

Article

Generation and Inhibition of SO₃ in Lead Smelting Flue Gas

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Abstract: The thermodynamic equilibrium of the gas-phase system in lead smelting flue gas was studied using FactSage 8.2 software, and the effects of temperature, the main components of the gas phase, and other factors on the SO₃ content in the equilibrated flue gas were investigated. In addition, experimental research was conducted on a solid-phase catalysis experimental platform to investigate the effect of lead smelting ash on SO₂ catalytic oxidation. The results show that temperature and initial O₂ content in flue gas have a significant impact on the equilibrium concentration of SO₃, while the initial SO₂ content in flue gas has a relatively small impact on the equilibrium concentration of SO₃; the fly ash from the lead smelting flue promotes the conversion of SO₂ to SO₃ in the flue gas. SO₃-suppression experiments show that PbS can adequately inhibit SO₃ formation in a simulated flue gas environment, and the content of SO₃ after adding PbS under different oxygen contents and SO₂ atmospheres does not exceed 0.6%. Through the method of thermodynamic simulation and experimental verification, this study reveals the catalytic oxidation mechanism of SO₂ in lead dust and proposes the use of PbS as an in situ SO₃ inhibitor.

Keywords: lead smelting; SO₃; flue gas; thermodynamics of SO₃ oxidation

1. Introduction

In China, the lead smelting industry mainly relies on the sintering-blast furnace process, followed by the closed-blast furnace smelting process. The smelting flue gas generated by these two processes contains a significant amount of sulfur oxides. In particular, the sintering-blast furnace process can produce approximately 0.5 t of SO₂ gas for every 1 t of crude lead produced [1]. The specific flue gas composition of some process furnace types is shown in Table 1 [2]. In addition to the high emissions of sulfur oxides, lead smelting smoke exhibits a high dust concentration. The main components of lead smelting smoke are lead, elemental zinc and zinc compounds, and small amounts of Cd, Se, Te, Tl, Sb, Sn, In, Al, and other elements and compounds [3,4].

Table 1. Smoke composition of different furnace types in lead smelting.

Process	Num	Smoke Components, %				
		SO ₂	O ₂	CO ₂	CO	H ₂ O
Direct lead smelting method	1#	10	5	20		33
	2#	7.5	8.4	8.4		27.4
Sinter	3#	4.10	10.38	2.0		14.51
Blast furnace	4#	0.68	2.36	16.55	6.62	3.55
	5#	<1	7.81	13.56	4.56	



Received: 7 March 2025

Revised: 9 April 2025

Accepted: 14 April 2025

Published: 17 April 2025

Citation: Liu, H.; Zhang, Q.; Gao, H.; Yang, H. Generation and Inhibition of SO₃ in Lead Smelting Flue Gas. *Appl. Sci.* **2025**, *15*, 4449. <https://doi.org/10.3390/app15084449>

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The pyrometallurgical processing of lead sulfide ores generates significant sulfur oxide emissions (SO_x), predominantly sulfur dioxide (SO_2) with minor quantities of sulfur trioxide (SO_3) [5–7]. These byproducts pose substantial operational and environmental challenges. Below the acid dew point temperature, SO_3 reacts with moisture to form corrosive acid mists and micro-droplets that degrade metal surfaces through low-temperature corrosion. Mitigation strategies include maintaining cold-end temperatures above the dew point or employing acid-resistant construction materials [8,9]. A secondary corrosion mechanism involves SO_3 reacting with alkali metals and iron to form aggressive compounds such as alkali metal iron trisulfate, which contributes to furnace wall degradation [10,11]. In the environment, unreacted SO_3 escapes as blue plume emissions through flue stacks, primarily through the formation of sulfuric acid (H_2SO_4) aerosols.

The flue gas cooling profile (1100 °C to 300 °C) introduces complex technical constraints for SO_3 mitigation. Effective solutions must achieve three objectives: (1) substantial SO_3 reduction without disrupting smelting operations, (2) compatibility with existing gas treatment infrastructure, and (3) economic viability in construction and operation. Chemical inhibitors present a potential solution but require careful evaluation; they must demonstrate minimal process interference while enabling the recovery of valuable components from heterogeneous flue streams containing gas-phase species, particulate matter, and complex decomposition/oxidation products [12,13]. Process simplicity and cost-effectiveness remain critical implementation criteria.

Fundamentally, SO_3 generation in lead smelting originates from high-temperature oxidation reactions during sulfide ore processing [14,15]. While SO_2 constitutes the primary sulfur oxide, catalytic conversion mechanisms (particularly in the presence of metal oxides and oxygen) enable partial SO_2 oxidation to SO_3 . This conversion intensifies corrosion risks through two pathways: acid condensation below dew points (in the 250–150 °C range) and high-temperature sulfate salt formation. The resulting corrosion products—whether liquid acid films or solid alkali sulfates—progressively degrade refractory linings and metallic components [16,17].

The current mitigation approaches present technical tradeoffs. SO_3 -specific removal systems could theoretically protect downstream acid plants relying on SO_2 feedstock, but they need to address secondary pollution risks and byproduct management challenges. Process modifications that suppress SO_3 formation at the source (e.g., oxygen control, catalytic inhibitors, etc.) show promise but demand the thorough understanding of reaction mechanisms across the thermal gradient [18–20]. Material solutions using advanced ceramics or alloy liners offer localized protection but increase capital costs. This analysis underscores the need for holistic strategies combining the following:

- Process optimization to minimize SO_3 generation;
- Targeted removal technologies preserving SO_2 for acid production;
- Selection of corrosion-resistant materials;
- Continuous monitoring of flue gas composition and thermal profiles.

Further research should quantify SO_3 formation kinetics under operational conditions and evaluate inhibitor performance in complex, particulate-laden gas streams. This fundamental understanding will inform the development of cost-effective, integrated solutions for sulfur oxide management in lead pyrometallurgy.

Through the method of thermodynamic simulation and experimental verification, this study reveals the catalytic oxidation mechanism of SO_2 in lead dust and proposes the use of PbS as an in situ SO_3 inhibitor. This discovery not only provides a theoretical breakthrough for understanding the kinetics of metallurgical multiphase reactions but also can guide smelters to achieve a reduction in SO_3 generation by more than 60% (the target value is <0.6%) through the synergy of process parameter optimization and material

modification, while avoiding the side effects of traditional technologies. This achievement has direct engineering significance for promoting the transformation of the lead industry towards the direction of low emissions and high energy.

2. Experimental

2.1. Experimental Setup

FactSage 8.0 software was used to simulate the SO_2/SO_3 thermodynamic equilibrium.

Elemental composition analysis was conducted using X-ray fluorescence spectroscopy [21,22].

A dedicated catalytic platform was developed, comprising the following:

A gas distribution system with precision mass flow controllers for gas blending;

A reaction system with a high-temperature tube furnace ($\pm 1^\circ\text{C}$ accuracy) and a customizable quartz reactor (8–12 mm in diameter and 800–1000 mm in length);

An absorption system using isopropanol trapping for SO_3 quantification.

The platform supported both homogeneous experiments (with an empty reactor) and heterogeneous tests with lead smelting ash catalysts.

2.2. Experimental Materials

The main reagents used in this experiment were lead glance and isopropanol, which were purchased in high purity forms from China. Furthermore, high-pressure gases such as SO_2 , O_2 , and N_2 (99.9%) were also utilized in this experiment.

2.3. Experiment

The Equilib module of FactSage 8.0 was used to simulate the SO_2/SO_3 thermodynamic equilibrium. Using FactSage, multiple multiphase equilibrium conditions can be calculated under multiple constraints, and the results can be output in the form of graphs or tables. This is based on the principle of Gibbs free energy minimization.

With the actual production data from a local lead smelter as a reference, the changes in the remaining components when a group changed in the equilibrium were calculated.

Experimental studies under homogeneous (gas-phase) and heterogeneous (catalytic) conditions were conducted to analyze SO_2/SO_3 conversion mechanisms. These investigations, combined with catalytic SO_3 generation patterns and inhibitor-based suppression strategies, provide actionable insights for SO_3 control in non-ferrous smelting operations.

The SO_3 measurement method used was as follows: collect the absorption liquid in the absorption bottle of the porous glass plate and the connecting tube between the absorption bottles, and record the volume of the solution in mL. Take 20 mL of the collected absorption solution, put it in a conical flask, and dilute it by adding 40 mL of 80% isopropanol solution. Titrate with a 0.025 mol/L strontium perchlorate titration solution. If the titration is finished, it will not change color, or if the color change effect is not obvious, the titration solution concentration is halved and the above operation is repeated. Take three titrations and take the average and record the volume of the titrant consumed as b mL $n_{\text{SO}_3} = c \times b \times \frac{a}{20}$, where n_{SO_3} is the number of moles of SO_3 produced during the experiment, and c is the concentration of the titrant used.

In this experiment, the effects of varying initial O_2 and SO_2 contents on PbS decomposition/oxidation behavior and SO_3 generation were studied.

3. Results and Discussion

3.1. Generation of SO_3 in Simulated Lead Smelting Flue Gas

The Equilib module in FactSage 8.2 was employed to investigate the equilibrium concentration and conversion rate of SO_3 in the gas phase under varying temperatures

(300–1300 °C). The simulated flue gas composition comprised the following molar fractions: 1% CO, 5% CO₂, 15% SO₂, 0.5% SO₃, 8% O₂, 8% H₂O, and 62.5% N₂.

3.1.1. The Effect of Equilibrium Temperature on SO₃ Generation

As illustrated in Figure 1, temperature exerts a significant thermodynamic influence on both the equilibrium SO₃ concentration and its conversion rate. A strong inverse correlation was observed: lower temperatures correspond to higher equilibrium SO₃ concentrations. At 400 °C, the equilibrium SO₃ concentration reached 15.83%, whereas it plummeted to 0.14% at 1300 °C. Notably, an inflection point in SO₃ concentration occurs at 400 °C, attributed to partial SO₃ consumption through sulfuric acid (H₂SO₄) formation within the 300–400 °C range.

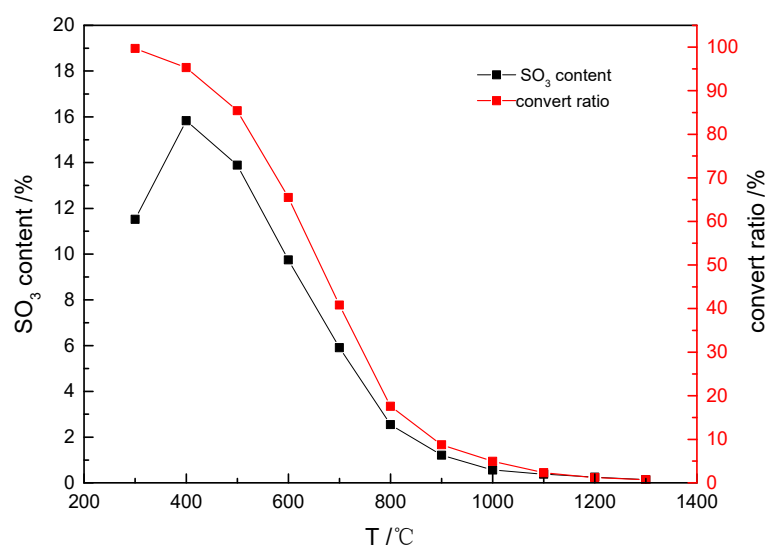
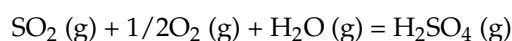
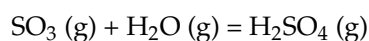


Figure 1. Effect of equilibrium temperature on final-gas-phase sulfur trioxide.

The SO₃ conversion rate followed a trend similar to that of its concentration profile, with the maximum conversion (99.70%) achieved at 300 °C, indicating the near-complete oxidation of sulfur species to SO₃. Conversely, the conversion rate declined sharply to 0.74% at 1300 °C, reflecting the thermodynamic instability of SO₃ at elevated temperatures. These results demonstrate that low-temperature regimes (<500 °C) strongly favor SO₃ formation and retention in the gas phase, while high-temperature conditions promote SO₃ decomposition.

This analysis highlights the critical role of thermal management in controlling SO₃ levels during pyrometallurgical processes, with implications for corrosion mitigation and emission control strategies.

An increase in the SO₃ concentration in a flue gas system proportionally increases the ADP, thereby exacerbating the corrosion risk of downstream equipment. SO₃ levels should be kept below 1 vol% through engineered suppression strategies to mitigate the degradation of waste heat boilers and particulate control systems. The complexity of SO₃ formation in lead smelting flue gases stems from its diffuse generation pathways, heterogeneous catalytic oxidation, homogeneous gas-phase reactions, and sulfate decomposition mechanisms. The dominant formation route is as follows:



3.1.2. The Effect of Initial SO₂ Content on SO₃ Generation

Assuming the fixed temperatures of 200 °C, 400 °C, 900 °C, and 1300 °C, the effects of the initial SO₂ content (0–20% range) on the content of various substances during the final equilibrium of the reaction were studied, as shown in Figure 2.

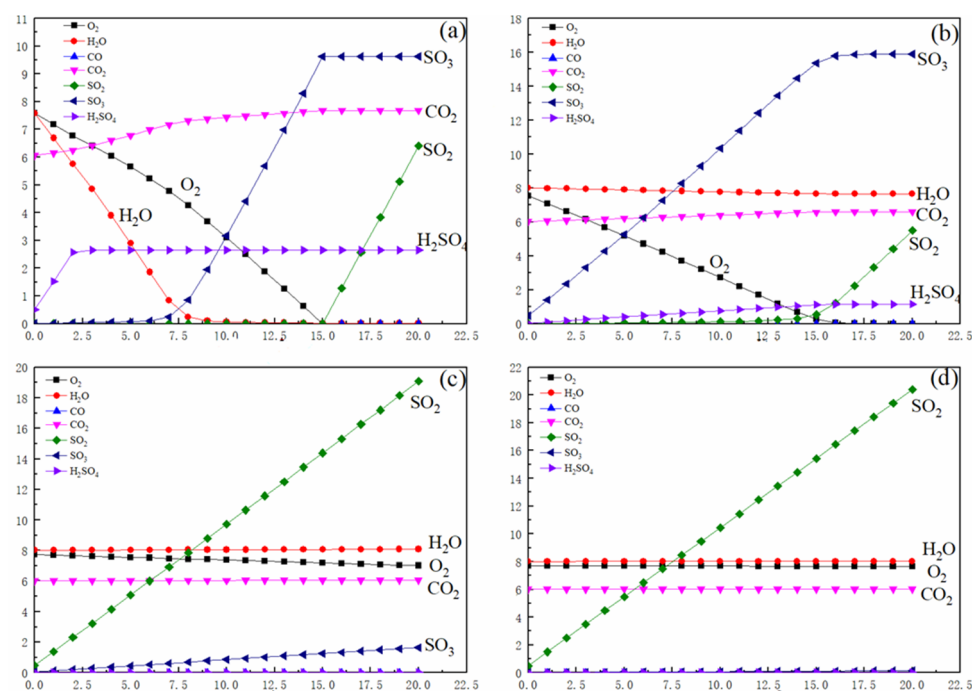


Figure 2. Effect of initial SO₂ on content of final-gas-phase components, X: SO₂ content, mol%; Y: content of component at equilibrium: (a) 200 °C; (b) 400 °C; (c) 900 °C; (d) 1300 °C.

As depicted in Figure 2a, the equilibrium SO₃ concentration exhibits a three-stage response to increasing initial SO₂ levels: initial stability, followed by a marked increase and eventual stabilization. When the SO₂ concentration exceeds 7%, SO₃ begins accumulating in the gas phase. This phenomenon arises because the limited moisture content at low temperatures becomes insufficient to sustain sulfuric acid (H₂SO₄) formation via SO₃ hydration. At SO₂ concentrations of >15%, SO₃ plateaus at 9.62% due to oxygen depletion, i.e., insufficient O₂ availability, preventing further SO₂-to-SO₃ oxidation and leading to additional inconsequential SO₂ increases.

Figure 2b reveals similar SO₃ trends under 400 °C conditions. Notably, thermodynamic calculations confirm the absence of liquid H₂SO₄ across all SO₂ concentrations, with sulfur species existing exclusively as gaseous SO₃, SO₂, and H₂SO₄ vapor. The initial linear SO₃ increase demonstrates near-complete SO₂ conversion efficiency (up to 15% SO₂), constrained ultimately by O₂ limitations. Figure 2c,d show analogous SO₃ trends at elevated temperatures. While 1300 °C conditions suppress SO₃ formation due to thermal instability, a weak positive correlation persists between SO₂ and SO₃ concentrations. This subdued response highlights temperature-dependent reaction kinetics overriding stoichiometric drivers.

Key conclusions from the analysis of Figure 2 are as follows: when the temperature is <500 °C, SO₂ enrichment promotes SO₃ generation until O₂ depletion imposes thermodynamic constraints; the maximum achievable SO₃ concentration is 9.62% (15% SO₂ threshold); and at a temperature >1200 °C, thermal decomposition dominates, minimizing SO₃ yields despite SO₂ availability, and residual SO₃ shows a weak dependence on initial SO₂ concentrations.

3.1.3. The Effect of Initial O₂ Content on SO₃ Generation

Assuming the fixed temperatures of 200 °C, 400 °C, 900 °C, and 1300 °C, the effects of initial O₂ content (0–10% range) on the content of various substances during the final equilibrium of the reaction were studied, as shown in Figure 3.

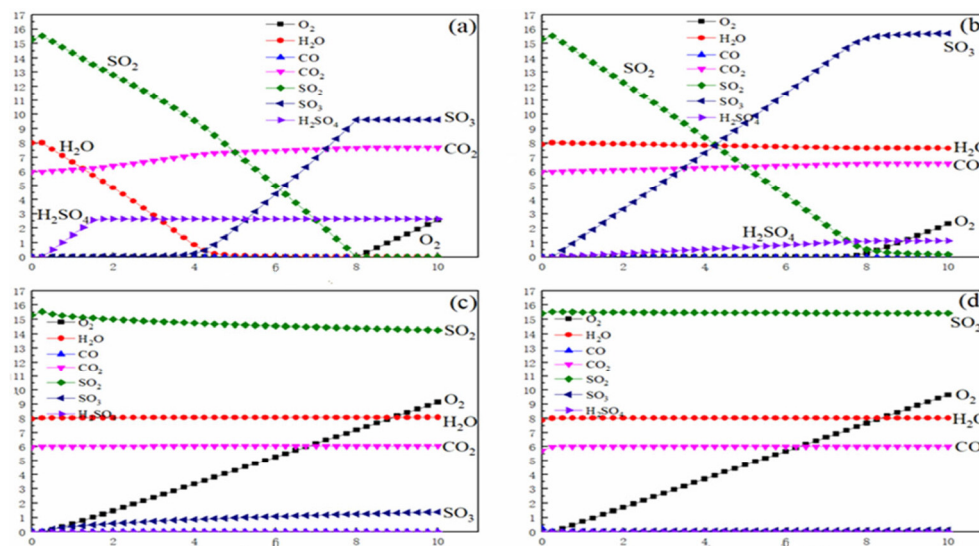


Figure 3. Effect of initial oxygen content on content of final-gas-phase components, X: O₂ content, mol%; Y: content of component at equilibrium: (a) 200 °C; (b) 400 °C; (c) 900 °C; (d) 1300 °C.

According to the thermodynamic analysis results of Figure 2a,b, in the low-temperature region below the thermodynamic decomposition temperature of SO₃ (at approximately 783 °C), reducing the oxygen concentration in the reaction atmosphere can significantly inhibit SO₃ formation. When the temperature is 400 °C, and as the volume fraction of O₂ decreases from 5% to 1%, the concentration of SO₃ in the system drops sharply from 8.5% to 1.0%. This phenomenon confirms the crucial regulatory role of oxygen concentration in the oxidation reaction of SO₂ → SO₃: this reaction is essentially an oxygen-dependent process, and the absence of O₂ in the system directly leads to the interruption of the formation pathway of SO₃. The thermodynamic calculation results indicate that, in the ultra-low oxygen range of 0–0.5%, sulfur-containing components mainly stably exist in the form of S₂(g), which essentially explains the complete inhibition of SO₂ formation at the molecular level.

By comparing and analyzing the data in the high-temperature region ($T > 783$ °C) of Figure 2c,d, it can be found that the influence of oxygen concentration regulation on SO₃ formation exhibits a significant temperature dependence. Above the thermodynamic decomposition temperature, even if the O₂ concentration is decreased from 5% to 1%, the SO₃ concentration decreases from 3.6% to 1.2%, which is mainly attributed to the enhanced effect of the spontaneous decomposition of SO₃ under high-temperature conditions. At this time, the sulfur components in the system mainly follow the dynamic equilibrium of $2\text{SO}_3 \leftrightarrow 2\text{SO}_2 + \text{O}_2$. Although the change in oxygen concentration can still affect the equilibrium shift according to Le Chatelier's principle, its regulatory efficiency is significantly weakened compared to that in the low-temperature region.

3.1.4. The Effect of Initial CO₂, CO, SO₃, and H₂O Contents on SO₃ Generation

Additional equilibrium simulations were conducted at fixed temperatures (200 °C, 400 °C, 900 °C, 1300 °C) to evaluate the effects of initial CO₂ (0–15%), CO (0–5%), SO₃ (0–5%), and H₂O (0–10%) concentrations on final equilibrium compositions. As these

parameters demonstrated a limited influence on SO₃ generation with minimal graphical variations, the key findings related to these parameters are summarized below:

CO₂ Influence: Variations in the initial CO₂ concentration showed a negligible impact (<0.5% deviation) on the equilibrium component distributions across all temperatures. The practical implications are that CO₂ injection primarily alters flue pressure and SO₃ partial pressure rather than chemical equilibria.

CO Effects: CO concentrations >2% significantly suppress SO₃ formation via O₂ depletion ($\Delta\text{SO}_3 \leq -34\%$ at 200 °C) when temperatures are <400 °C. Minimal SO₃ inhibition ($\Delta\text{SO}_3 < 3\%$) is observed due to thermal decomposition dominance at elevated temperatures (>900 °C).

H₂O Interactions: A high H₂O content (>6%) induces sulfuric acid condensation below 250 °C, exacerbating flue corrosion risks. Moisture control strategies should focus on maintaining a feedstock humidity of <5% and preventing ambient moisture ingress during processing.

SO₃ Feedstock Analysis: The initial SO₃ concentration is strongly correlated with the final equilibrium SO₃ concentration in low-temperature systems (200–400 °C). SO₃ decomposes into SO₂ and O₂ (up to 89% conversion) in high-temperature systems (>900 °C).

This systematic analysis quantifies secondary parameter influences, enabling optimized gas composition control in pyrometallurgical operations [23–25].

3.2. Generation of SO₃ in Experimentally Simulated Lead Smelting Flue Gas

Based on the simulated SO₃ generation data in lead smelting flue gas, the reaction temperature (200–1200 °C), O₂ content (3–15%), and SO₂ content (5–20%) were identified as dominant factors, with minimal influence from other flue gas components. Experimental studies under homogeneous (gas-phase) and heterogeneous (catalytic) conditions were conducted to analyze SO₂/SO₃ conversion mechanisms. These investigations, combined with catalytic SO₃ generation patterns and inhibitor-based suppression strategies, provide actionable insights for SO₃ control in non-ferrous smelting operations. The key findings revealed that catalytic conditions significantly enhance SO₃ yields compared to homogeneous reactions, particularly at mid-range temperatures (400–600 °C). These results underscore the importance of temperature management and catalytic material selection in SO₃-suppression strategies.

3.2.1. The Effect of Reaction Temperature on SO₃ Generation in Experimental Simulations

Assuming a reaction range of 400–1000 °C, a total gas flow rate of 200 mL/min was maintained, and the gas-phase composition was set as follows: an O₂ content of 8%, an O₂ content of 15%, and a N₂ content of 77%. The experimental results are shown in Figure 4.

Figure 4 demonstrates that gas-phase reactions alone yield minimal SO₃ conversion (<1%) across all temperatures. However, lead dust catalysis substantially enhances SO₃ generation, revealing catalytic activity in smelting particulates. Three thermal regimes govern SO₃ formation in lead smelting flue gas:

1. **High-Temperature Zone (>800 °C):** Despite intense molecular collisions, SO₃ decomposition dominates due to unfavorable thermodynamics ($\Delta G > 0$). Conversion rates decline sharply above 800 °C.
2. **Medium-Temperature Zone (600–800 °C):** Peak SO₃ conversion occurs here (exceeding 15%), where thermodynamics ($\Delta G < 0$) and kinetics align. Catalysts reduce the activation energy, enabling efficient SO₂ oxidation.
3. **Low-Temperature Zone (<600 °C):** While thermodynamically favorable ($\Delta G < 0$), the low molecular kinetic energy restricts conversion to 4–5%.

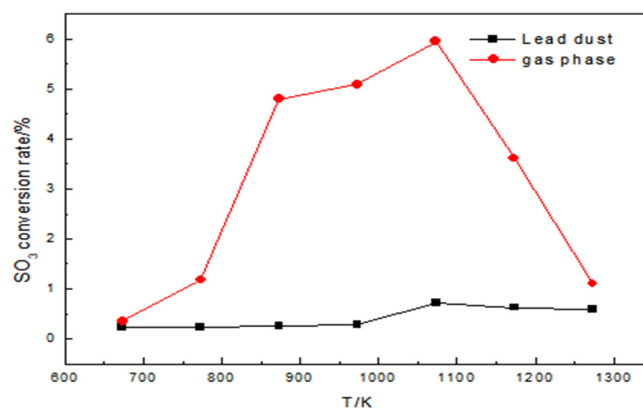


Figure 4. Comparison of SO₃ conversion under homogeneous and heterogeneous conditions at different temperatures.

This behavior stems from competing thermodynamic and kinetic drivers. At high temperatures, SO₃ becomes unstable despite rapid molecular motions. Low temperatures maintain thermodynamic favorability but lack the activation energy. The medium-temperature “window” uniquely balances both factors.

Operational variability (± 50 °C) in temperature zones may occur due to the furnace design or feedstock differences. Practical mitigation strategies should focus on the following: (1) rapid gas cooling throughout the 600–800 °C range to limit SO₃ formation; (2) optimizing catalyst composition at lower effective activation temperatures; and (3) implementing real-time temperature monitoring to account for process fluctuations.

These findings emphasize the critical role of thermal management in controlling SO₃ emissions. By targeting the medium-temperature regime through operational adjustments and catalytic optimizations, smelters can significantly reduce SO₃ generation while maintaining production efficiency.

3.2.2. The Effect of Initial O₂ Content on SO₃ Generation in Experimental Simulations

This study examined SO₃ formation at 600 °C with a fixed gas flow rate (200 mL/min) under varying oxygen concentrations (2–40%). Figure 5 reveals the distinct catalytic impacts: Under homogeneous conditions, SO₃ conversion remains minimal (<1%) despite oxygen concentration increases, confirming the limited gas-phase reactivity. Introducing lead dust catalysts dramatically enhances SO₃ yields. The catalytic effect is amplified with oxygen availability, suggesting O₂ participation in both SO₂ oxidation and catalyst activation [26,27].

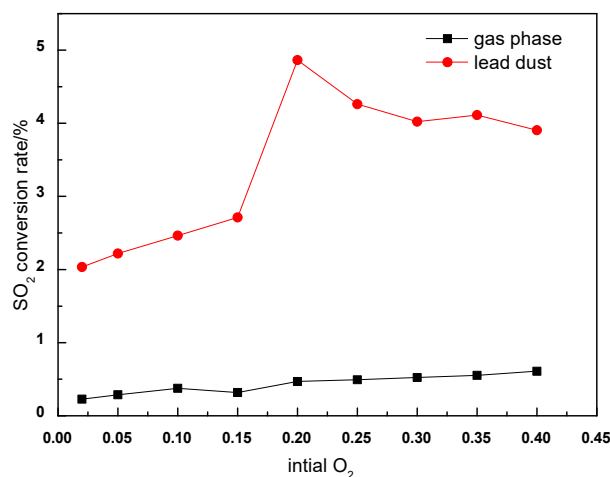


Figure 5. SO₃ conversion under different oxygen contents in homogeneous and heterogeneous conditions.

The two mechanistic regimes that emerge are as follows:

Low O₂ concentration (2–15%): rate limited by oxygen supply (a linear increase);

High O₂ concentration (>15%): plateauing kinetics due to SO₂ depletion.

The results highlight oxygen management as critical for optimizing the catalytic SO₃ control. While higher O₂ concentrations boost conversion, practical implementation requires balancing oxidation efficiency with operational costs and downstream corrosion risks.

3.2.3. The Effect of Initial SO₂ Content on SO₃ Generation in Experimental Simulations

Experimental investigations at 600 °C with a fixed gas flow rate (200 mL/min) reveal the limited sensitivity of SO₃ conversion to SO₂ concentration variations (10–30 vol%), as shown in Figure 6.

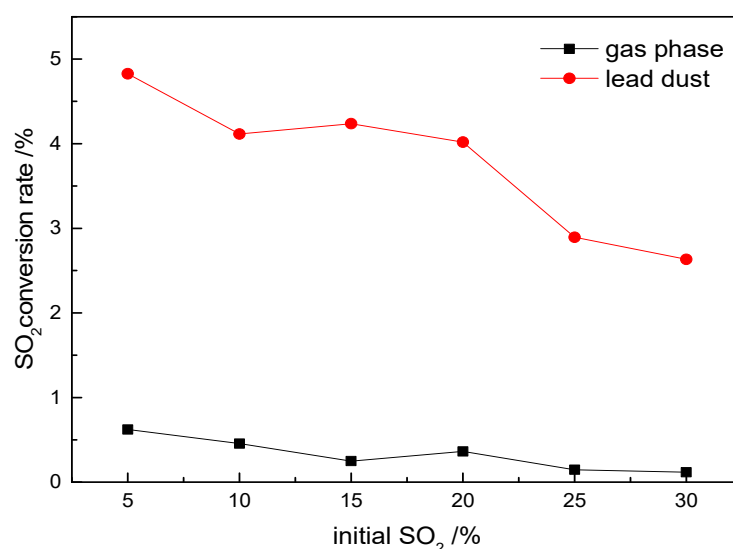


Figure 6. SO₃ conversion rate for different SO₂ contents in homogeneous and heterogeneous conditions.

Under homogeneous conditions, the SO₃ conversion rates remain consistently low (0.5–1.8%) with minimal fluctuations, demonstrating a weak dependence on SO₂ levels. In contrast, lead dust catalysis elevates the conversion rates to 12–14%, about an 8-fold enhancement over gas-phase reactions, though still exhibiting limited responsiveness to SO₂ increases (<2% change across tested concentrations).

These findings align with thermodynamic simulations showing decreasing SO₃ concentrations at elevated temperatures despite the rising SO₂/O₂ levels. The weak correlation between SO₂ content and SO₃ generation stems from oxygen availability being the dominant controlling factor: every 1% increase in the initial O₂ concentration boosts the conversion rates by 0.8%, whereas SO₂ variations show a negligible impact. The experimental conversion rates lag theoretical predictions by 15–22% due to kinetic limitations preventing a full thermodynamic equilibrium.

Lead ash catalysis operates through three synergistic mechanisms: (1) surface-mediated oxidation pathways that lower the activation energy, (2) oxygen activation at metal oxide sites, and (3) the stabilization of intermediate sulfur species. This catalytic system demonstrates remarkable robustness, maintaining a stable performance across wide SO₂ ranges (10–30%) and temperature fluctuations (±50 °C), suggesting adaptability to variable smelting feedstocks.

Practical implications emphasize oxygen optimization (>18 vol%) over SO₂ adjustments for effective SO₃ control. The catalytic approach reduces sensitivity to the feedstock

sulfur content while providing consistent and critical advantages for emission mitigation in industrial applications. These insights establish catalytic modification as a superior strategy compared to gas-phase oxidation for SO₃ management in lead smelting operations.

3.3. Effect of SO₃ Inhibition on the Oxidation Behavior of PbS in a Simulation of Lead Smelting Flue Gas

By investigating the influence of O₂ content on the conversion of SO₂ to SO₃, as well as the thermodynamics and kinetics of PbS decomposition and oxidation behavior under flue gas system conditions, it was found that PbS and its decomposition products exhibit a significantly stronger binding affinity with O₂ compared to SO₂ within the temperature range of 100–1300 °C. Under flue reaction conditions, O₂ is preferentially consumed through chemical reactions with PbS and its decomposition products rather than by reacting with SO₂ to form SO₃. By injecting PbS particles of specific sizes into the flue gas, the decomposition and oxidation reactions of PbS can be utilized to consume oxygen, thereby controlling the reaction direction, extent, and SO₃ partial pressure at equilibrium ($2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$). This approach effectively reduces the SO₃ content in lead smelting flue gas [28]. Experimental verification was conducted using a simulated flue gas platform designed and established by the research team. Under the simulated flue system conditions, the effects of varying initial O₂ and SO₂ contents on PbS decomposition/oxidation behavior and SO₃ generation were studied.

The following flue gas composition was maintained in the laboratory simulation: a baseline gas composition of SO₂ (18%), O₂ (4%), and N₂ (78%). The variable conditions included a fixed initial O₂ content of 4%, with the SO₂ content adjusted to 10%, 14%, 18%, and 22%, while the N₂ content decreased proportionally to maintain a constant total of 96% for SO₂ + N₂. The experimental results (Figure 7) demonstrate the amount of SO₃ formed after PbS addition under these conditions: at the initial SO₂ contents of 10%, 14%, 18%, and 22%, the corresponding SO₃ concentration is below 0.1% after PbS addition.

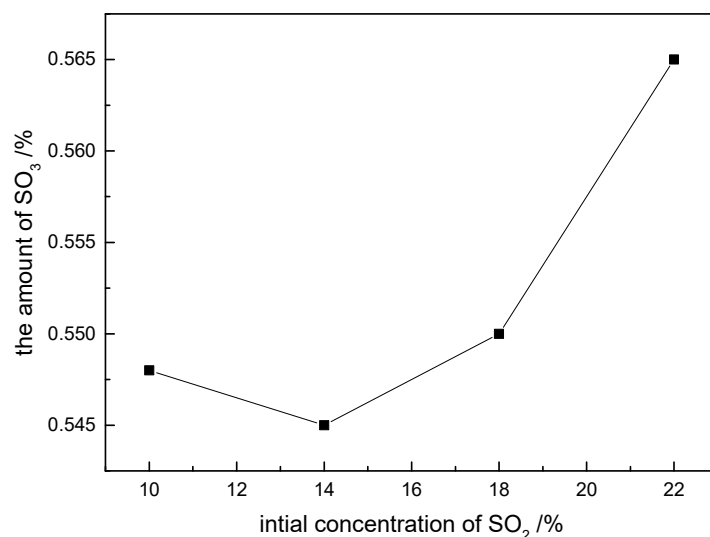


Figure 7. The amount of SO₃ formed after adding PbS at different initial contents of SO₂.

These values are significantly lower than the theoretical SO₃ levels calculated for scenarios without PbS addition. The minimal variation in SO₃ generation across different initial SO₂ concentrations indicates that the final SO₃ content is largely independent of the initial SO₂ level under simulated flue conditions at 600 °C, consistent with the theoretical predictions.

Consistently, as the oxygen content increases from 2% to 8%, under varying oxygen concentrations, the gas-phase SO_3 concentration is reduced to below 1% after the addition of PbS. In contrast, without an inhibitor, the SO_3 content increases with the rising oxygen levels, consistently exceeding 2%.

In summary, the formation behavior of SO_3 in the flue gas from lead smelting is regulated by both thermodynamic equilibrium and reaction kinetics. There are significant differences in its homogeneous and heterogeneous reaction mechanisms. In an industrial context, the strategies of thermodynamic inhibition, high-temperature decomposition, and kinetic regulation using catalyst passivation to minimize SO_3 emissions should be integrated into designs of flue gas purification systems. The inhibition of SO_3 formation by consuming oxygen using PbS is also a feasible and economical method. Utilizing the lead smelting by-product PbS to consume residual oxygen has inherent economic advantages and can realize the recycling of waste. Firstly, it is manifested in the fact that there is no need to purchase reagents externally (such as ammonia or activated carbon), which can save raw materials. Secondly, it can simplify the process, reduce the complexity of the gas treatment system, and lower the investment and operation costs.

4. Conclusions

- (1) From a thermodynamic perspective, the lower the temperature, the more conducive this is to SO_3 formation. The contents of SO_2 , O_2 , CO, SO_3 , and H_2O in the gas phase have a certain effect on SO_3 formation, but their effect becomes significant at high temperatures. The O_2 and SO_2 contents are the key parameters that control the SO_3 concentration in lead smelting flue gas.
- (2) The conversion of SO_3 is clearly influenced by the smoke and dust present in the flue gas. Due to the inability to achieve complete thermodynamic equilibrium in the experiment and under certain kinetic limitations, lead ash has a significant effect on the conversion of SO_2 to SO_3 .
- (3) Thermodynamic analysis shows that the reaction of PbS and O_2 takes precedence over the reaction of SO_2 and O_2 to form SO_3 under the same atmospheric conditions. SO_3 -suppression experiments show that PbS can adequately inhibit SO_3 formation in a simulated flue gas environment, and the content of SO_3 after adding PbS under different oxygen contents and SO_2 atmospheres does not exceed 0.6%.

Author Contributions: H.L. performed the main experiment, the dynamic experiment, data analysis, and wrote the manuscript; Q.Z. proposed the topic and comprehensively supervised the experiment and its data analysis; H.G. used computational software to perform data calculations and revised the manuscript; H.Y. formulated the research topic and provided guidance throughout the experiment and paper revisions. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financially supported by the National Key Research and Development Program of China (2018YFC1902005).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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