

Review

Flue Gas Deacidification Technologies for Waste-to-Energy Plants in China: A Review of Progress, Mechanisms, and Perspectives

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Abstract

Municipal solid waste (MSW) incineration power generation has become the dominant waste treatment technology in China. However, acid flue gas dominated by HCl and SO₂ induces severe boiler corrosion, a surge in hazardous fly ash, and uncontrolled operational costs, significantly hindering the industry's low-carbon transition. While conventional dry, semi-dry, and wet deacidification processes meet emission standards, they face an irreconcilable trilemma, failing to concurrently optimize removal efficiency, economic viability, and solid waste reduction. This review clarifies that high-temperature in-furnace deacidification represents a future development direction yet identifies two critical limitations: above 700 °C, external mass transfer remains the rate-controlling step, and the combined effects of CaSO₃ decomposition and sorbent sintering lead to inefficient desulfurization. Meanwhile, in the 130–400 °C range, HCl preferentially occupies active sites, inhibiting SO₂ adsorption. To address these challenges, this study proposes an innovative staged temperature–gradient synergistic deacidification pathway driven by catalytic oxidation. This strategy utilizes transition metals at high temperatures to oxidize SO₂ into SO₃, which is subsequently converted into thermally stable CaSO₄, while decoupling SO₂ pre-removal from the targeted capture of HCl in their respective optimal windows. Finally, four executable development directions are systematically proposed: industrial waste-based bifunctional sorbents, multi-field coupled gas–solid mass transfer intensification, staged deacidification processes, and full-process AI closed-loop control. These findings provide systematic theoretical support and actionable technical references for upgrading MSWI technology under China's "Dual Carbon" and "Waste-Free City" initiatives.



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Keywords: waste to energy; gas purification; deacidification mechanism; deacidification technologies; optimization strategies

1. Introduction

With the rapid advancement of urbanization in China, the yield of municipal solid waste (MSW) keeps rising substantially, and the harmless disposal of MSW has emerged as a crucial issue for ecological environmental protection and urban sustainable development. Benefiting from its prominent merits of reduction, recycling and harmless treatment,

waste-to-energy (WtE) incineration technology has replaced conventional sanitary landfill and become the dominant approach for municipal solid waste treatment in China [1–5]. Industrial statistical data demonstrate that more than 900 waste incineration power plants have been constructed and commissioned across the country up to now, with approximately 2174 incinerator units in service. The daily treatment capacity of MSW reaches 1.128 million tons, and the share of incineration in the total harmless disposal of MSW exceeds 70%. This indicates that China has built the world’s largest waste incineration treatment system with the most complete industrial chain, and the relevant technologies, equipment and engineering services have gradually realized international export [6–9].

The distribution of waste incineration treatment capacity in major countries and regions worldwide is illustrated in Figure 1. China’s waste incineration scale has far exceeded that of developed countries and regions such as Europe, the United States, Japan, and South Korea, making China the core market driving the global development of the waste incineration industry. Nevertheless, three critical engineering challenges persist during the industry’s transition toward high-quality and low-carbon development [10]. First, high-concentration acid gases in incineration flue gas cause high-temperature corrosion of key equipment, including boilers and superheaters, shortening service life, raising operation and maintenance costs, and restricting the improvement of steam parameters and power generation efficiency [11–13]. Second, current flue gas purification systems struggle to balance deacidification efficiency, operational costs, and secondary pollution control, and conventional processes require excessive de-acidifier dosage, leading to soaring operating expenses [14,15]. Third, prevailing deacidification technologies drastically increase fly ash output, significantly intensifying the pressure of harmless fly ash disposal and associated environmental risks. Notably, the core control node for resolving the above three dilemmas lies in the efficient, low-carbon, and stable removal of acid gases from incineration flue gas [16,17].

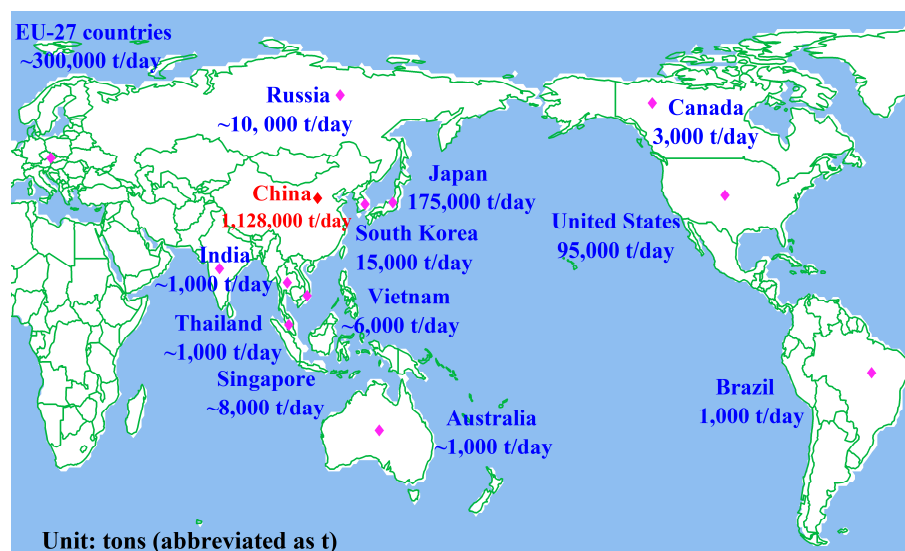


Figure 1. Global distribution of major municipal solid waste incineration treatment volume; the data are compiled from the Ministry of Housing and Urban–Rural Development of China, Eurostat, national environmental agencies, and industry reports (e.g., ISWA, CEWEP).

Municipal solid waste features a complex composition, and the flue gas generated during incineration contains high-concentration acidic pollutants. These pollutants are dominated by hydrogen chloride (HCl, approximately 1200 mg/Nm³) and sulfur dioxide (SO₂, approximately 800 mg/Nm³), accompanied by trace acidic components such as hydrogen fluoride (HF) and hydrogen bromide (HBr) [18]. At present, the mainstream “semi-dry + dry + wet” combined deacidification process in the industry can achieve

ultra-low emission of acid gases, yet its technical limitations have become increasingly prominent. The dry and semi-dry processes are constrained by the mass transfer efficiency and reaction kinetics of gas–solid reactions [19], thereby necessitating the addition of deacidifiers at 2–3 times the stoichiometric ratio in practical operation. This not only drives up the chemical cost but also increases the fly ash output by 20–40%, considerably intensifying the pressure of fly ash disposal [20–22]. Although the wet process can achieve a deep deacidification efficiency of over 98%, it suffers from complex systems, high investment and operating costs. Meanwhile, it gives rise to high-salinity wastewater and “white smoke” from flue gas, which require supporting flue gas reheating and wastewater treatment facilities, resulting in a marked rise in energy consumption and carbon emissions. This is incompatible with the low-carbon development goal of the industry [23,24].

Recently, remarkable strides have been made in the abatement technologies for SO₂ and HCl in WtE systems [25–27]. A comprehensive and critical review of updated deacidification techniques is, therefore, essential to support the high-quality, low-carbon development of the global WtE industry. Nevertheless, most existing review articles merely summarize the published literature, while rarely incorporating on-site operational data and practical industrial constraints. Specifically, few studies have explored the performance degradation mechanisms of deacidification systems or systematically discussed the inherent “efficiency–cost–environment” trilemma under full-scale operating conditions, creating a notable gap between theoretical research and industrial application [28,29]. To fill this gap, this review systematically summarizes the latest progress in flue gas deacidification, covering process optimization, adsorbent modification, and artificial intelligence-driven process intensification, while integrating in-depth critical analyses and original perspectives. It reveals that conventional technical routes only yield marginal performance improvements and cannot resolve the fundamental limitations of traditional deacidification methods. From the perspective of chemical reaction engineering, the underlying thermodynamic barriers, kinetic hysteresis, and mass transfer limitations that restrict acid gas removal are comprehensively elucidated herein. Integrating state-of-the-art engineering practice and frontier theoretical research, this review confirms, through rigorous analysis, that the synergistic deacidification pathway of “transition metal catalytic oxidation coupled with calcium-based acid-base immobilization” is technically viable. This strategy strategically harnesses the inherent high-temperature windows in furnace flues and waste heat boilers, enabling the efficient source control of acid gases. This review is expected to serve as a useful reference for overcoming technical bottlenecks in deacidification and promoting technological transformation within the global WtE industry.

2. Literature Search and Analytical Methodology

This work presents a critical review of flue gas deacidification technologies for municipal solid waste incineration (MSWI). To ensure comprehensive coverage of state-of-the-art research and engineering practices in this field, the literature retrieval, screening, and analytical framework adopted in this review are described as follows.

2.1. Literature Sources and Retrieval Strategy

Core academic publications were identified through searches across four major authoritative databases: the Web of Science Core Collection, Scopus, ScienceDirect, and Google Scholar. National emission standards, industrial technical reports, and selected operational data were collected from official public sources, including the Ministry of Ecology and Environment of China and official industry publications. Site-specific engineering data (mostly covering 2024–2026) were sourced from Shenzhen Energy Environment Co., Ltd. The search covered publications released from January 2000 to March 2026, with particular

attention paid to cutting-edge research advances and engineering applications emerging over the past decade.

The core search terms used to identify the relevant literature include municipal solid waste incineration, waste-to-energy, flue gas desulfurization, calcium-based deacidification sorbent, semi-dry flue gas desulfurization, and deacidification reaction mechanism.

2.2. Inclusion and Exclusion Criteria

A set of criteria was applied to screen for high-quality, thematically relevant studies to underpin the critical analysis:

Inclusion Criteria: (1) Original experimental research or full-scale engineering case studies focused on MSWI flue gas deacidification, with complete and reliable datasets; (2) review articles summarizing deacidification technologies or reaction mechanisms; and (3) studies addressing high-temperature deacidification, sorbent modification, and process intensification.

Exclusion Criteria: (1) Conference abstracts, short communications, and patent documents without complete research data; (2) duplicated publications and retracted papers; and (3) the literature not relevant to the core theme of flue gas deacidification.

2.3. Screening Procedure and Analytical Framework

Initial database searches returned 6946 records related to municipal solid waste incineration (MSWI) and 5260 records focused on flue gas desulfurization. To balance thematic breadth and relevance, the scope was further refined by combining core terms for MSWI power generation and flue gas desulfurization, supplemented with technical terms specific to deacidification processes. Ultimately, approximately 130 highly relevant publications were selected as the core basis for the critical synthesis and discussion in this review (Figure 2).

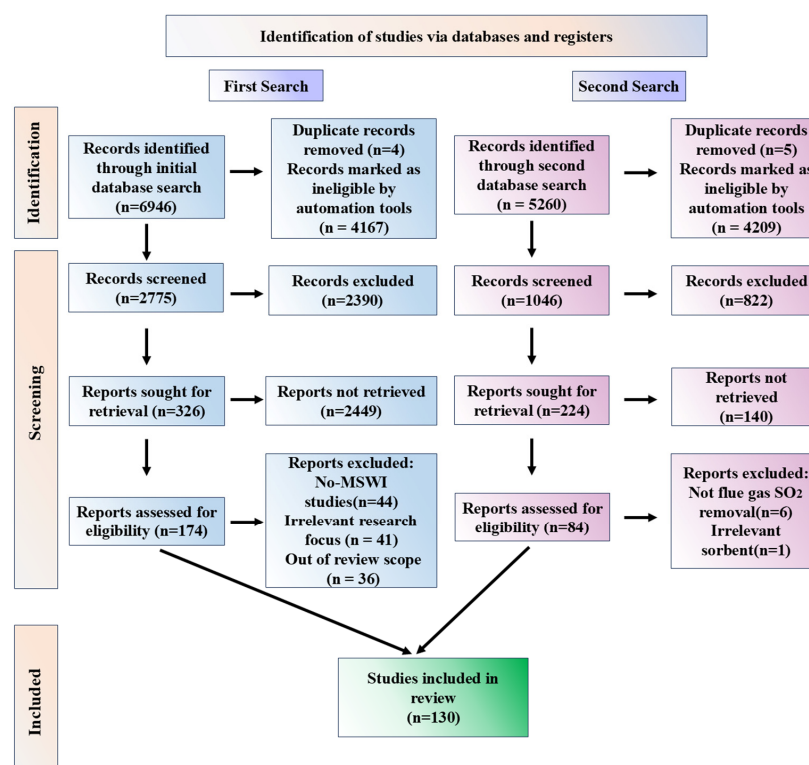


Figure 2. Flowchart of literature screening.

The selected literature is synthesized and critically discussed from three perspectives: (i) performance comparison of mainstream deacidification processes; (ii) analysis of ther-

modynamic and kinetic reaction mechanisms; and (iii) summary of optimization strategies covering material development, process design, and intelligent control. On this basis, key bottlenecks restricting the advancement of deacidification technologies are identified, and targeted directions for future development are proposed.

3. Status and Performance Comparison of Mainstream Flue Gas Deacidification Technologies in Waste Incineration

At present, a seven-stage integrated flue gas purification process, namely “SNCR denitrification + semi-dry deacidification + dry deacidification + activated carbon adsorption + Bag filter + wet deacidification + SCR denitrification”, is predominantly adopted in waste incineration power plants in China (Figure 3).

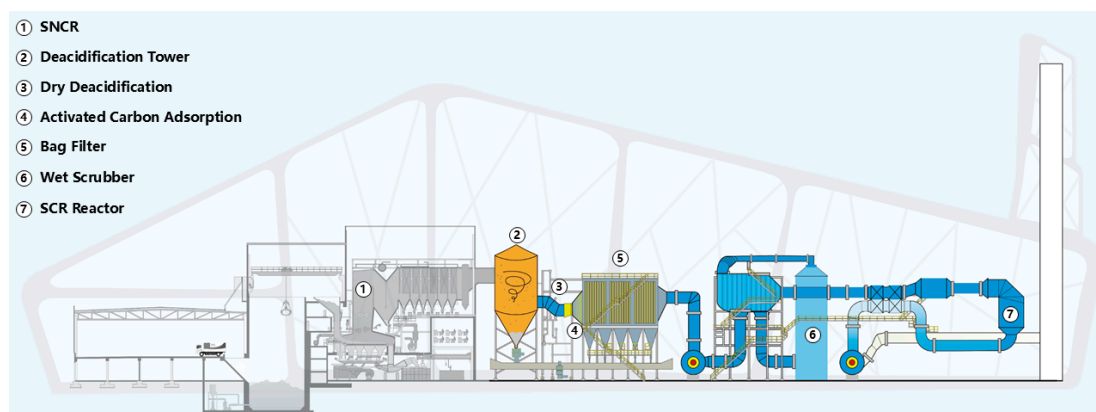


Figure 3. Seven-stage flue gas treatment process for waste-to-energy incineration, Shenzhen Energy Environment Co., Ltd. (Shenzhen, China).

Specifically, acidic pollutants including HCl, SO₂, HBr and HF are removed primarily through the synergistic action of dry, semi-dry and wet deacidification processes [30–32]. Nitrogen oxides are reduced to harmless N₂ via a two-stage denitrification configuration: in-furnace selective non-catalytic reduction (SNCR) [33] and tail-end selective catalytic reduction (SCR) [34,35]. As highly toxic persistent organic pollutants, dioxins are mainly decomposed at high temperatures inside the furnace, in compliance with the “3T+E” principle (temperature ≥ 850 °C, residence time ≥ 2 s, turbulence, and excess air). Notably, existing studies have demonstrated that SCR catalysts can also achieve the oxidative decomposition of dioxins into non-toxic compounds [36,37]. The pollutant treatment performance of the flue gas purification system in a waste incineration power plant in Shenzhen is presented in Table 1. This combined process achieves ultra-low acidic gas emissions, with all indicators surpassing the Directive 2010/75/EU standard [38].

Table 1. Comparison of pollutants before and after flue gas purification in a waste incineration plant in Shenzhen.

Pollutant	Concentration Before Purification	Concentration After Purification	Main Process
HCl	~1200 mg/Nm ³	≤ 2 mg/Nm ³	Semi-dry + dry + wet combined deacidification Process
SO ₂	~800 mg/Nm ³	≤ 8 mg/Nm ³	Semi-dry + dry + wet combined deacidification Process
NO _x	~400 mg/Nm ³	≤ 35 mg/Nm ³	SNCR + SCR combined denitrification process
Particulate	≤ 6000 mg/Nm ³	≤ 5 mg/Nm ³	Bag filter
HF	~10 mg/Nm ³	≤ 0.15 mg/Nm ³	Semi-dry + dry + wet combined deacidification Process
Dioxins	~10 ng-TEQ/Nm ³	≤ 0.05 ng-TEQ/Nm ³	3T+E combustion control and activated carbon adsorption

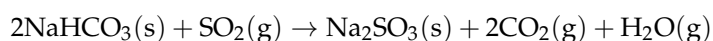
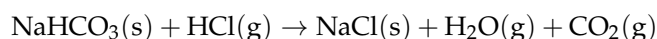
Note: The 3T+E refers to: incinerator furnace temperature ≥ 850 °C, flue gas residence time in high-temperature zone ≥ 2 s, sufficient flue gas turbulence, and appropriate excess air coefficient, so as to realize complete combustion of organic matters and source control of dioxins.

3.1. Dry Deacidification

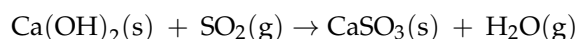
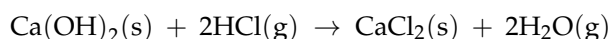
Dry deacidification refers to a process where alkaline powder sorbents are directly injected into the flue duct or dry reactor at a flue gas temperature range of 130–250 °C to remove acidic gases via gas–solid neutralization reactions. The resulting neutral salt particles are captured together with fly ash in the downstream bag filter, ultimately achieving the removal of acidic gas [39–41]. This process features a simple system configuration, low energy consumption, and zero wastewater discharge. As the dominant auxiliary deacidification technique for waste incineration power plants, it is mainly employed to address abnormal operating conditions including sudden concentration fluctuations of acidic flue gas components and start–stop events of the main deacidification system, thereby ensuring continuous and stable compliance with emission standards.

At present, the commonly used deacidification sorbents for dry deacidification are mainly slaked lime ($\text{Ca}(\text{OH})_2$) and sodium bicarbonate (NaHCO_3). The main reaction equations are as follows:

1. Using NaHCO_3 as the deacidification sorbent:



2. Using $\text{Ca}(\text{OH})_2$ as the deacidification sorbent:



Theoretical studies have shown that the removal efficiencies of HCl and SO_2 by the NaHCO_3 dry process can exceed 95% and 90%, respectively, under ideal reaction conditions of 130–250 °C with a stoichiometric ratio close to 1:1. However, in engineering applications, limited by short gas–solid contact time, low mass transfer efficiency, and fluctuations in flue gas components, the actual deacidification efficiency is considerably lower than the theoretical value. An excessive deacidification sorbent dosage is, therefore, required to meet emission standards, resulting in low sorbent utilization efficiency.

In recent years, dry deacidification centered on calcium injection into the furnace has emerged as a research hotspot in the field [15]. and leading domestic enterprises in China have carried out relevant engineering applications. The mechanism of this technology involves the direct injection of calcium carbonate (CaCO_3) or modified calcium-based deacidification sorbents into the first and second flue ducts of the incinerator, where the temperature is ≥ 850 °C. At such high temperatures, CaCO_3 decomposes rapidly to generate highly reactive calcium oxide (CaO), which then removes acidic gases at the source via gas–solid neutralization reactions in the furnace. Nevertheless, this technology still faces distinct bottlenecks in practical engineering applications. First, calcium sulfite (CaSO_3), the primary deacidification product, exhibits inferior thermal stability above 850 °C and readily undergoes thermal decomposition, leading to SO_2 re-emission. Second, calcium-based sorbents tend to undergo severe sintering at high temperatures, resulting in pore structure collapse, reduced specific surface area, and rapid loss of reactivity. Third, in-furnace calcium injection significantly increases the fly ash concentration in flue gas, which aggravates the abrasion of boiler heating surfaces and alkaline-earth metal ash deposition [12,42–45], lowers heat transfer efficiency, and simultaneously increases the operating load of the downstream dust removal system, as well as the corrosion risk in high-temperature zones.

3.2. Semi-Dry Deacidification

Semi-dry deacidification [24,46,47] is the most widely applied primary deacidification process in waste incineration plants. The core mechanism involves the preparation of lime slurry with $\text{Ca}(\text{OH})_2$ as the main component at a mass concentration of 6–15% and a pH of 12–13. The slurry is atomized into micron-sized droplets of 50–100 μm by a high-speed rotary atomizer with a rated speed of approximately 12,000 r/min and injected into the deacidification tower (Figure 4). The alkaline droplets fully contact the hot flue gas, accompanied by simultaneous heat and mass transfer, as well as acid–base neutralization reactions, thereby removing acidic gases such as HCl and SO_2 from the flue gas.



Figure 4. Semi-dry deacidification tower, Shenzhen Energy Environment Co., Ltd.

Most solid reaction products enter the subsequent baghouse filter along with the flue gas and are captured, while a small fraction of large particles settle in the ash hopper at the bottom of the reactor. Meanwhile, unreacted $\text{Ca}(\text{OH})_2$ forms a fixed-bed-like filter cake layer on the surface of the filter bags, which undergoes secondary deacidification reactions with residual acidic gases in the flue gas, further enhancing the overall deacidification efficiency.

Semi-dry deacidification efficiency is governed by both the physical drying process and the chemical reaction process.

For the physical processes, droplet size, flue gas temperature, residence time in the reactor, and the approach to adiabatic saturation temperature (AAST) after reaction serve as the key influencing parameters [48–50]. Studies have demonstrated that, when the atomized droplet size is controlled at approximately 50 μm , an optimal balance between specific surface area and evaporation rate is achieved, leading to the peak deacidification efficiency. An overly large droplet size results in an insufficient mass transfer area, while an excessively small size shortens the gas–liquid reaction duration due to rapid droplet evaporation. Both scenarios lead to a deteriorated deacidification efficiency. Engineering practices indicate that controlling the flue gas residence time within 10–12 s in the reactor can ensure sufficient reaction while striking a balance between capital investment and operational economy. AAST represents the core parameter determining the deacidification efficiency and operational stability of the system. Research has shown that deacidification efficiency increases approximately exponentially with decreasing AAST. A lower AAST corresponds to a higher relative humidity of flue gas, a slower droplet evaporation rate, a longer gas–liquid mass transfer reaction period, and thus a higher acidic gas absorption

efficiency [51–54]. Nevertheless, an excessively low AAST may cause flue gas condensation, which induces equipment corrosion and flue duct blockage. Therefore, AAST is generally maintained at ≥ 10 °C in engineering applications to achieve a favorable trade-off between deacidification efficiency and operational safety [49,55,56].

For the chemical reaction process, the specific surface area of the sorbent, reaction time, and system calcium-to-sulfur (Ca/S) molar ratio are identified as the core controlling parameters. In industrial operations, the Ca/S ratio is generally controlled within the range of 1.2–2.0 to strike a balance between deacidification efficiency and reagent consumption. Compared with the dry deacidification process, the semi-dry process exhibits a distinct mass transfer advantage originating from gas–liquid two-phase reactions, leading to a considerably higher deacidification efficiency. Specifically, the removal efficiency can exceed 95% for HCl and 85% for SO₂ [57–60]. Meanwhile, the process produces no wastewater and features moderate capital and operating costs, rendering it the mainstream primary deacidification technology in the industry.

3.3. Wet Flue Gas Deacidification

Wet flue gas deacidification [61–65] is generally installed at the end of the flue gas cleaning train (Figure 5), downstream of the baghouse filter, functioning as a polishing process for the deep abatement of acidic gas. Its core mechanism involves the use of alkaline absorbents (e.g., NaOH) in countercurrent contact with flue gas within packed or spray towers, enabling deep removal of acidic gases through efficient gas–liquid mass transfer. A typical wet deacidification system consists of two key sections: a flue gas cooling zone and an absorption zone. This process exhibits excellent deacidification performance, with the HCl removal efficiency exceeding 98% and an SO₂ removal efficiency above 95%, featuring stable operational performance and strong adaptability to fluctuations in flue gas load and composition, thus meeting the most stringent ultra-low emission standards. Shenzhen Longgang Energy Eco-Park, a waste-to-energy plant, has adopted a combined “semi-dry + dry + wet” purification process, which ultimately reduces the HCl concentration in flue gas to below 1 mg/Nm³, demonstrating the remarkable superiority of the wet process for deep flue gas purification [58,66,67].

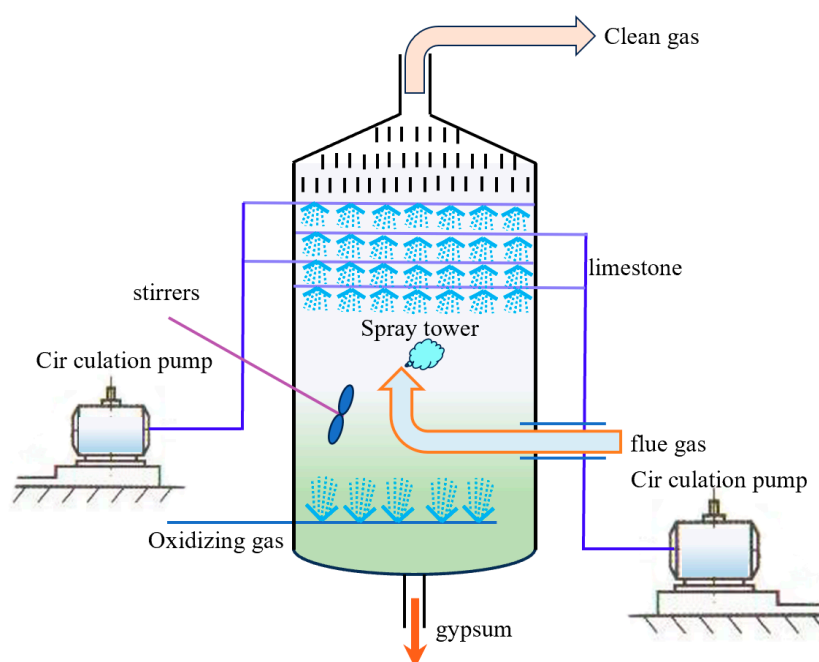


Figure 5. Diagram of a wet flue gas deacidification tower, Shenzhen Energy Environment Co., Ltd.

Nevertheless, the wet deacidification process also exhibits distinct limitations in engineering applications. First, the system features a complicated flow configuration accompanied by high construction and operation costs and requires a supporting high-salinity wastewater treatment unit. The corresponding capital investment is more than 40% higher than that of the semi-dry process. Second, the treatment process produces high-chloride, high-salinity wastewater that is difficult and costly to handle; improper disposal poses a considerable risk of secondary pollution. Third, the temperature of the treated flue gas decreases to 60–70 °C, which readily causes white plume formation at the stack outlet. This necessitates the configuration of flue gas reheating equipment (e.g., GGH), which further elevates system energy consumption and operational complexity. According to engineering data, the energy consumption of the wet deacidification system is over 15% higher than that of the dry process, leading to a substantially higher overall life-cycle cost [68,69].

3.4. Performance Comparison of Typical Deacidification Technologies

A performance parameters comparison of the three deacidification technologies is presented in Table 2. These technologies differ significantly in deacidification efficiency, capital and operating costs, system complexity, and other aspects, resulting in distinct application boundaries. Overall, state-of-the-art deacidification technologies face an inherent dilemma, characterized by the inability to concurrently optimize decontamination efficiency, economic feasibility, and environmental sustainability.

Table 2. Flue gas deacidification technologies: dry, semi-dry and wet processes.

Characteristic	Wet Process	Semi-Dry Process	Dry Process
Deacidification agent form	Liquid	Slurry	Dry powder
HCl removal efficiency	High (>98%)	Medium (90–95%)	Low (70–85%)
SO ₂ removal efficiency	High (>95%)	Medium (80–92%)	Low (70–85%)
Capital cost	$250\text{--}450 \times 10^3 \text{ CNY}/(10^4 \text{ m}^3 \cdot \text{h}^{-1})$	$150\text{--}300 \times 10^3 \text{ CNY}/(10^4 \text{ m}^3 \cdot \text{h}^{-1})$	$100\text{--}250 \times 10^3 \text{ CNY}/(10^4 \text{ m}^3 \cdot \text{h}^{-1})$
Operating cost	40–80 CNY/10 ⁴ m ³	35–70 CNY/10 ⁴ m ³	30–60 CNY/10 ⁴ m ³
System complexity	Complex	Medium	Simple
Land area	Large	Medium	Small
Wastewater issue	Exists	None	None
Reheat requirement	Required	Not required	Not required
Corrosion issue	Severe	Slight	None

On the one hand, combined processes centered on dry and semi-dry technologies are limited by gas–solid/gas–liquid–solid reaction kinetics and mass transfer resistance, thus requiring excessive sorbent injection to ensure emission compliance. This gives rise to the dual problems of elevated reagent costs and increased fly ash generation, forming a contradiction between environmental compliance and process economy.

On the other hand, although the wet process enables the deep removal of acidic gases, it is accompanied by high investment, intensive energy consumption, and secondary environmental pressure from the disposal of high-salinity wastewater, leading to a contradiction between ultra-low emission targets and low-carbon development. In addition, high-temperature in-furnace source deacidification can realize the pre-control of acidic gases yet is restricted by issues such as thermal decomposition of reaction products and activity decay of deacidification sorbents, making it difficult to achieve stable and efficient removal.

4. Optimization Strategies and Research Progress of Deacidification Technologies

To address the inherent bottlenecks of conventional deacidification processes and advance flue gas deacidification technologies for MSWI toward the goals of high efficiency with low consumption, low-carbon environmental friendliness, and precise regula-

tion, researchers and engineers have carried out systematic innovations focusing on three core pathways: sorbent modification, process route optimization, and intelligent process control [70–74].

4.1. Optimization of Process Routes and Their Inherent Limitations

During MSWI, most reaction by-products of calcium-based deacidification sorbents are incorporated into fly ash [22,75–77]. As a hazardous waste, fly ash is associated with prohibitive disposal costs, which have become a key constraint on cost reduction and efficiency enhancement in the MSWI industry. To address this, domestic incineration power plants have carried out extensive attempts at process route optimization, aiming to achieve synergistic management of fly ash yield and sorbent consumption while ensuring compliance with stringent environmental emission standards.

Common engineering attempts have focused on the regulation of process unit configurations, including reducing the reagent dosage in the dry deacidification unit, adopting a single-stage semi-dry deacidification process, and applying a two-stage “semi-dry + wet” deacidification process [24,78]. Nevertheless, these adjustments have achieved only limited effects: they generally achieve a marginal reduction in fly ash yield (0.1–0.5%) at the cost of an increase in specific sorbent consumption per ton of waste (0.5–1.5%), failing to realize the synergistic optimization of deacidification efficiency, material consumption, and fly ash generation. There have also been case studies attempting the “in-furnace calcium carbonate injection + wet deacidification” process, which failed to achieve large-scale popularization due to the ultra-high consumption of calcium carbonate, approximately 20 kg per ton of incinerated waste, and the large volume of refractory wastewater generated by the wet deacidification unit.

Overall, it can be concluded that, without material innovation of deacidification sorbents, mere adjustment of the process routes can hardly systematically achieve the core development goals of high efficiency, low consumption, and low carbon emission.

4.2. Modification and Innovation of Deacidification Sorbent Materials

Deacidification sorbents are the core component that determines the upper performance limit of flue gas deacidification systems. Material modification and functional innovation thus represent the fundamental pathway to break through the inherent bottlenecks of conventional calcium-based materials, achieve enhanced deacidification efficiency, and reduce reagent consumption and fly ash generation.

For the medium- and low-temperature scenarios (130–250 °C) corresponding to tail-end semi-dry and dry deacidification processes, the modification and optimization of high-reactivity calcium-based materials have been well-established with mature engineering applications [15,79–82] (Figure 6). For instance, modified $\text{Ca}(\text{OH})_2$ sorbents with a hierarchical porous structure and high specific surface area can be synthesized via the targeted regulation of pore structure, pore size distribution, and surface active sites [14]. The well-developed porous framework of this sorbent markedly enhances gas–solid interphase mass transfer and the kinetic performance of interfacial neutralization reactions. Engineering application data demonstrate that, under equivalent deacidification efficiency and emission control requirements, the reagent consumption of this modified sorbent (produced by a Beijing-based environmental protection enterprise) is reduced by 30–50% compared with commercially available conventional hydrated lime, along with a 15–25% reduction in fly ash yield and a 10–30 °C increase in the outlet flue gas temperature of the deacidification unit.

Material innovation has directly driven the development of novel deacidification process configurations. Based on the temperature gradient distribution characteristics of

the full incineration boiler flow path, targeting the industry pain points of poor working condition adaptability of conventional in-furnace calcium injection and insufficient gas–solid contact time in tail-end deacidification processes, a Shenzhen-based environmental protection enterprise has proposed a synergistic process system of medium-temperature pre-deacidification coupled with tail-end semi-dry deep deacidification. In this process, the aforementioned high-reactivity modified-calcium-based sorbent is injected into the flue duct between the boiler superheater and economizer, where the flue gas temperature ranges from 350 °C to 550 °C, enabling the sorbent to sequentially complete medium-temperature pre-deacidification and subsequent tail-end deep deacidification along with the flue gas flow. This design avoids the sintering-induced deactivation of the sorbent caused by ultra-high temperatures above 700 °C in the furnace chamber, while simultaneously extending the effective gas–solid reaction contact time by virtue of the sorbent’s high specific surface area and porous structure. Engineering operation data show that this process achieves a 70–90% pre-removal efficiency for SO₂, and the system Ca/S can be stably controlled at around 2.0. This significantly reduces the operating load and reagent consumption of the tail-end deacidification system, and realizes the synergistic optimization of deacidification efficiency, material consumption, and fly ash yield.



Figure 6. From laboratory to industry, high-activity calcium hydroxide desulfurizer in low-temperature dry desulfurization [79].

Nevertheless, such medium- and low-temperature deacidification sorbents are only applicable to tail-end flue gas purification. They cannot mitigate the high-temperature corrosion of boiler heating surfaces induced by acidic gases in the furnace chamber at the source, nor can they effectively inhibit the formation of dioxins in fly ash. Accordingly, the research and development of deacidification materials suitable for the high-temperature zone (700–1000 °C) in the furnace chamber is of critical engineering necessity and application value. Current studies have mainly focused on technical breakthroughs in two core modification strategies:

1. Constructing a high-temperature stable porous framework: By introducing inert components such as Al₂O₃, SiO₂, and magnesium–aluminum spinel into the calcium-based sorbent [82–87], the sintering resistance of the sorbent is enhanced, and the collapse of pore structure under high-temperature conditions is avoided, thereby ensuring the active sites required for the reaction;
2. Optimizing the reaction path: By adding thermally stable solid catalysts like MnO_x, Fe₂O₃, and CuO into the adsorbent, SO₂ is oxidized to SO₃, which then reacts with the calcium-based sorbent to form thermally stable calcium sulfate, fundamentally solving the problem of SO₂ re-emission caused by the thermal decomposition of calcium sulfite [15,88–92].

At present, the engineering application of high-temperature deacidification sorbents is still constrained by multiple factors, including safety control, environmental compatibility, and economic viability, and further breakthroughs are required for their large-scale industrial deployment.

4.3. Intelligent Control of the Deacidification Process

Currently, insufficient upstream monitoring configuration represents a pervasive industrial bottleneck restricting precision flue gas deacidification in operating municipal solid waste incineration (MSWI) plants. Most in-service facilities are only equipped with online flue gas pollutant monitoring systems at the stack outlet, while key nodes with dramatic fluctuations in acid gas concentrations, such as the furnace outlet and deacidification tower inlet, generally lack dedicated monitoring instrumentation. This layout deficiency forces sorbent dosing to rely heavily on operator experience or delayed regulation based solely on terminal emission data. Such practice readily leads to excessive reagent consumption, elevated operating costs, and increased fly ash yield, and poses non-negligible risks of transient pollutant exceedance [93–95].

AI-enabled intelligent control technology for flue gas purification provides a viable technical pathway to address this bottleneck. The overall framework of the intelligent flue gas purification control system developed by Shenzhen Energy Environment Co., Ltd. is presented in Figure 7. The system adopts a layered architecture, sequentially comprising a multi-source data input layer, a feature-mapping hidden layer, dual-core algorithm modules, and an intelligent precise regulation output terminal from left to right.

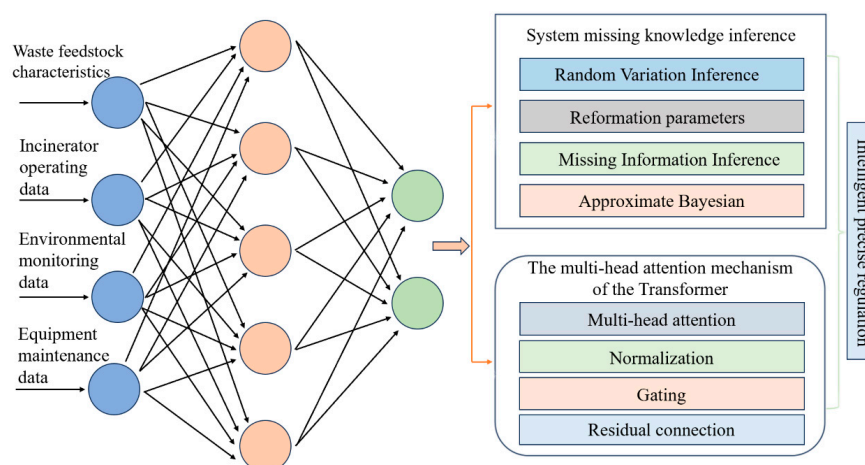


Figure 7. Intelligent control system for municipal solid waste incineration flue gas purification, Shenzhen Energy Environment Co., Ltd.

The input layer integrates four categories of multi-source heterogeneous data: waste feedstock characteristics, incinerator operating data, environmental monitoring data, and equipment maintenance data, which comprehensively cover operational conditions across the entire incineration–flue gas purification chain. After feature extraction and nonlinear mapping through the neural network hidden layer, the processed data are fed into two core algorithmic modules [96–99]:

1. **System missing knowledge inference module:** This module integrates four algorithmic components, namely random variation inference, parameter reformation, missing information inference, and approximate Bayesian computation. It performs soft-sensing and reconstruction of key unmeasurable parameters (e.g., incoming waste composition, real-time acid pollutant generation potential), thus compensating for the shortage of upstream monitoring points;

2. Transformer multi-head attention mechanism module: Built with a combined structure of multi-head attention, normalization, gating, and residual connection, this module constructs a dynamic prediction model for deacidification reagent demand, which effectively captures the long-range coupling effects and large time-delay characteristics between incineration combustion states and flue gas pollutant emissions.

The collaborative prediction outputs from the two modules are transmitted to the intelligent precise regulation unit, which implements dynamic closed-loop optimization of deacidification sorbent dosage. This control scheme specifically overcomes the limitations of conventional proportional–integral–derivative (PID) control in handling the inherent strong nonlinearity, large time delay, and multivariable coupling of MSWI processes.

Such AI-enabled intelligent deacidification technical routes have been validated in multiple domestic engineering projects, including applications by Green Dynamic Group and Beijing Chaoyang Environment Group. According to public reports from *Beijing Daily*, after deploying a homologous intelligent system, Beijing Chaoyang Environment Group achieved comprehensive performance improvements while maintaining long-term stable compliance of flue gas emissions: the main steam stability was enhanced by 36–48%, the automatic operation rate of process units exceeded 98%, on-site manual operation intensity was reduced by 80%, and the consumption of deacidification and denitration reagents decreased by over 3% year on year. These findings preliminarily corroborate the engineering feasibility of AI-driven flue gas purification optimization.

It must be explicitly clarified that the above data are only publicly disclosed results from a single project. Owing to discrepancies in process configuration, waste physico-chemical properties, and operational management levels among different MSWI plants, the reported performance cannot be directly generalized to the entire industry. Furthermore, the core technical implementation details and standardized statistical calibers of the indicators have not been fully disclosed. Accordingly, such cases serve solely as reference evidence for the industry's technological development trend and are not regarded as quantitative validation for the core conclusions of this work. At present, the large-scale deployment of this technology remains constrained by factors including sensor configuration conditions, data quality, and project-specific retrofitting costs, and its universality requires further verification through more independent engineering practices.

For the future development of low-cost deep AI empowerment for deacidification systems in existing MSWI plants, research priorities will focus on the soft sensing of critical unmeasurable parameters utilizing on-site multi-source data. Specifically, unmonitored acid gas concentrations and incoming waste composition will be reconstructed via the system missing knowledge inference module, supported by multi-sensor data fusion and dynamic analysis of furnace combustion flame states. Subsequently, a full-process incineration–deacidification dynamic prediction model will be established using a deep neural network optimized by the Transformer multi-head attention mechanism to effectively characterize the long-range dependencies and coupling interactions among multiple variables in the incineration process. Ultimately, global control system optimization will be achieved via deep reinforcement learning. This pathway enables the forward-looking prediction of pollutant generation and full-process optimization, establishing a novel data- and algorithm-driven intelligent operation paradigm for MSWI plants.

Despite preliminary progress in the above three directions, critical bottlenecks remain: poor thermal stability of calcium-based products, insufficient sorbent sintering resistance, competitive S/Cl adsorption limiting synergistic HCl/SO₂ removal, and high modified sorbent costs restricting scale-up. Addressing these requires fundamental studies on acid gas removal mechanisms to elucidate their thermodynamic and kinetic regulation under

varied conditions, underpinning the development of next-generation efficient, low-cost, stable deacidification technologies.

5. Mechanism of Deacidification Reaction and Problem Analysis

5.1. SO₂ Removal Reaction Mechanism and Core Bottlenecks

SO₂ removal is primarily achieved via the neutralization reaction between SO₂ and alkaline deacidification sorbents. According to the differences in reaction temperature regimes and phase behaviors, the deacidification process can be categorized into two fundamental systems: the gas–solid reaction system in the high-temperature zone of MSWI, and the multiphase reaction system in the medium–low temperature regime corresponding to semi-dry/dry deacidification processes [100–102]. These two systems present fundamental differences in reaction pathways, kinetic characteristics, and engineering bottlenecks, and the relevant reaction mechanisms and technical limitations are elaborated separately below.

In the high-temperature environment of ≥ 850 °C within the furnace chamber and the primary and secondary flue ducts of MSWI, both Ca(OH)₂ and CaCO₃ undergo rapid thermal decomposition to generate nascent CaO. The SO₂ removal process follows the classic shrinking core model for gas–solid non-catalytic reactions [103–105], with the core sequential elementary processes listed as follows (Figure 8): (1) external diffusion of SO₂ from the bulk gas phase to the outer surface of CaO particles; (2) internal diffusion of SO₂ through the pore structure of CaO particles to the active sites on the inner surface of the unreacted core; (3) physisorption and chemisorption of SO₂ on the surface active sites of CaO; (4) surface chemical reaction between the adsorbed SO₂ and CaO to generate CaSO₃, and under the oxygen-rich conditions of incineration furnaces, the formed CaSO₃ can be further oxidized to CaSO₄ with stronger thermal stability (MSWI, ≤ 1100 °C) [106]; and (5) lattice reconstruction of the reaction products and solid-state diffusion within the product layer.

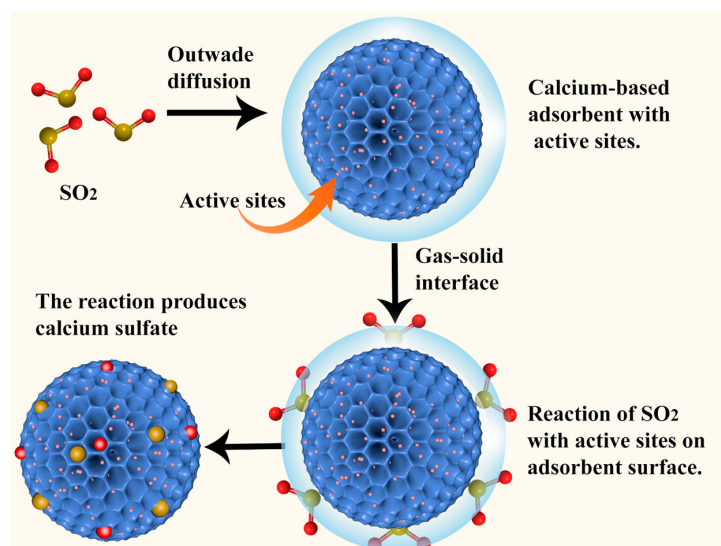
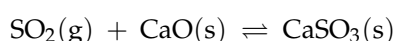
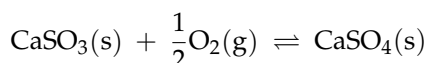


Figure 8. Schematic diagram of the typical dry desulfurization reaction mechanism over Ca-based adsorbent [105].

The core reaction equations are presented as follows:

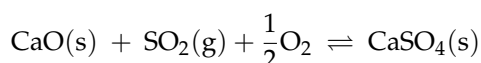




Notably, the main desulfurization reaction between CaO and SO₂ is a typical strongly exothermic reaction. Calculations based on the approximate Gibbs free energy change Equation (1) show that [107,108], under the in-furnace desulfurization conditions of 600–1100 °C in MSWI furnaces, the critical decomposition temperature of the dominant desulfurization product CaSO₄ under actual working conditions is approximately 1200 °C in the oxygen-rich atmosphere corresponding to the actual partial pressures of SO₂ and O₂ in the flue gas. When the furnace temperature exceeds this critical value, the thermodynamic prerequisite for the spontaneous forward reaction disappears, the desulfurization products undergo rapid thermal decomposition, and the desulfurization reaction proceeds completely in the reverse direction [109–112]. However, in practical MSWI operation, the high-temperature deacidification zone exhibits flue gas velocities of 5–10 m/s. Even with calcium-based sorbent injection, the effective reaction temperature generally stays below 850 °C, which is substantially lower than the thermodynamic decomposition threshold of CaSO₄. The persistently low desulfurization efficiency observed under these thermodynamically favorable conditions indicates that thermodynamic factors alone do not govern the overall reaction process.

$$\Delta_r G_m^\theta(T) \approx \Delta_r H_m^\theta - T * \Delta_r S_m^\theta \quad (1)$$

The main reaction for in-furnace calcium injection desulfurization is expressed as:



The thermodynamic parameters for this reaction are adopted from the 298 K standard data in the NIST-JANAF Thermochemical Tables. For engineering calculations within the temperature range of 600–1800 K, the error introduced by neglecting the temperature dependence of molar heat capacity is less than 5%, thus $\Delta_r H_m^\theta$ and $\Delta_r S_m^\theta$ can be reasonably approximated as temperature-independent constants. The relevant thermodynamic parameters are listed in Table 3.

Table 3. Standard thermodynamic parameters of reactants and products at 298 K.

Substance	(kJ/mol)	(J/(mol·K))
CaO (s)	−635.09	39.75
SO ₂ (g)	−296.83	248.22
O ₂ (g)	0	205.14
CaSO ₄ (s)	−1434.11	106.70

Data source: NIST-JANAF Thermochemical Tables (2023 edition).

Based on these data, the standard molar enthalpy change and the standard molar entropy change of the in-furnace calcium injection reaction are calculated as:

$$\Delta_r H_m^\theta = \Delta_f H_m^\theta(\text{CaSO}_4) - \Delta_f H_m^\theta(\text{CaO}) - \Delta_f H_m^\theta(\text{SO}_2) - \frac{1}{2} \Delta_f H_m^\theta(\text{O}_2) = -502.19 \text{ KJ/mol}$$

$$\Delta_r S_m^\theta = S_m^\theta(\text{CaSO}_4) - S_m^\theta(\text{CaO}) - S_m^\theta(\text{SO}_2) - \frac{1}{2} S_m^\theta(\text{O}_2) = -283.84 \text{ J/(mol * K)}$$

When the reaction reaches thermodynamic equilibrium, $\Delta_r G_m^\theta(T) = 0$, and substituting into Equation (1) yields a critical decomposition temperature of approximately 1769 K (1496 °C) under standard conditions ($p_{\text{SO}_2} = p_{\text{O}_2} = 1 \text{ bar}$).

$$T_\theta = \frac{|\Delta_r H_m^\theta|}{|\Delta_r S_m^\theta|} = \frac{502190}{283.84} \approx 1769 \text{ K} \approx 1496 \text{ °C}$$

However, the flue gas composition in actual MSWI furnaces differs significantly from standard conditions, with SO₂ partial pressures ranging from 5×10^{-5} to 5×10^{-4} bar (50–500 ppm) and O₂ partial pressures ranging from 0.04 to 0.12 bar (4–12%). Therefore, the Gibbs free energy change under non-standard conditions must be corrected using the van't Hoff isotherm (Equation (2)):

$$\Delta_r G_m(T) = \Delta_r G_m^\theta(T) + RT \ln Q \quad (2)$$

where the reaction quotient $Q = \frac{1}{p_{\text{SO}_2} * p_{\text{O}_2}^{1/2}}$ (the activity of pure solids is taken as unity).

Setting $\Delta_r G_m^\theta(T) = 0$ at equilibrium and combining with Equation (1) gives the general expression for the actual critical decomposition temperature T_C as Equation (3):

$$T_C = \frac{|\Delta_r H_m^\theta|}{|\Delta_r S_m^\theta| - R(\ln p_{\text{SO}_2} + \frac{1}{2} \ln p_{\text{O}_2})} \quad (3)$$

The calculation results for typical MSWI operating conditions are presented in Table 4. Under these conditions, the thermodynamic equilibrium decomposition temperature of CaSO₄ ranges from 1050 to 1138 °C, far exceeding the practical operating range of in-furnace calcium injection desulfurization. However, operational data reveal that desulfurization efficiency deteriorates significantly once temperatures exceed 850–900 °C. It is crucial to emphasize that surpassing this practical threshold does not alter the thermodynamic equilibrium direction or directly induce CaSO₄ decomposition. Rather, the observed efficiency decline is primarily governed by kinetic constraints, as elaborated below.

Table 4. Critical decomposition temperatures of CaSO₄ under typical MSWI operating conditions.

p_{SO_2} (bar)	p_{O_2} (bar)	Thermodynamic Equilibrium T_C (°C)
5×10^{-4}	0.12	1138
3×10^{-4}	0.1	1118
2×10^{-4}	0.08	1102
1×10^{-4}	0.06	1076
5×10^{-5}	0.04	1050

Notes: Thermodynamic equilibrium temperatures calculated by Equation (3) using parameters from Table 3.

The specific mechanisms are as follows:

- (1) High-temperature sintering and deactivation: At elevated temperatures, CaO undergoes irreversible sintering, resulting in grain growth and pore collapse, which drastically reduces the number of available active sites;
- (2) Product layer diffusion barrier: The molar volume of the reaction product CaSO₄ is approximately 3.2 times that of CaO. It rapidly fills the internal pores of the CaO particles and forms a dense shell on the surface, blocking the diffusion pathways for SO₂ to reach the unreacted core;
- (3) Non-equilibrium residence time: The actual gas–solid residence time within the furnace is only 0.5–2 s, which is far too short for the reaction system to reach thermodynamic equilibrium.

From the perspective of mass transfer and reaction kinetics, elevated temperature exerts dual opposing effects on the desulfurization process. On the one hand, increasing the temperature enhances the gas-phase molecular diffusion coefficient and reduces the gas film boundary layer thickness, further weakening the external diffusion (gas film mass transfer) resistance of SO₂ [113]. Concurrently, in accordance with the Arrhenius Equation (4),

temperature exponentially increases the surface chemical reaction rate constant, exerting a consistent positive effect on the intrinsic reaction kinetics.

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

On the other hand, a quantitative analysis based on typical industrial operating conditions of MSWI furnaces (50 μm calcium-based sorbent particles, flue gas velocity of 5 m/s, atmospheric pressure) confirms that at temperatures above 700 °C, external gas–solid mass transfer actually constitutes the rate-limiting step in the deacidification process. The external mass transfer coefficient (k_g) is calculated using the widely recognized classic Ranz–Marshall correlation (Equation (5)), which is applicable for single-particle gas–solid mass transfer calculations:

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \quad (5)$$

where $Sh = \frac{k_g d_p}{D_{AB}}$ (Sherwood number), $Re = \frac{\rho v d_p}{\mu}$ (particle Reynolds number), $Sc = \frac{\mu}{\rho D_{AB}}$ (Schmidt number), d_p is the sorbent particle diameter, and D_{AB} is the gas-phase molecular diffusion coefficient of SO_2 in flue gas.

The Damköhler number (D_a), a dimensionless group representing the ratio of the characteristic time scale of physical transport to that of chemical reaction, serves as a fundamental criterion for identifying the rate-controlling step. While the general definition encompasses various transport processes, in the context of this study, focusing on external mass transfer limitations, D_a is specifically defined as the ratio of the intrinsic reaction rate (k_s) to the external mass transfer coefficient (k_g) (Equation (6)):

$$D_a = \frac{k_s}{k_g} \quad (6)$$

The corresponding rate-controlling regimes are classified as follows:

- (1) When $D_a \gg 1$, the intrinsic chemical reaction rate is far higher than the external mass transfer rate. The overall deacidification process is external mass transfer-limited, and the surface neutralization reaction proceeds nearly instantaneously once SO_2 molecules reach the sorbent surface;
- (2) When $D_a \approx 1$, the characteristic time scales of chemical reaction and external mass transfer are comparable. The process is co-controlled by both kinetics and mass transfer, and neither factor can be simplified or neglected;
- (3) When $D_a \ll 1$, external mass transfer proceeds much faster than the surface chemical reaction. The overall process is kinetically controlled, and external diffusion resistance can be completely ignored.

The calculation results for key parameters at typical furnace temperatures are summarized in Table 5.

Table 5. Quantitative calculation of mass transfer and kinetic parameters for in-furnace calcium desulfurization.

Temperature (°C)	SO_2 Molecular Diffusion Coefficient (cm^2/s)	External Mass Transfer Coefficient (m/s)	Intrinsic Reaction Rate Constant (m/s)	Damköhler Number
600	~0.84	~5.09	~0.1	~0.02
700	~1.02	~5.97	~1.0	~0.17
800	~1.21	~6.91	~10	~1.45
900	~1.42	~7.90	~50	~6.33
1000	~1.63	~8.94	~100	~11.20

Data sources: NIST Chemistry WebBook; Full computational details are available in Supplementary Materials.

As shown in Table 5, when the temperature exceeds 700 °C, the D_a exceeds 10, indicating that the intrinsic reaction rate surpasses the mass transfer rate. Under these conditions, external mass transfer instead becomes the critical limiting factor and cannot be neglected.

More critically, high furnace temperatures induce irreversible sintering of nascent CaO, causing grain growth, pore structure collapse, and a drastic reduction in specific surface area and active site density, which severely impedes the intra-pore diffusion of SO₂. Compounding this structural degradation, the reaction products CaSO₃ and CaSO₄ have molar volumes 2.7 and 3.2 times that of CaO, respectively. This significant volume expansion rapidly fills the internal pores of CaO particles and forms a dense, impermeable product layer on the particle surface. This synergistic effect of sintering-induced pore closure and product layer blockage drastically exacerbates internal diffusion resistance, which becomes the dominant rate-controlling step in the middle and late stages of the desulfurization reaction. Thus, the high-temperature in-furnace desulfurization process via calcium injection is constrained by the coupled effects of external mass transfer, internal diffusion mass transfer, and calcium sulfite instability. Despite its inherent advantage in the source control of acid gases, the technology still suffers from a persistently low practical desulfurization efficiency.

In the medium-low temperature range of 130–250 °C, corresponding to dry and semi-dry (Figure 9) deacidification processes, the efficient reaction of SO₂ with calcium-based deacidification sorbent Ca(OH)₂ and sodium-based deacidification sorbent NaHCO₃ is strictly dependent on the participation of trace water molecules in the flue gas. The reaction pathways of both sorbents follow the classic gas–liquid–solid multiphase reaction mechanism [114–116]. Taking the mainstream sorbent Ca(OH)₂ as an example, water molecules in the flue gas form a nanoscale thin liquid film on the surface of Ca(OH)₂ particles. SO₂ diffuses to the interface of the liquid film, then dissolves and hydrates rapidly to form sulfurous acid, followed by a neutralization reaction with dissolved Ca(OH)₂ in the liquid film. The stepwise reaction equations are as follows:

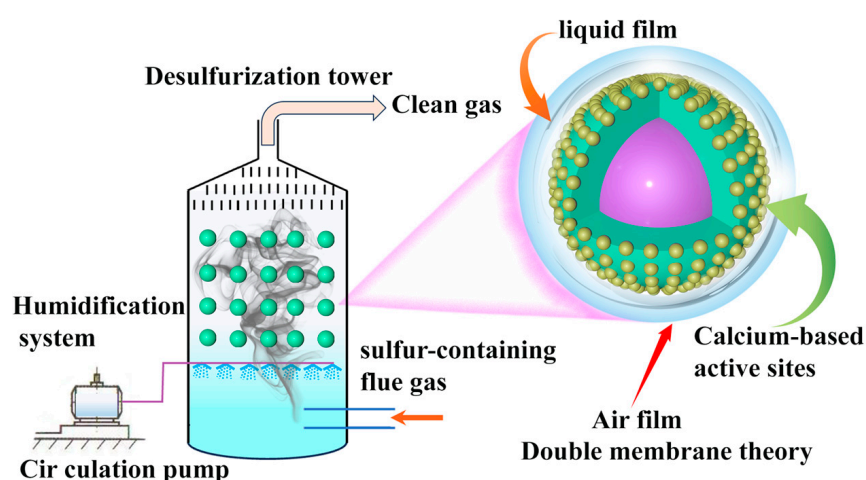
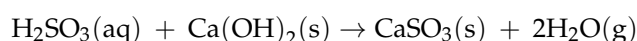
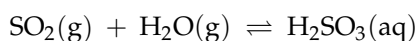


Figure 9. The fundamental mechanisms of the semi-dry desulfurization process [116].

The semi-dry desulfurization process follows the classical dual-film theory [116] (Figure 8): SO₂ diffuses through the gas film, dissolves in the aqueous film on Ca-based sorbent particles, and reacts with Ca(OH)₂. The overall reaction rate is co-controlled by

external diffusion, SO₂ dissolution, internal ion diffusion, and interfacial neutralization. Unlike high-temperature in-furnace desulfurization, CaSO₃ formed at medium-low temperatures is thermally stable. Nevertheless, the desulfurization efficiency is still restricted by the coupling of three inherent bottlenecks:

1. The coupling limitation of mass transfer and reaction in the multi-step sequential process, where the rate limitation of any individual step will reduce the overall reaction efficiency;
2. The significantly slowed intrinsic reaction rate at medium-low temperatures: coupled with the limited flue gas residence time in the reactor in practical engineering, insufficient effective gas–solid contact time prevents the reaction from reaching thermodynamic equilibrium, which directly limits the upper limit of desulfurization efficiency;
3. The remarkably higher reactivity of HCl with alkaline deacidification sorbents than that of SO₂: HCl will preferentially occupy the alkaline active sites on the sorbent surface, exerting a strong competitive inhibition effect on SO₂ removal (Figure 10a).

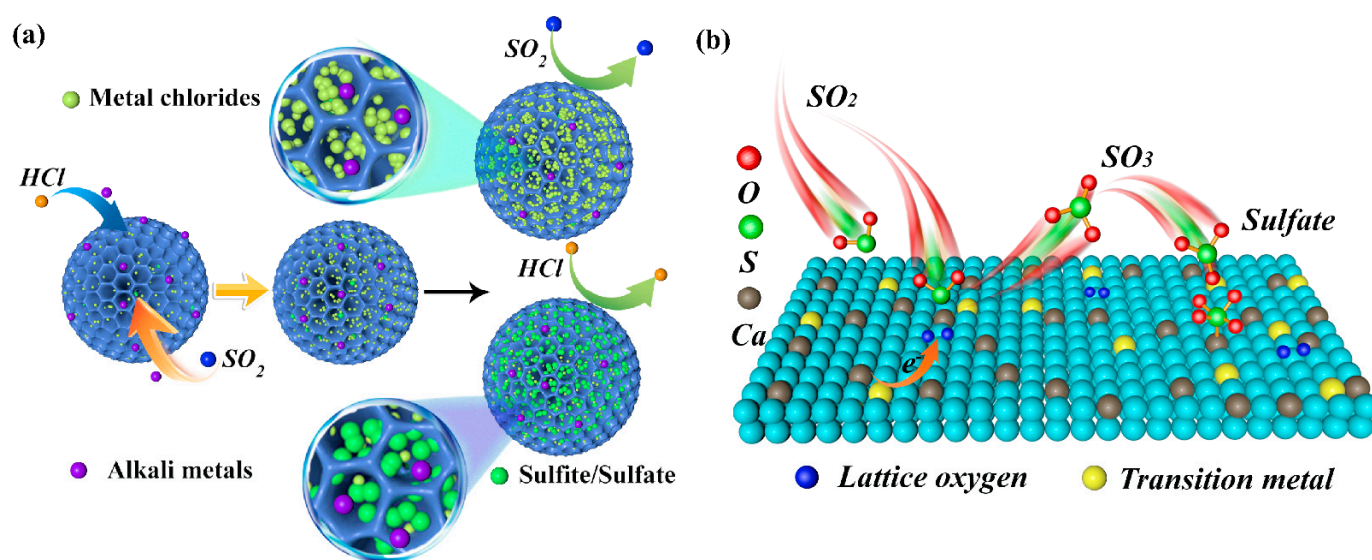
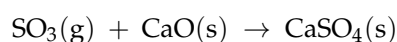


Figure 10. (a) Reaction of SO₂ and HCl with active sites in the medium-low temperature range. (b) Catalytic oxidation of SO₂ via the introduction of transition metal oxide catalytic oxidation sites.

The combined effect of the above multiple bottlenecks results in the requirement of excessive dosage of deacidification sorbents in engineering applications to ensure stable and compliant removal of SO₂.

To address the aforementioned flue gas desulfurization bottlenecks, reaction pathway optimization via introducing catalytically active transition metal oxide sites is developed for efficient and stable SO₂ removal (Figure 10b). This strategy catalytically oxidizes SO₂ to SO₃, simplifying the traditional multi-step reaction into two core reactions (equations below), with the SO₃–alkaline sorbent reaction featuring lower activation energy and faster kinetics than conventional SO₂-involved reactions [117–121].



Within the defined operational window of MSWI (≤ 1100 °C), the generated CaSO₄ exhibits thermal stability, effectively mitigating SO₂ re-emission risks comparable to those triggered by CaSO₃ decomposition [106]. This establishes a viable strategy for high-efficiency

deacidification, while also alleviating kinetic limitations arising from limited gas–solid contact time in downstream medium-to-low temperature treatment processes.

Shi et al. achieved a sulfur capacity of 234.80 mg/g at 380 °C over Cu-modified CaO via pre- and post-synthesis modification, with DFT calculations revealing efficiency restrictions from adsorption saturation and competitive acid gas adsorption. Yang et al. [122], Ma et al. [123] and Ye et al. [124] further verified excellent SO₂ catalytic oxidation performance of manganese-based oxides, with α -MnO₂ exhibiting the lowest reaction energy barrier and highest sulfur capacity (304.11 mg/g).

Despite the enhanced SO₂ removal efficiency, large-scale engineering application is still restricted by three core constraints: high preparation cost of modified sorbents, aggravated tail flue equipment corrosion from SO₃-induced acid dew point reduction, and catalyst deactivation via active site coverage by high-concentration furnace fly ash.

5.2. Removal Characteristics of HCl

The reaction between HCl and alkaline deacidification sorbents is a typical exothermic acid–base neutralization reaction. Compared with the multi-step gas–solid reaction of SO₂, its reaction pathway is simpler without additional hydration and oxidation processes. Based on thermodynamic and reaction kinetic analyses, the intrinsic activation energy of this reaction is significantly lower than that of the reaction between SO₂ and deacidification sorbents, and its standard Gibbs free-energy change is more negative with a stronger thermodynamic driving force. Thus, the intrinsic reaction kinetic rate of HCl is much higher than that of SO₂ under identical working conditions [125], which enables HCl to preferentially occupy the surface alkaline active sites of the sorbents and exert a strong competitive inhibition effect on SO₂ removal (Figure 11).

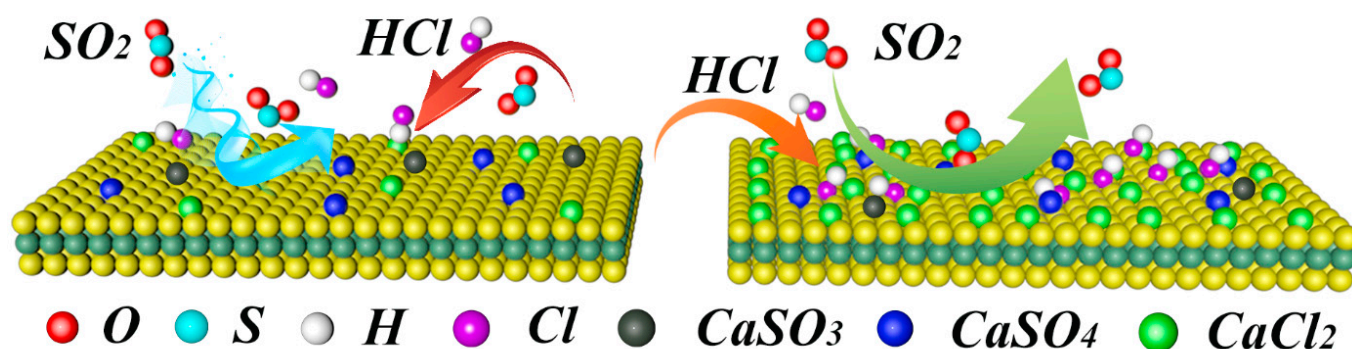


Figure 11. Competitive adsorption between HCl and SO₂.

Consistent with experimental investigations and engineering practices, the gas–solid reaction between HCl and Ca(OH)₂ or CaO exhibits a significant active temperature window effect: the deacidification sorbents present the highest surface alkaline activity and the fastest gas–solid mass transfer rate in the range of 300–400 °C, which is identified as the optimal reaction temperature range for HCl removal.

As described previously, the reaction products of SO₂ and calcium-based deacidification sorbents can rapidly fill the internal pores of sorbent particles and form a dense product layer on the particle surface, resulting in a sharp decline in the specific surface area and the number of available active sites of the sorbents. This not only limits the removal of SO₂ itself, but also further hinders the contact between HCl and the active sites inside the particles, aggravating the attenuation of deacidification efficiency. Therefore, based on the above-mentioned competitive reaction characteristics between HCl and SO₂, the product-induced pore-blockage effect, and their differentiated optimal reaction

temperature ranges, a staged temperature-gradient deacidification strategy can be adopted in engineering to achieve the efficient and synergistic removal of the two acid gases. In the high-temperature zone (≥ 850 °C) of the primary and secondary flue ducts of the furnace, the aforementioned strategy of “transition metal catalytic oxidation coupled with calcium-based acid-base immobilization” is applied to achieve efficient source removal of SO_2 . In the optimal medium-temperature window of 300~400 °C [126] at the economizer section of the boiler, calcium-based deacidification sorbents are precisely injected to achieve targeted and efficient removal of HCl, ultimately avoiding the competitive adsorption and cross-inhibition effects between the two acid gases.

5.3. Deacidification Material Modification and Process Optimization

Based on the above analysis of the reaction mechanism, core bottlenecks, and regulation strategies of flue gas deacidification from municipal solid waste incineration, the breakthrough of future flue gas deacidification technologies relies on the collaborative innovation of material design and process optimization, with three core development directions as follows:

1. Development of bifunctional composite deacidification sorbents: Transition metal catalytic oxidation components (such as Fe_2O_3 , MnO_2 , CuO , V_2O_5 , etc.) are introduced into the calcium-based matrix to construct bifunctional composite deacidification sorbents with both alkaline reactive sites and catalytic oxidation sites, which enables in situ catalytic oxidation and stable solid-phase immobilization of SO_2 , and fundamentally breaks the thermodynamic and kinetic bottlenecks of traditional calcium-based materials. Meanwhile, the synergistic capture efficiency of multi-component acid gases is further improved via regulating the microscopic pore structure of the material and optimizing the high dispersion of active sites (Figures 12a and S1–S3);
2. Optimization of staged temperature-gradient deacidification process: Combined with the full-process flue gas temperature gradient characteristics of the boiler, a staged deacidification strategy of “preferential SO_2 removal via deep oxidation in the ≥ 850 °C high-temperature zone + targeted HCl removal in the 300~400 °C medium-temperature zone + deep purification in the 130~250 °C medium-low temperature zone” is adopted. Highly selective removal of HCl is achieved in the optimal active temperature range of 300~400 °C, and deep conversion of SO_2 is realized via catalytic oxidation assistance in the furnace and semi-dry reaction tower. Meanwhile, gas–solid mass transfer enhancement methods such as swirl injection and nano atomization are applied to compensate for the kinetic and mass transfer defects of traditional processes, including insufficient intrinsic reaction rate and inadequate gas–solid contact (Figure 12b);
3. Full-process collaborative system integration: The in-furnace high-temperature deacidification, tail medium-low temperature deacidification, and intelligent precise injection control technology linked with on-line flue gas monitoring are systematically integrated. Combined with the real-time changes of furnace combustion conditions, flue gas components and concentrations, dynamic adaptive regulation of the injection position, dosage, type and formula of deacidification sorbents is realized. On this basis, a full-process collaborative, efficient and low-carbon deacidification technology system is constructed, which realizes the organic combination of source control and ending deep purification of acid gases while reducing the excessive dosage ratio of deacidification sorbents and the output of by-product solid waste (Figure 12c).

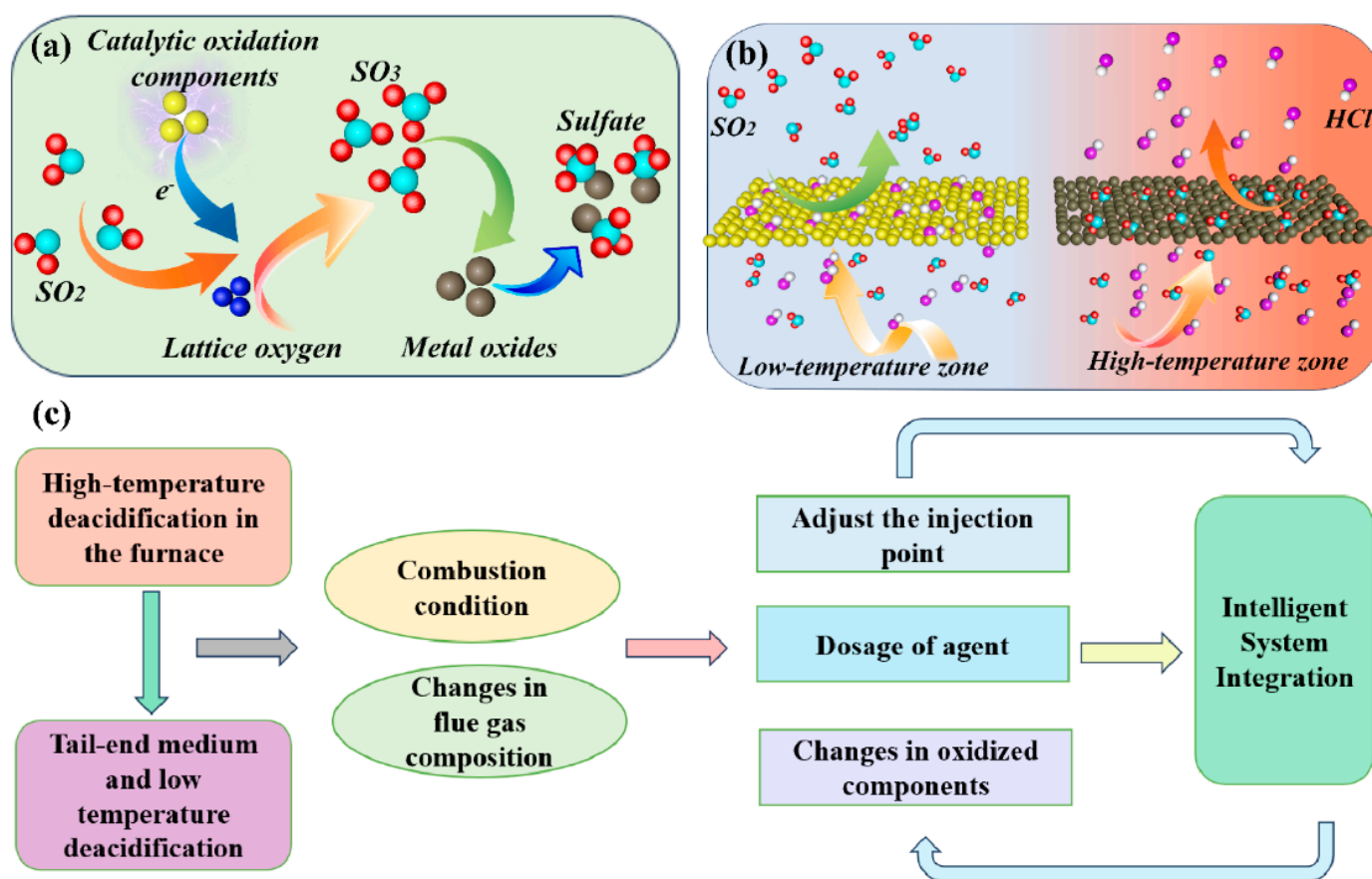


Figure 12. (a) Deacidification pathway of bifunctional composite sorbents, (b) schematic diagram of staged deacidification, (c) full-process system integration.

6. Conclusions

Municipal solid waste incineration (MSWI) for power generation is the dominant approach for municipal solid waste disposal in China, whose high-quality development is restricted by three core challenges induced by acidic flue gas components: equipment corrosion, insufficient multi-pollutant synergistic purification, and increased deacidification by-product fly ash. Efficient and low-carbon removal of HCl and SO_2 is the core to address these challenges. Current mainstream wet, semi-dry, and dry deacidification technologies can achieve ultra-low acid gas emissions, but fail to balance efficiency, cost, and environmental load, restricted by bottlenecks including limited intrinsic kinetics, poor product thermal stability, low sorbent utilization, and multi-component competitive adsorption. In-furnace calcium injection, despite the advantages of source control and short process, is limited by $CaSO_3$ thermal decomposition, sorbent sintering deactivation, and competitive adsorption.

Reaction pathway optimization via the introduction of transition metal catalytic sites to directionally oxidize SO_2 to SO_3 , which forms ultra-stable $CaSO_4$ with calcium-based sorbents, can thermodynamically eliminate SO_2 secondary release, reduce activation energy, and accelerate intrinsic reaction kinetics, serving as the core pathway to break through in-furnace deacidification bottlenecks. Combined with the differentiated optimal temperature windows of HCl and SO_2 , a staged temperature-gradient synergistic deacidification strategy can achieve targeted removal of HCl and SO_2 , alleviate competitive adsorption, and improve sorbent utilization.

Future breakthroughs in MSWI deacidification technology will focus on four core directions: (1) Development of low-cost bifunctional sorbents: industrial solid wastes such

as red mud and fly ash are adopted as the matrix, and bifunctional sites with high alkaline activity and catalytic oxidation are constructed via in situ loading of transition metals. This approach reduces raw material costs by over 30% while leveraging high-temperature stable phases to suppress sintering and deactivation; (2) multi-field coupling intensification of gas–solid reactions: injection points and feeding methods are differentiated according to furnace structural characteristics, and a multi-dimensional coupled field of temperature, velocity, and concentration is formed inside the combustion chamber, which lowers mass transfer resistance and optimizes the gas–solid reaction pathway from the mechanism perspective; (3) system integration of in-furnace and tail-end synergy: implementing a staged gradient temperature control strategy, the in-furnace process undertakes over 70% of the deacidification load, significantly reducing reagent consumption at the tail end, which, when integrated with tail-end processes to ensure ultra-low emissions, reduces fly ash output by 20–25%, balancing source control with end purification; and (4) full-process intelligent precision regulation: based on a multi-parameter real-time monitoring platform, closed-loop feedback algorithms are employed to dynamically match sorbent dosage with transient flue gas loads. This strategy cuts excessive sorbent usage by 10–20%, achieving low-carbon and low-consumption operation throughout the entire process.

Aligned with China's Dual Carbon goals and Waste-Free City initiative, MSWI deacidification technologies must simultaneously meet ultra-low emission requirements, reduce operational costs, cut carbon footprints, and minimize solid waste output. A high-efficiency, low-cost full-process synergistic deacidification system enabled by mechanism innovation, material breakthroughs, system integration and intelligent upgrading will provide critical support for the high-quality growth of China's MSWI industry.

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