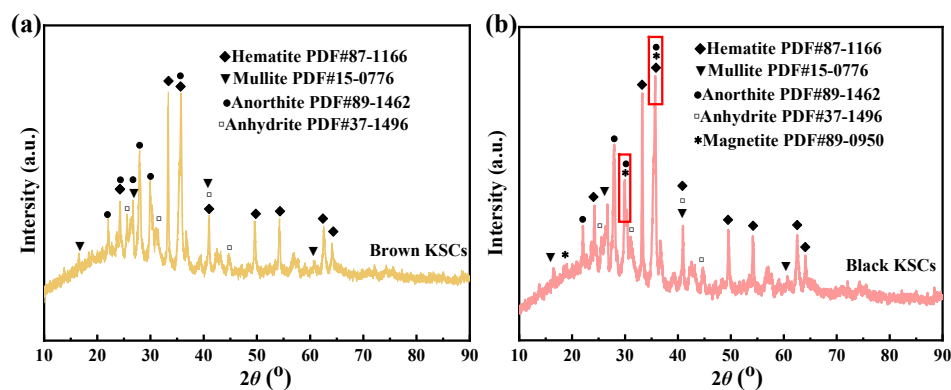


Figure 4. XRD patterns of KSCs at 1150 °C: (a) brown KSCs; (b) black KSCs.

Black ceramsites uniquely contained magnetite (Fe_3O_4), indicating localized reducing conditions during sintering. This color differentiation arises from temperature and atmospheric gradients within the kiln. The central zone exhibited higher temperatures than peripheral regions, resulting in elevated sintering intensity for centrally located ceramsites. In the sintering process, the oxidation atmosphere of the furnace center area was lower than the edge area because the air permeability was lower than that of the edge area.

The carbon–sulfur analysis results of KSCs, as presented in Table 2, revealed that both carbon and sulfur contents in brown KSCs were significantly lower than those in black KSCs. During the sintering process of KSCs, the carbon and sulfur in the brown KSCs reacted more fully and became gases released into the air. In the sintering process of black KSCs, due to the central region, there was insufficient oxygen in the reaction process, and C had not been fully burned to form CO_2 gas.

Table 2. The carbon–sulfur analysis results of KSCs (wt%).

KSCs	Carbon Content	Sulfur Content
Brown KSCs	0.1	1.0
Black KSCs	1.4	2.0

Figure 5 displayed the internal microstructure of KSCs at 1150 °C under an optical microscope. Brown KSCs exhibited a dense matrix with minimal observable pores. Black KSCs demonstrated a compact overall structure containing irregularly dispersed pores ranging from several to tens of micrometers in size. Water absorption rates were measured using a ceramic-specific absorption tester (DT, Vicometer WKT-300C, Taizhou, China). After the instrument detection, the water absorption rate of black KSCs was 8.5%, and the water absorption rate of brown KSCs was 6.7%.

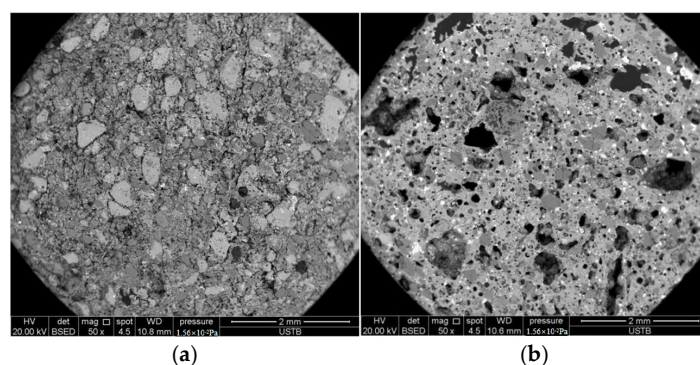


Figure 5. Micrograph of the inside of KSCs: (a) brown KSCs; (b) black KSCs.

3.2. Thermal Process Analysis of KSCs

Figure 6 illustrates KSCs samples after a 72 h efflorescence test. White crystalline deposits uniformly developed on all surfaces, with significantly higher accumulation observed on black KSCs compared to brown counterparts. The picture of the collected efflorescent salts is shown in Figure 7. The XRF results shown in Table 3 showed up to 60.07% sulfur oxide and 21.99% calcium oxide in the white crystal; the XRD patterns in Figure 8 showed that the dominant crystalline phase of the white crystal was water-containing calcium sulfate.

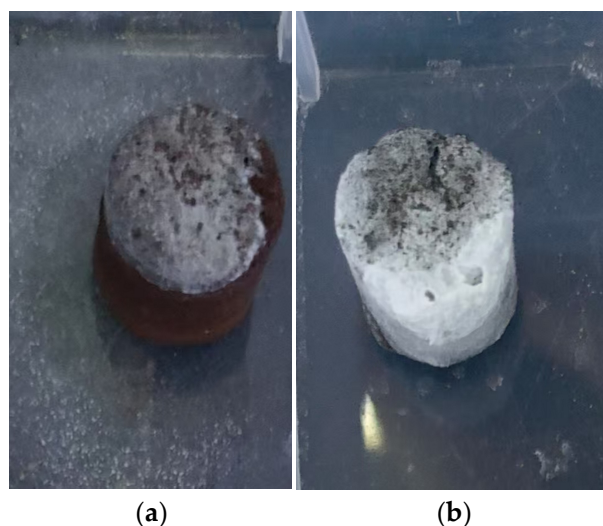


Figure 6. Images of efflorescence on brown and black KSCs: (a) brown KSCs; (b) black KSCs.



Figure 7. Surface white crystalline deposits from efflorescence on KSCs.

Table 3. Chemical composition of white crystalline deposits from efflorescence on KSCs (wt%).

Material Composition	SO ₃	CaO	K ₂ O	Cl	MgO	ZnO	SiO ₂	Al ₂ O ₃	MnO	Fe ₂ O ₃	Total
white crystalline	60.07	21.99	7.45	4.96	2.14	1.32	0.62	0.58	0.47	0.21	99.81

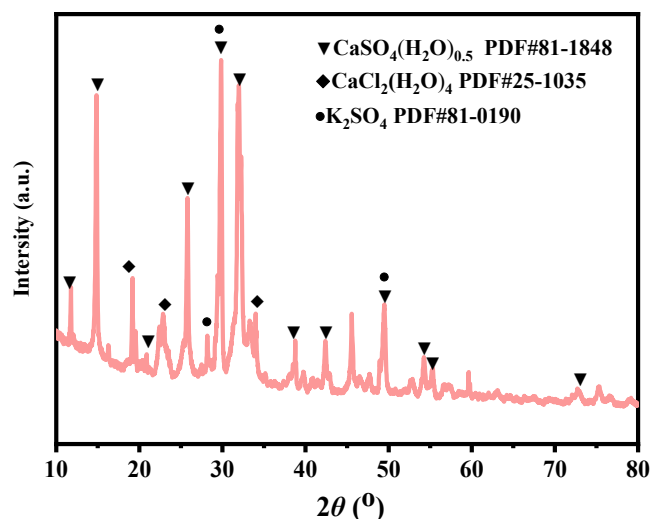


Figure 8. XRD patterns of main surface white crystalline deposits from efflorescence on KSCs.

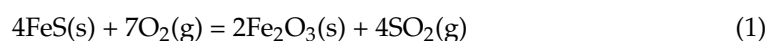
4. Discussion

4.1. Analysis of Conditions for Efflorescent Mineral Formation in KSCs

The occurrence of efflorescence in KSCs required both sufficient and necessary conditions; sufficient condition had the presence of soluble salts, while necessary conditions had the existence of migration channels for dissolution. The formation of soluble salts was attributed to the conversion of iron sulfide in the kiln slag into FeS during the sintering process. Calcium in the ceramsites did not combine with silicates but instead reacts with FeS to form CaSO₄. Therefore, during the sintering of KSCs, it was necessary to reduce the FeS content. Additionally, since the migration channels in KSCs accelerate the dissolution of salts, the sintering process should enhance densification and reduce the water absorption rate of KSCs.

XRD analysis results indicated distinct CaSO₄ diffraction peaks in KSCs, confirming the material basis for efflorescence. Higher sulfur content correlated with increased formation of soluble sulfates during sintering, thereby elevating post-service efflorescence risks. During sintering, sulfur reacted with calcium and potassium in raw materials to generate soluble sulfates (e.g., CaSO₄). To reduce sulfate content, process optimization must prioritize sulfur volatilization as gaseous SO₂ through controlled oxidation. This requires identifying the critical sintering temperature at which sulfur oxidizes to SO₂ and extending the duration at this temperature, while simultaneously determining the temperature range where sulfur tends to form sulfates and minimizing the processing time within that range.

The TG-DTG-MS analysis spectrum of KSCs is shown in the Figure 9, revealing the release patterns of volatile components in KSCs at various stages. Below 200 °C, the TG curve declined, with an endothermic peak observed at 140 °C. Figure 9b1 indicates that the mass loss during this stage corresponds to the volatilization of bound water in the sample. The fastest desulfurization phase occurred between 485 and 600 °C, where the MS curve demonstrated the release of SO₂ and CO₂ gases within the 450–600 °C temperature range. The oxidative combustion reaction of FeS occurring within the temperature region of 400–600 °C produced Fe₂O₃ and SO₂. Among them, iron oxide (primarily Fe₂O₃ and Fe₃O₄) was the main product of pyrite oxidation. Therefore, reaction Equations (1)–(3) were as follows:



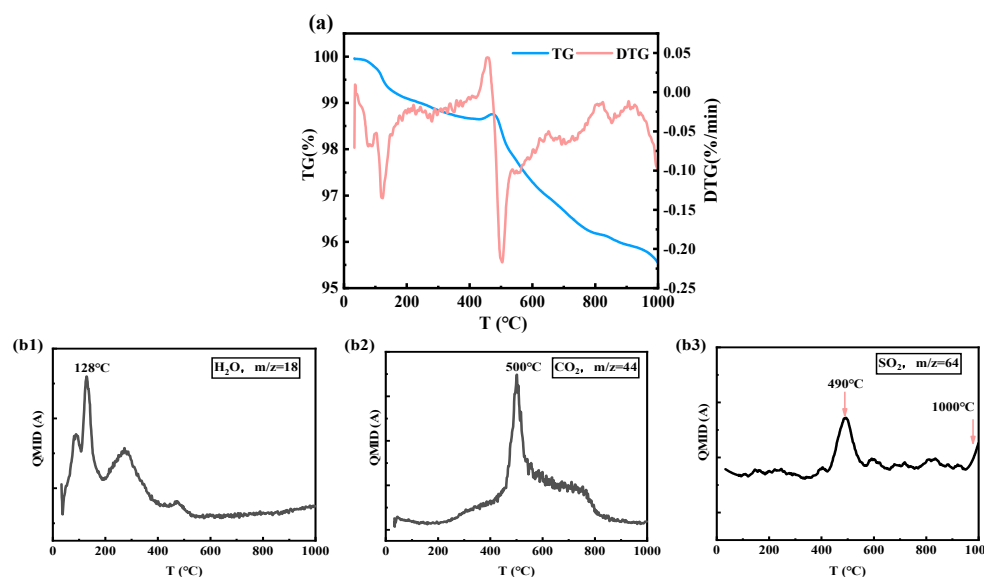
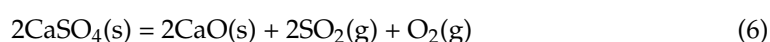


Figure 9. TG-DTG-MS curve of KSCs under air atmosphere: (a) TG-DTG curve of KSCs; (b1–b3) MS of volatile products in TG analysis.

At this point, KSCs entered a rapid oxidation-combustion stage, during which C was oxidized to CO_2 and FeS was oxidized to SO_2 . In the 600–800 °C range, the MS curve revealed that this stage was dominated by the oxidation of C to CO_2 . Beyond 800 °C, the oxidation of carbon was nearly complete. However, minimal sulfur oxidation was observed between 600 and 1000 °C. Based on the TG-DTG-DSC curves in Figure 9 and the XRD patterns in Figure 4, it can be observed that CaSO_4 was formed within the temperature region of 600–800 °C in KSCs. A second desulfurization phase emerged within 1000–1150 °C, as evidenced by the rising SO_2 gas released curve in the MS curve starting at 1000 °C. Therefore, reaction Equations (4)–(6) were as follows:



By combining Equations (2) and (4), we obtain the sulfation reaction as Equation (5). When CaO and FeS were present during the sulfation reaction in Equation (5), the main factors influencing it from a thermodynamic perspective were temperature and O_2 concentration. The Gibbs function for the forward reaction in Equation (7) of sulfation was:

$$\Delta G_{8,298}^\theta = 2\Delta G_{\text{Fe}_2\text{O}_3,298}^\theta + 4\Delta G_{\text{CaSO}_4,298}^\theta - 4\Delta G_{\text{CaO},298}^\theta - 9\Delta G_{\text{O}_2,298}^\theta - 4\Delta G_{\text{FeS},298}^\theta \quad (7)$$

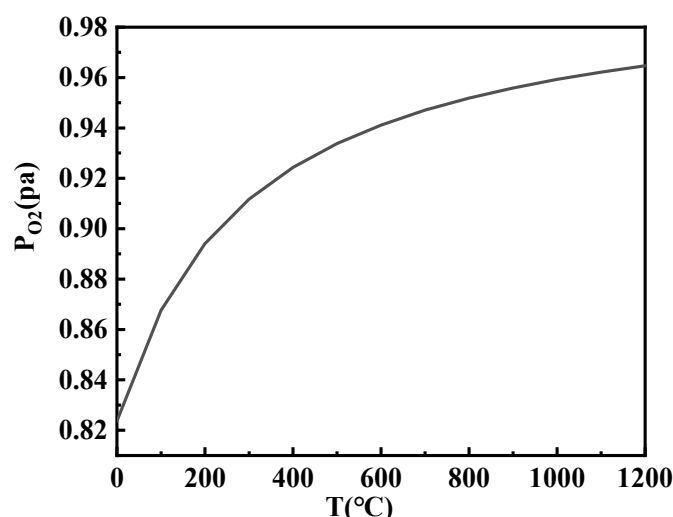
Gibbs free energy ΔG was defined as $\Delta G = \Delta H - T\Delta S$, and the thermodynamic data in Table 4 can derive the Gibbs function for the forward reaction as Equation (8) of sulfation Equation (5):

$$\Delta G_2 = \Delta G_{2,298}^\theta + RT \ln \frac{1}{P_{\text{O}_2}^9} = 39961.619 - 74.826T \ln P_{\text{O}_2} \quad (8)$$

Table 4. Thermodynamic data of reactants.

	ΔH_{0298}	ΔS_{0298}	ΔG_{0298}
	KJ·mol ^{−1}	KJ·mol ^{−1} ·K ^{−1}	KJ·mol ^{−1}
CaSO ₄ (s)	−1437.62	106.692	−1469.43
FeS(s)	−101.671	60.321	−119.656
Fe ₂ O ₃ (s)	−823	87.4	−849.058
CaO(s)	−634.92	38.1	−646.28
O ₂ (g)	0	205.149	−61.165
SO ₂ (g)	−296.813	248.22	−370.82

As can be seen from Figure 10, as the temperature increased, the P_{O_2} rapidly increased when ΔG_3 was zero. This could also be understood as the easier decomposition of calcium sulfate at higher temperatures, necessitating a higher concentration of oxygen to maintain the forward reaction. This further demonstrated that the primary reason for the occurrence of sulfation reactions was the presence of high CaO content in the KSCs, followed by the completion of carbon oxidation to carbon dioxide during the sintering process at 600–800 °C, which enhanced the oxidizing atmosphere.

**Figure 10.** P_{O_2} and temperature when ΔG_3 was zero.

The results indicated that SO₂ was released within two temperature ranges: 450–600 °C and 1000–1150 °C. Between these temperature ranges, a sulfur fixation reaction occurred, where CaO in KSCs reacted with the released SO₂ to form CaSO₄, leading to the formation of new sulfur-containing compounds (e.g., sulfates) within KSCs. To reduce the internal sulfur content of KSCs, the sintering process should prolong the duration within these two desulfurization temperature ranges to ensure thorough release of SO₂, thereby minimizing sulfur retention in the final product.

4.2. Effect of Sintering Process on the Efflorescence of KSCs

The occurrence of efflorescence in KSCs required the presence of leaching channels within the ceramsites structure. To mitigate this, it was critical to identify the densification temperature of KSCs, enhance its degree of densification, and reduce its water absorption rate. Uneven temperature and atmosphere distribution within the sintering furnace arose due to the exothermic oxidation of FeS during the sintering process. This reaction caused a rapid temperature spike in the central zone of the furnace, accompanied by a sharp decline in oxidative conditions.

According to carbon and sulfur testing results, the black KSCs exhibited higher carbon and sulfur content compared to the brown samples. Experimental results revealed that the black KSCs displayed more severe efflorescence than the brown KSCs. SEM observations indicated that the brown KSCs had a dense internal structure with no significant voids, whereas the black high-sulfur KSCs exhibited a porous structure. This was attributed to the reaction of FeS forming Fe_3O_4 during the densification of the black KSCs. The internally generated SO_2 was not fully released, causing carbon and sulfur to become trapped in the liquid phase. These elements subsequently formed sulfates within the ceramsites, leading to the development of numerous internal pores.

For the brown KSCs, although it was located near the furnace wall and experienced slower heating rates, CaSO_4 did not reach its decomposition temperature during the final sintering stage. As a result, sulfur was not sufficiently released and remained trapped within the material.

Wang et al. [6] demonstrated in their analysis of ceramsites production using zinc-extraction kiln slag that 1050–1180 °C was the critical temperature range for ceramsites densification. As shown in Figure 11, the water absorption of KSCs sintered at 1090–1190 °C rapidly decreased within the 1130–1150 °C interval, indicating active densification. Therefore, during the ceramsites sintering process, precise temperature control was critical. The oxidation of FeS within the ceramsites must be fully completed before raising the temperature to the 1130–1150 °C range.

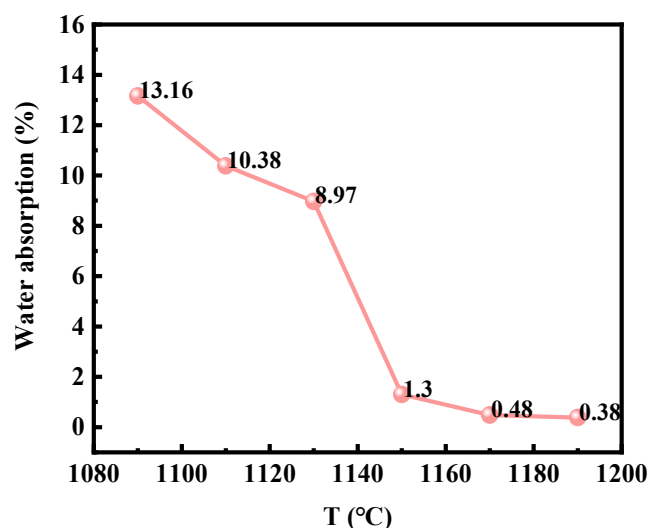


Figure 11. Water absorption rate of KSCs at different temperatures.

During sintering, it was essential to avoid rapid heating rates that could trap SO_2 —released from CaSO_4 decomposition—inside the ceramsites due to premature densification, ensuring the final sintering temperature was reached to prevent residual sulfur (S) retention caused by insufficient decomposition of CaSO_4 .

To optimize the sintering parameters for KSCs, the following adjustments were critical. The desulfurization duration in the low-temperature stage (e.g., 450–600 °C) was prolonged and the oxidative atmosphere enhanced during this phase to ensure complete oxidation and decomposition of FeS in KSCs, thereby fully releasing SO_2 . The high-temperature sintering time (e.g., 1000–1150 °C) was extended while reducing the oxidative atmosphere in this stage to accelerate the decomposition of CaSO_4 , facilitating the release of additional SO_2 . This dual strategy reduced the soluble salt content (e.g., CaSO_4) within the ceramsites, effectively suppressing efflorescence by minimizing residual sulfates.

Based on the above analysis, the sintering parameters for KSCs were optimized as follows. Low-temperature stage (400–600 °C): a 15 min holding time with enhanced oxidative atmosphere to ensure complete oxidation of FeS and SO₂ release. High-temperature stage (1000–1100 °C): a 15 min holding time with reduced oxidative atmosphere to promote CaSO₄ decomposition and minimize sulfate retention. After re-sintering 50 kg of KSCs under these conditions, post-test results showed a water absorption rate of 1.2% and a sulfur content of 0.72%, indicating a significant reduction in sulfur retention compared to previous batches.

5. Conclusions

This study investigated the inhibition mechanism of efflorescence in high-sulfur KSCs. Through 50 kg scale sintering experiments, a novel process strategy for efflorescence control was developed. Conclusions were as follows:

1. The mechanism of efflorescence in KSCs required both sufficient and necessary conditions; sufficient conditions had the presence of soluble salts CaSO₄, while necessary conditions had the existence of migration channels for dissolution. High-sulfur kiln slag inherently contained elevated sulfur content (4.53%) and alkaline substances such as CaSO₄. The porous structure of ceramsites (ceramsites exhibiting a water absorption rate of 8.5%) exacerbated the efflorescence phenomenon.

2. The formation of soluble CaSO₄ in KSCs was revealed and a novel sintering process to reduce sulfur was proposed. During the sintering process, the desulfurization duration was extended and meantime the oxidative atmosphere at the low-temperature period was enhanced, ensuring enough oxidation of FeS to release more SO₂ in ceramsites. Simultaneously, the high-temperature sintering period was prolonged while reducing the oxidative atmosphere during this phase to accelerate the decomposition of CaSO₄ to release SO₂ gas. These strategies effectively reduced soluble calcium sulfate content in ceramsites, thus suppressing the efflorescence phenomenon.

3. Another effective method to enhance the sintered densification of ceramsites was to change the mineral phase. The Fe₃O₄ formed in KSCs lowered the densification temperature, causing SO₂ gas released from decomposed CaSO₄ to be trapped within the ceramsites due to premature densification before escaping into the atmosphere. This results in the formation of multiple internal voids. By maintaining the KSCs in an oxidizing atmosphere at 400–600 °C for 15 min followed by a reducing atmosphere at 1000–1100 °C for 15 min prior to its densification temperature, more Fe₂O₃ and less Fe₃O₄ formed in ceramics, resulting in an increasing sintering temperature, and sulfur inside the ceramsites was fully released. This process promoted uniform internal densification of the ceramsites, resulting in a reduction in its water absorption rate from 8.5% to 1.2%. Additionally, the efflorescence phenomenon of the ceramsites was significantly alleviated.

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Abbreviations

The following abbreviations are used in this manuscript:

KSCs	Kiln slag ceramsites
XRD	X-ray diffraction
TG-MS	thermogravimetric–mass spectrometry

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