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Avoiding PCDD/F Formation in Metal Chloride–Based Chlorination–Calcination Processes: Mechanisms, Risk Factors and Best Available Practices

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Abstract

Metal chloride–based chlorination–calcination routes are increasingly being revisited for processing complex ores, secondary resources, and metallurgical residues due to their high selectivity and compatibility with circular-economy strategies. However, the coexistence of chlorine species, transition metals, carbonaceous matter, and intermediate temperatures can favor the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), raising critical environmental and regulatory concerns. This critical review examines the fundamental chemical mechanisms governing PCDD/F formation in chlorination–calcination systems, with emphasis on precursor pathways, de novo synthesis on particulate surfaces, and the catalytic role of metal chlorides such as Cu, Fe, and Ni. Key operational risk factors—including temperature windows, oxygen potential, residence time, chlorine activity, and the nature of carbon sources—are systematically analyzed across laboratory, pilot, and industrial contexts. Building on this mechanistic framework, the review evaluates best available practices (BAPs) for PCDD/F prevention, including feed pretreatment, process atmosphere control, temperature management, catalyst suppression, rapid quenching, and off-gas treatment strategies. By integrating thermochemical insights with process engineering and environmental control perspectives, this work provides a rigorous basis for designing chlorination–calcination flowsheets that minimize PCDD/F formation while preserving metallurgical efficiency and regulatory compliance.

Keywords. PCDD/F; chlorination–calcination; dioxin formation; de novo synthesis; precursor pathways; best available practices

Highlights

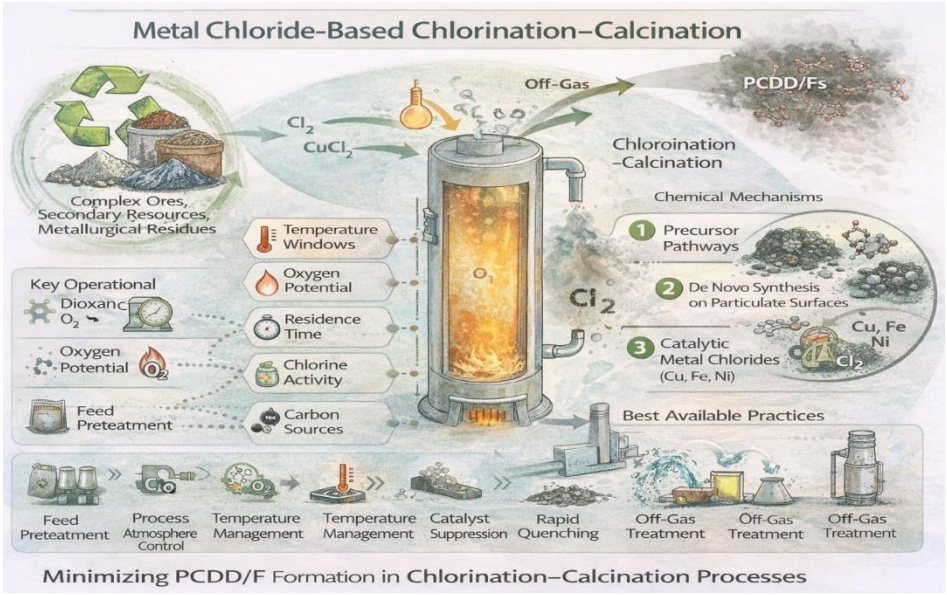
- Critically analyzes PCDD/F formation mechanisms specific to metal-chloride–based chlorination–calcination processes
- Identifies key thermochemical and operational risk factors that control dioxin and furan generation

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- Discusses the catalytic role of transition-metal chlorides and particulate carbon in de novo synthesis
- Reviews best available practices for PCDD/F prevention at process and off-gas levels
- Provides design-oriented guidance for environmentally robust chlorination–calcination flowsheets.

Graphical abstract



1. Introduction

Metal chloride–based chlorination–calcination routes are being re-examined in modern extractive metallurgy for practical reasons. Chlorination improves selectivity, streamlines flowsheets, reduces water use, and avoids large effluent circuits. A recent synthesis of “chlorine metallurgy” reflects this renewed momentum (Xue et al., 2024). Additionally, interest in chloride routes for complex ores, residues, and secondary resources has grown, driven by circular-economy goals.

Innovation accelerates progress, with high-intensity methods like electrothermal chlorination proposed for rapid metal separation. These alter residence times and temperature profiles, thereby shifting the locations of reactive chlorine species (Deng et al., 2024). While improving efficiency, they may also move emission-relevant chemistry to less obvious zones.

This revival has a notable weakness. PCDD/F formation is rarely treated as a design constraint in chlorination–calcination studies. This gap is evident even in broad reviews of chlorination roasting of solid wastes, where emission chemistry is not the

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main focus (Ge et al., 2022). Yet the ingredients for PCDD/F synthesis can coexist in chloride-based routes. Reactive chlorine is present. Fine particulate surfaces are generated. Transition metals and carbonaceous residues may be mobilized into off-gas circuits.

Mechanistically, the risk is not obscure. PCDD/Fs form via precursor pathways and surface-mediated routes. Surface chemistry is central to many thermal systems. Laboratory studies show that chlorinated aromatics can yield PCDD/F on metal oxide–bearing surfaces while generating persistent radicals (Chen, Sun, et al., 2020). Kinetic and modeling work confirm that formation and destruction compete within narrow temperature windows, especially during cooling and filtration (Stanmore, 2021). Evidence from gasification and pyrolysis further indicates that reducing atmospheres alone do not eliminate formation potential (Safavi et al., 2022; Sørmo et al., 2024).

Chloride metallurgy's process involves chlorination–evaporation steps that concentrate volatile metal chlorides and redistribute catalytic species across dust streams, modifying the reactive inventory in ducts, cyclones, and baghouses (Hamann et al., 2024). PCDD/F emissions are not exclusive to incineration; secondary copper and other high-temperature metallurgical processes also release these chlorinated pollutants in stack gases (Dat et al., 2020). Studies show these compounds favor associating with fine particulates and residues, not remaining evenly in the gas phase (Ren et al., 2020).

Control technologies are well established. Activated carbon remains a benchmark for PCDD/F capture in flue gas, depending on surface properties and operating conditions (Ding et al., 2023; Gao et al., 2024). Catalytic oxidation reactors provide destruction instead of capture, expanding control options (Duan et al., 2024). Operational measures like flue gas recirculation can indirectly reduce formation by stabilizing temperature and oxygen levels (Li, C. et al., 2023). However, these are reactive and don't replace prevention.

Beyond compliance, PCDD/Fs serve as environmental tracers, helping reconstruct emission sources and process histories, emphasizing upstream control (Bellucci & Giuliani, 2023). Evidence shows chlorinated organics can form on mineral dust atmospherically, extending relevance beyond plants (Chen, M. et al., 2025). These findings support process-level prevention.

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This review explores PCDD/F formation in metal chloride–based chlorination–calcination, focusing on prevention. It aims to consolidate mechanistic knowledge, identify controllable risks, and evaluate practices that prioritize preventing formation over remediation. This aligns efficiency with standards and sustainability, including the use of dioxin-free materials (Aysa, 2025).

The next section outlines the review methodology. It defines the search strategy, inclusion criteria, and the framework for classifying evidence. It also explains how each reference is mapped to text, tables, or figures, ensuring traceability across the full bibliography.

2. Methodology

This review followed PRISMA 2020 guidelines for transparency and reproducibility (Page et al., 2021). A brief version of PRISMA was applied, suited for a critical narrative review rather than a meta-analysis.

2.1. Literature search and data sources

A literature search was conducted on Web of Science, Scopus, and Google Scholar, covering 2000 to early 2025. Core search terms included chlorination, calcination, metal chlorides, PCDD/F, dioxin formation, de novo synthesis, and off-gas control. Additional records were obtained through backward citation tracking of key reviews and process papers.

2.2. Eligibility criteria

Studies were included when they met at least one of the following conditions:

(i) direct discussion of PCDD/F formation mechanisms under thermal or chlorinated conditions.

(ii) experimental or industrial evidence of PCDD/F formation, suppression, or partitioning.

(iii) relevance to chloride-assisted thermal processing, metallurgical roasting, calcination, or off-gas treatment.

Studies that focused solely on toxicology, biomonitoring, or analytical detection, without process relevance, were excluded. Regulatory documents were considered only when they provided mechanistic or design-relevant insight.

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2.3. Screening and selection

Titles and abstracts were initially screened to exclude unrelated material. Full texts were then assessed for mechanistic depth and relevance to chloride-based thermal systems. Disagreements were resolved by prioritizing process relevance and transferability to metallurgical contexts.

At the end of this process, 92 references were retained and consolidated. All references in the final list are explicitly cited in the text, tables, or figures, ensuring full traceability.

2.4. Data extraction and synthesis

Information was qualitatively extracted and organized into thematic categories: s:

(i) fundamental mechanisms of PCDD/F formation.
(ii) surface-mediated and *de novo* pathways.
(iii) process-specific risk factors in chlorination–calcination systems.
(iv) prevention and control strategies.

No statistical pooling was performed. Instead, emphasis was placed on mechanistic consistency, process analogies, and engineering implications, consistent with the objectives of a critical review.

Figure 1 shows the PRISMA 2020 flow diagram used in this review. It summarizes the identification, screening, eligibility assessment, and final inclusion of literature, providing transparency into the selection process that yielded 92 references. This structured approach ensures traceability, rigor, and alignment with best practices for systematic reviews.

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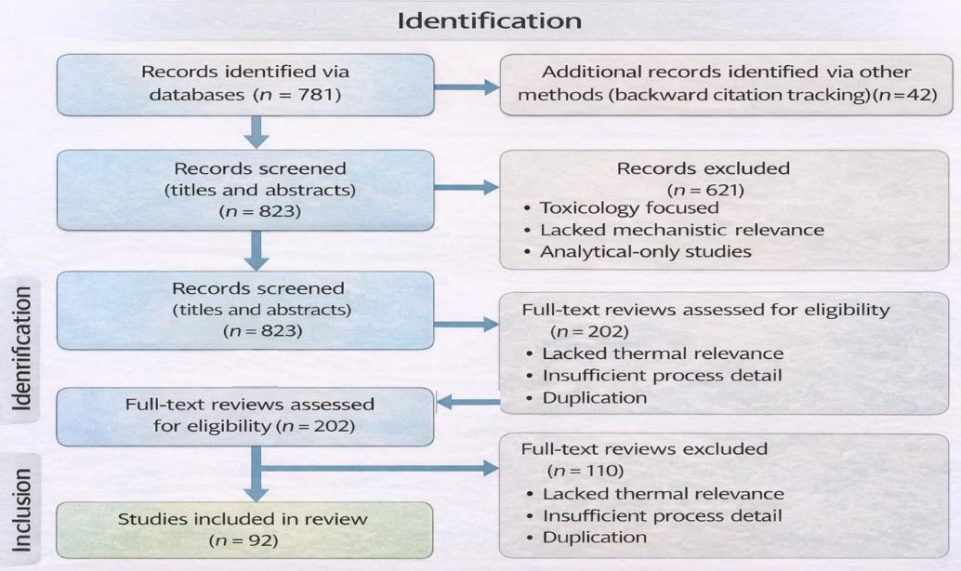


Figure 1. PRISMA 2020 flow diagram summarizing literature identification, screening, eligibility, and inclusion steps used in this review. Adapted from Page et al. (2021).

With the methodological framework established, the following section provides an overview of chloride-assisted calcination processes, focusing on how chlorine chemistry is applied at the process level and on the conditions under which conditions relevant to PCDD/F formation may arise.

3. Overview of chloride-assisted calcination processes

Chloride-assisted calcination employs high temperatures with chlorine to alter phase stability, boost volatility contrast, or facilitate selective reactions during heat treatment. Widely used in mineral processing, residue valorization, and extractive metallurgy, its design mainly relies on thermochemistry, reaction kinetics, and reactor configuration, not environmental factors (Xue et al., 2024).

3.1. Types of chlorination–calcination routes

Chlorination–calcination routes can be classified by the chemical form in which chlorine is introduced into the system. The choice of chlorinating agent directly affects reaction pathways, equilibrium constraints, and material compatibility.

Gaseous Cl_2 chlorination is highly reactive, enabling rapid formation of volatile metal chlorides, ideal for high selectivity and quick reactions. However, it requires strict control of gas–solid contact and the use of corrosion-resistant materials. (Bruffey et al., 2021; Deng et al., 2024)

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Gaseous HCl chlorination offers a milder alternative. Chlorination proceeds via acid–base and redox-assisted mechanisms. This route is commonly used when partial chlorination is sufficient or when Cl_2 handling is undesirable (Liu et al., 2023; Höber et al., 2022).

Solid metal chlorides, like alkali and alkaline-earth chlorides, act as internal chlorinating agents. They release chlorine in situ or form complexes for selective reactions, offering operational simplicity and compatibility with solid–solid processing (Guo et al., 2021; Gong et al., 2022).

Thermodynamic driving forces vary substantially across these routes. Chlorination with Cl_2 generally yields the most negative Gibbs free energy for oxide conversion. HCl-based systems are more sensitive to oxygen potential. Solid chlorides depend strongly on melting behavior and activity coefficients (Shamsuddin, 2021).

Compare chlorinating agents, reaction pathways, and thermochemical drivers for chloride-assisted calcination. Although all aim to transform or volatilize metals, their chlorine activity, reaction control, and robustness differ. Table 1 summarizes key features of common chlorination–calcination methods, aiding future risk and PCDD/F discussions.

Table 1. Comparison of chlorination–calcination routes based on chlorinating agent, dominant reactions, and thermochemical driving forces. Adapted from Shamsuddin (2021) and Xue et al. (2024)

Chlorinating agent	Typical chemical form	Dominant reactions	Thermochemical driving forces	Process implications
Cl_2 (gaseous)	Molecular chlorine (Cl_2)	Direct chlorination of metal oxides and sulfides; formation of volatile metal chlorides	Highly negative $\Delta G°$ for many metal–chloride systems; strong dependence on temperature	High reactivity and fast kinetics; high selectivity for volatile chlorides; requires strict control of gas handling and corrosion-resistant materials
HCl (gaseous)	Hydrogen chloride (HCl)	Acid–base assisted chlorination; redox-coupled reactions with oxides	Moderate thermodynamic driving force; sensitive to oxygen partial pressure and H_2O activity	Milder chlorination; lower corrosion risk than Cl_2; often used for partial or controlled chlorination
Solid metal chlorides	NaCl, KCl, $CaCl_2$, $MgCl_2$	Solid–solid or solid–liquid chlorination; in situ chlorine	Driving force driven by melting behavior, activity	Operational simplicity, compatibility with solid feeds;

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		release; complex formation	coefficients, and local equilibria	effectiveness depends on chloride dosage and phase state.
Chloride mixtures	Alkali/alkaline-earth chloride blends	Flux-assisted chlorination and mineralization	Synergistic lowering of reaction barriers and melting points	Enhanced mass transfer; useful for complex silicates and refractory feeds
Chlorination–reduction systems	Cl_2/HCl + reductant	Coupled chlorination and reduction reactions	Combined chemical potential of Cl and reducing species	Enables selective volatilization under reducing atmospheres; requires tight control of redox balance

The comparison shows that process selection is rarely universal. It depends on feed mineralogy, the target metal, and the downstream separation strategy.

3.2. Role of metal chlorides in mineral processing

Metal chlorides serve multiple functions beyond simple chlorination. Their behavior is strongly dependent on temperature, phase state, and interactions with the mineral matrix.

Chlorides, as fluxing agents, lower melting points and promote liquid-phase formation, boosting mass transfer and speeding up solid–solid reactions. This is used to roast complex silicates and refractory residues (Ge et al., 2022).

Chlorides, as mineralizers, facilitate phase transformation and recrystallization by destabilizing oxide lattices and promoting more reactive intermediates, especially in lithium- and magnesium-bearing minerals (Li, T. et al., 2025; Song et al., 2023).

Chlorides serve as selective chlorinating agents by exploiting differences in volatility. Metals like Zn, Pb, Nb, and Ti can be separated by boiling points of their chlorides (Hamann et al., 2024; Wei et al., 2025).

Interactions with oxides form volatile metal chlorides. Chlorides with silicates may break polymer networks and free metals. In carbonates, chlorination often induces decarbonation, altering gas-phase composition and reaction rates (Guo et al., 2021; Liu et al., 2023).

Metal chlorides do more than chlorinate; they modify calcination by affecting melting, mass transfer, and reactive species at interfaces. Understanding these roles

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is key to their effectiveness and influence on PCDD/F formation. Figure 2 shows their main functions as fluxing agents, mineralizers, and chlorination promoters.

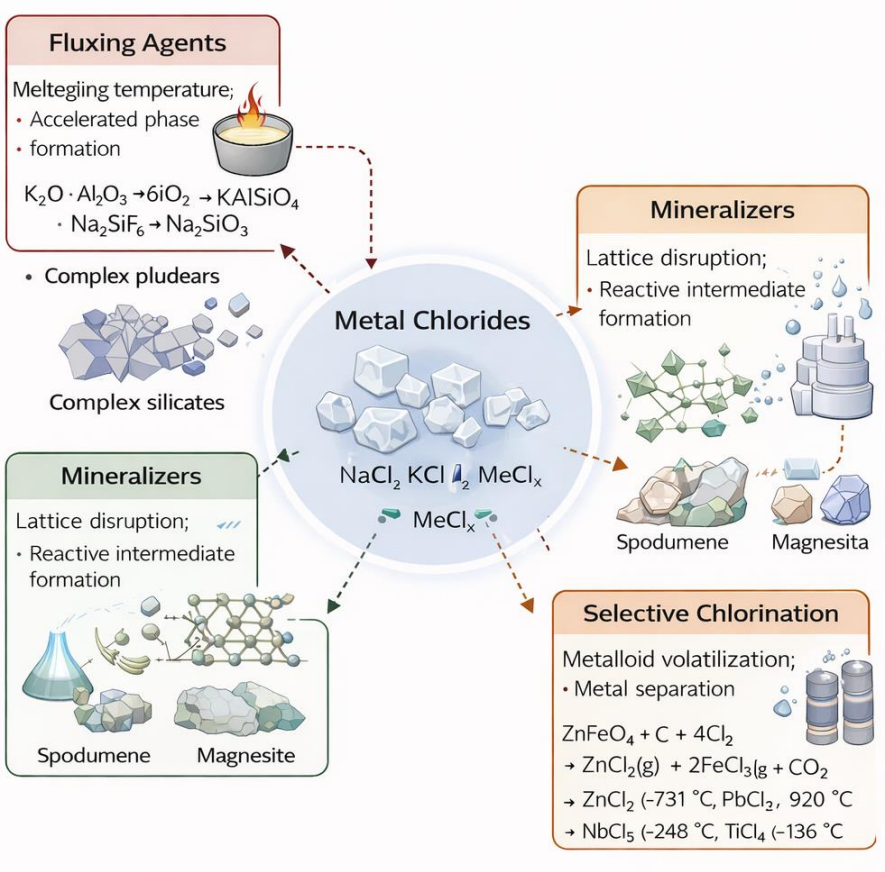


Figure 2. Schematic representation of the roles of metal chlorides in mineral processing: fluxing, mineralization, and selective chlorination pathways. Adapted from Ge et al. (2022).

This multifunctional behavior explains why chlorides are effective even at relatively low dosages.

3.3. Typical operating conditions

Operating conditions for chloride-assisted calcination are governed by chemical and mechanical constraints.

Most industrial and pilot-scale applications operate between 500 and 1000 °C. Lower temperatures favor solid-state reactions and controlled chlorination, whereas higher temperatures promote volatilization and phase separation (Guo et al., 2021; Hamann et al., 2024).

Process atmospheres vary with the objectives. Oxidizing atmospheres stabilize oxides and limit metal reduction. Inert atmospheres decouple chlorination from

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oxidation. Reducing atmospheres are used when simultaneous chlorination and reduction are desired (Hur et al., 2023).

Reactor selection is critical. Rotary kilns are durable with long residence times. Fluidized beds give better gas–solid contact and temperature uniformity. Muffle and fixed-bed furnaces are common at lab and pilot scales for precise control (Bruffey et al., 2021; Pereira, 2025).

The thermal reactor configuration determines how chlorination–calcination reactions proceed and where emission-related chemistry occurs. Reactor type affects gas–solid contact, temperature uniformity, particle entrainment, and residence time, thereby directly influencing the behavior of metal chlorides, particulates, and residual carbon. Figure 3 shows common reactor types in chloride-assisted calcination, highlighting differences in gas–solid interactions and residence time that are vital for metallurgical performance and PCDD/F risk.

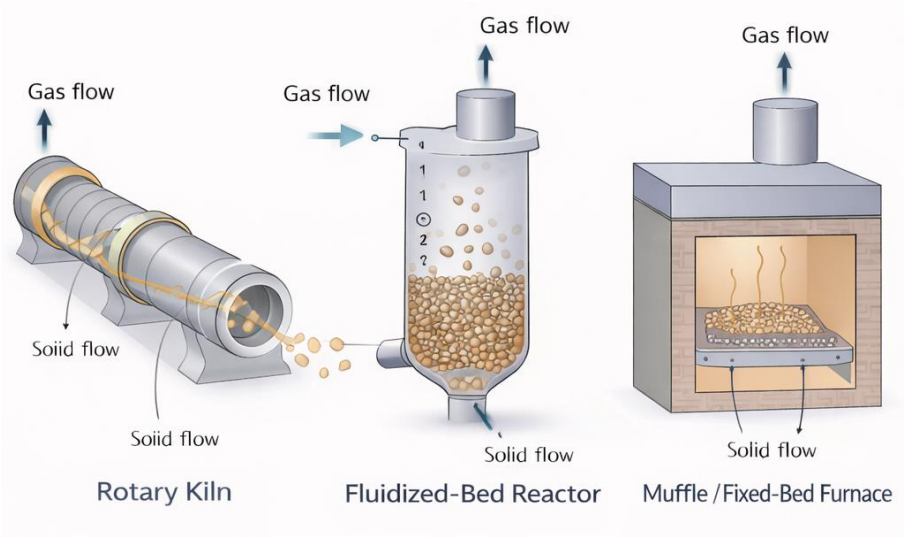


Figure 3. Typical reactor configurations used in chloride-assisted calcination, highlighting differences in gas–solid contact and residence time. Adapted from Bruffey et al. (2021).

These configurations strongly influence reaction extent, selectivity, and scalability.

This process-oriented overview outlines the chemical and operational framework for chloride-assisted calcination. The next section builds on this foundation to examine how these conditions create specific windows for PCDD/F formation, shifting the focus from process efficiency to mechanistic risk analysis.

4. Dioxins and furans: Chemical nature and formation pathways

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PCDD/Fs are persistent organic pollutants formed unintentionally across a wide range of thermal processes. Their relevance in high-temperature industrial systems stems from a combination of chemical stability, extreme toxicity, and regulatory stringency. Understanding their chemical nature and formation pathways is therefore a prerequisite for any prevention-oriented discussion.

To contextualize the formation mechanisms discussed in this section, it is essential to distinguish the basic chemical structures of dioxins and furans. Structural differences between PCDDs and PCDFs govern congener distribution, chlorine substitution patterns, and toxic potency. Figure 4 shows the general molecular frameworks of PCDDs and PCDFs, highlighting the structural features that underpin their behavior in thermal systems.

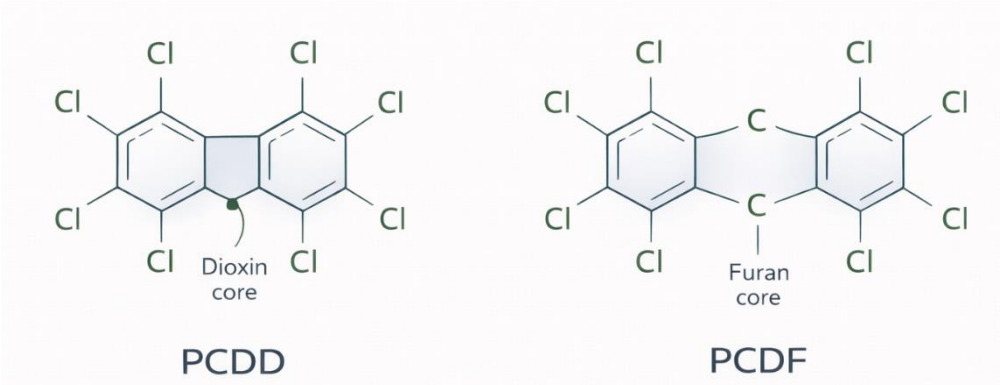


Figure 4. General chemical structures of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Adapted from Stanmore (2021).

4.1. Chemical structure and toxicological relevance of PCDD/F

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are structurally related compounds composed of two aromatic rings linked by oxygen atoms (PCDD) or by an oxygen bridge and a carbon–carbon bond (PCDF). The degree and position of chlorine substitution define individual congeners (Stanmore, 2021). Small structural differences translate into large variations in biological activity.

Not all congeners have the same toxicity. Toxicological relevance is assessed with the toxic equivalency (TEQ) concept, normalizing congener toxicity to 2,3,7,8-TCDD, the most toxic reference. This allows comparing complex emissions using a single weighted indicator (Ren et al., 2020) and supports regulatory limits and risk assessments.

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Table 2 summarizes the toxic equivalency factors (TEFs) assigned to selected PCDD and PCDF congeners and their relevance to regulatory assessment. By weighting individual congeners by their relative toxicity, the TEQ framework provides a standardized basis for comparing emission profiles across processes and operating conditions.

Table 2. Toxic equivalency factors (TEFs) for selected PCDD and PCDF congeners and their regulatory relevance. Adapted from Ren et al. (2020) and Themba et al. (2023).

Compound class	Congener	TEF (WHO)	Regulatory relevance
PCDD	2,3,7,8-TCDD	1.0	Reference compound; highest toxic potency; basis for TEQ calculations
PCDD	1,2,3,7,8-PeCDD	1.0	Major contributor to TEQ in many thermal processes
PCDD	1,2,3,4,7,8-HxCDD	0.1	Relevant in fly ash and off-gas particulate matter
PCDD	1,2,3,6,7,8-HxCDD	0.1	Commonly detected in industrial emissions
PCDD	1,2,3,7,8,9-HxCDD	0.1	Moderate contribution to total TEQ
PCDD	OCDD	0.0003	High mass concentration but low TEQ contribution
PCDF	2,3,7,8-TCDF	0.1	Frequently dominant PCDF congener in thermal systems
PCDF	1,2,3,7,8-PeCDF	0.03	Significant contributor to TEQ in metallurgical off-gas
PCDF	2,3,4,7,8-PeCDF	0.3	One of the most toxic PCDF congeners
PCDF	1,2,3,4,7,8-HxCDF	0.1	Associated with surface-mediated formation pathways
PCDF	1,2,3,6,7,8-HxCDF	0.1	Common in post-combustion particulate fractions
PCDF	OCDF	0.0003	Low toxicity despite frequent detection

The TEQ framework enables comparison of complex emission profiles through a single risk-weighted metric.

International regulations focus on TEQ values rather than total mass, setting emission limits at ng TEQ m^{-3} in industries such as waste treatment and metallurgy. The approach prioritizes potency over concentration regarding PCDD/F risks (Themba et al., 2023). These principles now also apply to brominated analogues (PBDD/Fs) with a similar structure and toxicity (Li, D. et al., 2025).25).

4.2. General formation mechanisms in thermal processes

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Two mechanistic pathways dominate PCDD/F formation in thermal systems: the precursor route and de novo synthesis.

The precursor route involves chlorinated aromatic compounds, such as chlorophenols or chlorobenzenes, condensing and oxidizing to form PCDD/F, which is favored when molecular precursors survive upstream thermal treatment and is sensitive to oxygen and catalysts (Zhang, Fujimori, Shiota, et al., 2021). Recent studies show that chlorobenzenes can also serve as intermediates under conditions associated with de novo synthesis, blurring pathway distinctions (Li, Y. et al., 2025).

De novo synthesis involves the formation of PCDD/Fs on carbonaceous residues via chlorine and oxygen, without precursors, primarily on metallic particulates, and is common in industrial systems (Safavi et al., 2022). Evidence shows that catalytic oxidation and destruction compete with formation, with the balance influenced by temperature and catalyst state (Li, B. et al., 2025).

Figure 5 shows the fundamental distinction between the two dominant formation routes. A simplified schematic representation is provided below, highlighting the chemical logic and surface involvement characteristic of each pathway.

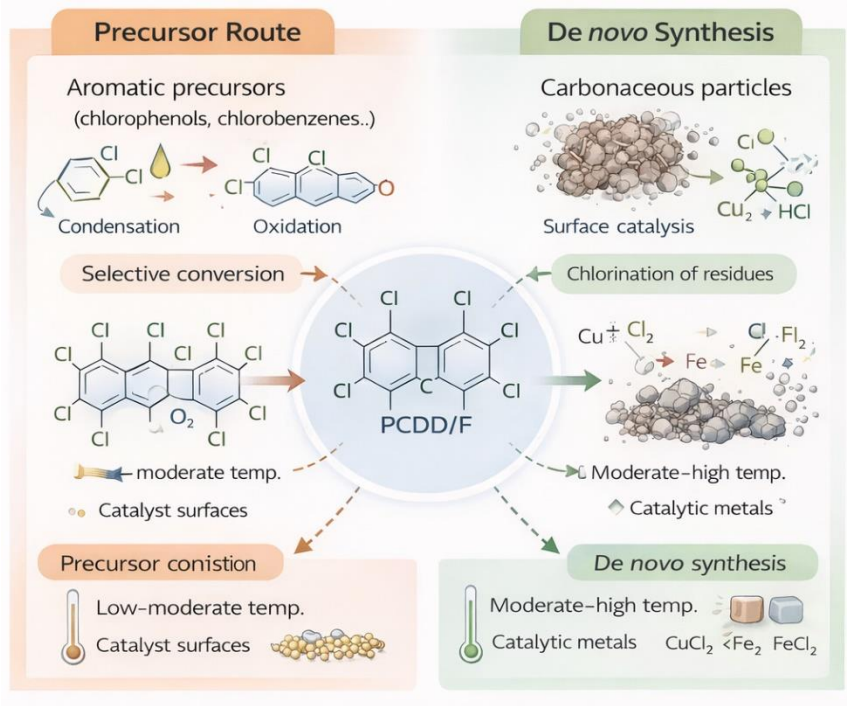


Figure 5. Simplified schematic of the main PCDD/F formation pathways in thermal processes: precursor route and de novo synthesis. Adapted from Safavi et al. (2022).

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Both pathways may coexist within the same system, but their relative contributions depend strongly on temperature history, surface availability, and chlorine activity rather than on bulk process conditions alone.

A critical feature of both pathways is their strong temperature dependence. Formation rates peak within the 200–450 °C range, which corresponds to post-combustion cooling zones, heat-recovery sections, and hot-gas filtration units. Kinetic studies indicate that formation and destruction reactions may overlap in this interval. Small changes in residence time or surface availability can therefore shift net emissions significantly (Palmer et al., 2021). This sensitivity explains why downstream control devices may also serve as secondary sites of formation.

Figure 6 shows that because temperature governs both the kinetics and thermodynamic stability of PCDD/F, it is useful to qualitatively represent how formation and destruction rates evolve across the temperature range relevant to industrial thermal systems.

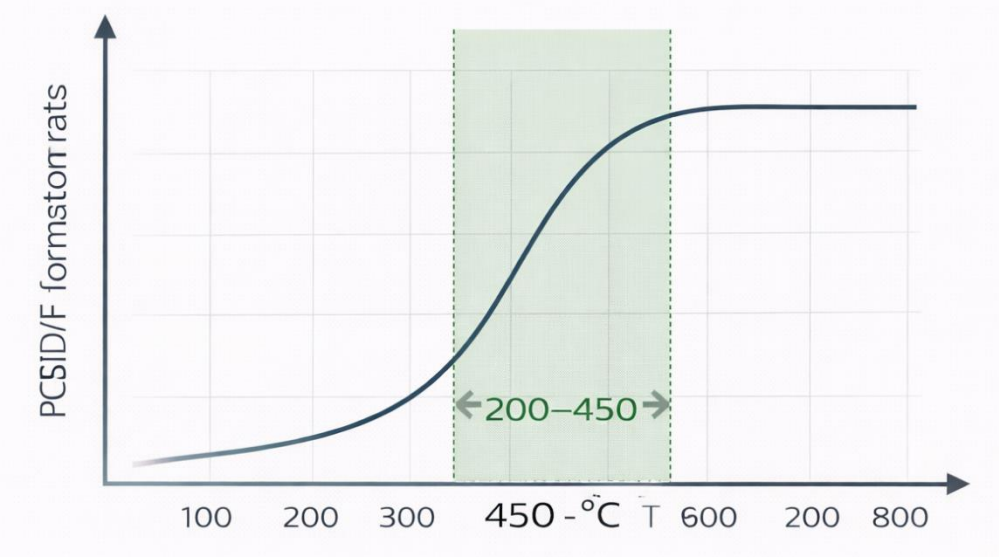


Figure 6. Qualitative relationship between temperature and net PCDD/F formation rate in thermal systems, indicating the critical 200–450 °C window. Adapted from Palmer et al. (2021).

This temperature window coincides with cooling and gas-cleaning sections in many industrial units, which explains why formation is often observed downstream rather than within the primary high-temperature reactor.

Recent work has highlighted the role of surface chemistry in promoting these pathways. Defect-rich metal oxides can stabilize environmentally persistent free radicals (EPFRs), which act as intermediates in PCDD/F formation. This finding

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underscores the importance of heterogeneous mechanisms over purely gas-phase reactions (Pan et al., 2024). These surfaces also strongly adsorb PCDD/F, underpinning capture-based mitigation strategies (Ding et al., 2023).

The participation of catalytic metals further amplifies formation rates. Copper and iron species are particularly effective at promoting chlorination and coupling reactions. Their presence on fly ash or dust surfaces correlates strongly with PCDD/F yields (Lin, Mao, et al., 2022). By contrast, calcium-based materials can partially suppress formation by capturing chlorine and modifying surface basicity, underscoring that catalyst chemistry can either enhance or inhibit formation (Li, X. et al., 2023).

Figure 7 highlights that, beyond temperature effects, heterogeneous surface chemistry controls the efficiency of PCDD/F formation by coupling particulate matter, catalytic metals, and reactive chlorine species.

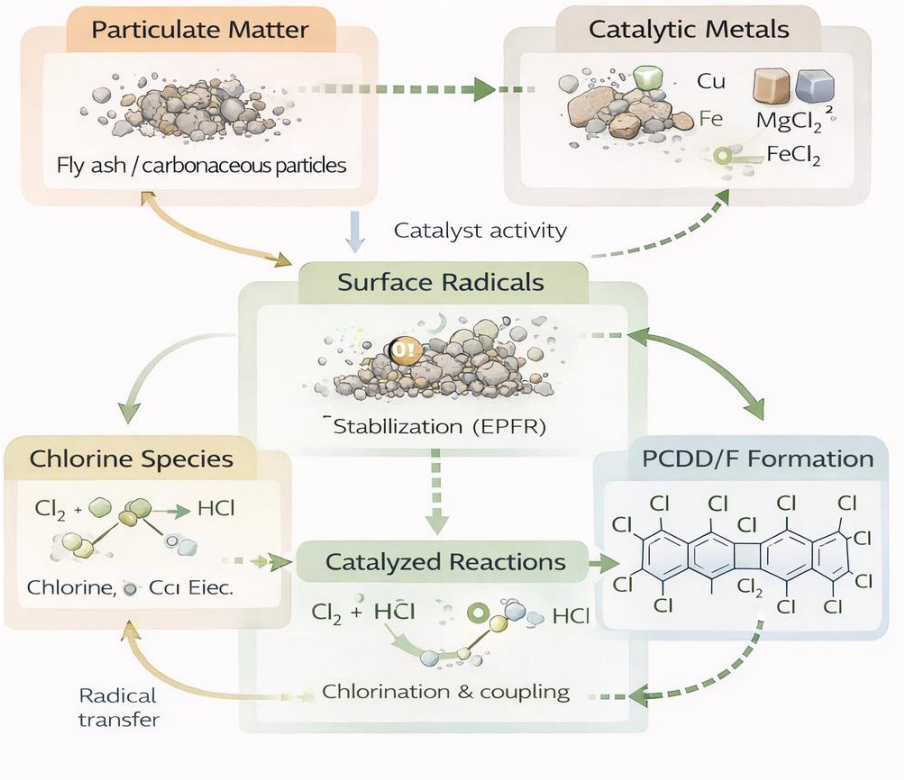


Figure 7. Interaction between particulate matter, catalytic metals, surface radicals, and chlorine species during heterogeneous PCDD/F formation. Adapted from Lin, Mao, et al. (2022) and Pan et al. (2024).

This sequence emphasizes the central role of heterogeneous surface chemistry in industrial-scale formation, where surface composition and catalyst distribution often outweigh bulk gas-phase conditions.

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Industrial observations confirm these mechanisms occur outside labs. Emission inventories from sintering, metallurgy, and thermal units show PCDD/F signatures linked to de novo formation in real conditions (Zhou et al., 2023). Similar trends appear in incineration, pyrolysis, and gasification, indicating these processes are widespread.

These fundamental concepts define what PCDD/Fs are and how they form in generic thermal environments. The next section applies these mechanisms to chloride-assisted calcination systems, identifying how chlorine chemistry, process design, and operating windows interact to create specific formation risks.

The literature highlights precursor-driven pathways and de novo synthesis as key to PCDD/F formation in thermal systems. Most evidence comes from waste incineration, which differs from metallurgical calcination, making direct application uncertain. Therefore, mitigation should prioritize engineering controls for surface and cooling processes over suppressing specific precursors.

5. Mechanisms of PCDD/F formation in metal chloride–Based calcination

Metal chloride–based calcination creates a distinct chemical environment that differs from conventional thermal systems. Chlorine availability, reactive solids, and catalytic metals coexist by design. This section examines how these features translate into PCDD/F formation mechanisms under realistic process conditions, drawing on evidence from related high-temperature systems where chlorine and particulate matter interact.

5.1. Thermodynamic feasibility

From a thermodynamic view, PCDD/F formation is unlikely at high calcination temperatures; chlorinated aromatics and PCDD/F congeners are unstable above ~700–800 °C. Net formation occurs during cooling, consistent with equilibrium analyses and Gibbs free energy trends (Stanmore, 2021).

In chloride-assisted systems, in situ Cl_2 and HCl alter local chemical potentials, maintaining chlorine activity at high temperatures. This shifts stability limits and promotes chlorination during cooling (Shamsuddin, 2021). Similar chlorine cycling occurs in other chloride-rich thermal systems, indicating chlorine can persist beyond the main reaction zone (Riley et al., 2021).

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Qualitative ΔG–T diagrams illustrate this contrast. While metal chlorides become more stable at higher temperatures, PCDD/F stability increases sharply as temperature decreases into the post-calcination range.

Figure 8 shows that placing PCDD/F formation within a thermodynamic context is useful, as it allows comparison of the temperature-dependent stability of metal chlorides with that of PCDD/F congeners, highlighting when formation becomes feasible.

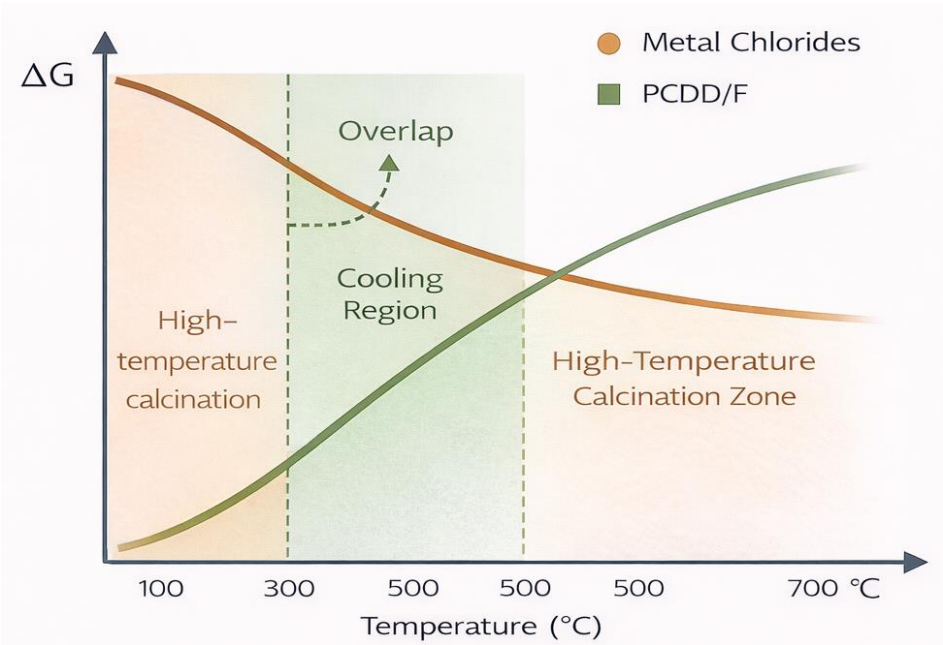


Figure 8. Qualitative Gibbs free energy trends for metal chloride formation and PCDD/F stability as a function of temperature. Adapted from Stanmore (2021) and Shamsuddin (2021).

The overlap between chloride stability and PCDD/F stability appears only during cooling, not during the main calcination step, reinforcing that formation risk is governed by post-reactor thermal history rather than by high-temperature chlorination.

The overlap between chloride stability and PCDD/F stability emerges only during cooling, not during the main calcination step.

5.2. Role of residual carbon and organic matter

Residual carbon is a prerequisite for heterogeneous PCDD/F formation, yet its origin is often underestimated in mineral processing contexts.

Carbon may be present as natural organic matter associated with ores. It may also derive from residual reagents, binders, or flotation chemicals. In some cases, added reductants or carbonaceous additives are intentional (Rao et al., 2021).

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Two forms are particularly relevant. Organic carbon provides molecular fragments and functional groups. Elemental carbon acts as a surface for radical stabilization and chlorination. Both can coexist in calcination residues (Ren et al., 2020).

Evidence from pyrolysis and gasification systems confirms that even low levels of carbonaceous residues can sustain PCDD/F formation when chlorine and catalytic metals are present, reinforcing the relevance of carbon control beyond incineration contexts (Lin, X., Qian, et al., 2025). Carbon removal upstream is therefore a critical control lever (Zhu & Huang, 2025).

Table 3 identifies practical control points for PCDD/F prevention. It is necessary to distinguish the main sources and forms of residual carbon typically present in mineral and residue calcination feeds.

Table 3. Typical sources and forms of residual carbon in mineral and residue calcination feeds. Adapted from Rao et al. (2021).

Carbon source	Carbon form	Typical origin in calcination feeds	Relevance to PCDD/F formation
Natural organic matter	Organic carbon	Sedimentary minerals, laterites, phosphate ores, clays	Provides functional groups and aromatic fragments that act as precursors
Residual flotation reagents	Organic carbon	Collectors, frothers, depressants retained on mineral surfaces	Enhances availability of chlorinatable organic species
Binders and additives	Organic carbon	Pelletizing agents, agglomeration binders	Decomposes into reactive intermediates during heating
Added reductants	Elemental carbon	Coke fines, charcoal, coal, carbon black	Acts as a substrate for *de novo* synthesis
Carbonaceous dust	Elemental / mixed	Attrition in kilns, cyclones, and ducts	High surface area favors radical stabilization
Unburned char	Elemental carbon	Incomplete oxidation during thermal treatment	Strongly associated with heterogeneous formation routes

Carbon origin influences not only quantity but also surface reactivity and the potential for radical formation.

5.3. Catalytic effects of transition metals

Transition metals play a central catalytic role. Copper is the most effective promoter, followed by iron and nickel. These metals accelerate chlorination, coupling, and oxidation reactions occurring on particle surfaces (Weidlich, 2021).

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In chloride-based systems, metals may form volatile or semi-volatile chlorides. These species redistribute catalytic activity along ducts and filters. Copper chlorides are especially active in promoting *de novo* synthesis (Zhang, Fujimori, Lin, et al., 2023).

Laboratory and pilot studies consistently show higher PCDD/F yields when Cu- or Fe-rich dust is present. The effect persists even when bulk metal concentrations are low (Lin, Wang, et al., 2023). Comparable catalytic amplification has been documented in complex waste-derived feeds, such as electronic waste, where metal-rich particulates dominate PCDD/F behavior (Lin, X., Ying, et al., 2023).

Figure 9 shows that because PCDD/F formation in chloride-assisted systems is strongly surface-driven, the catalytic role of transition metals must be considered explicitly, particularly when metal chlorides can redistribute along the gas path.

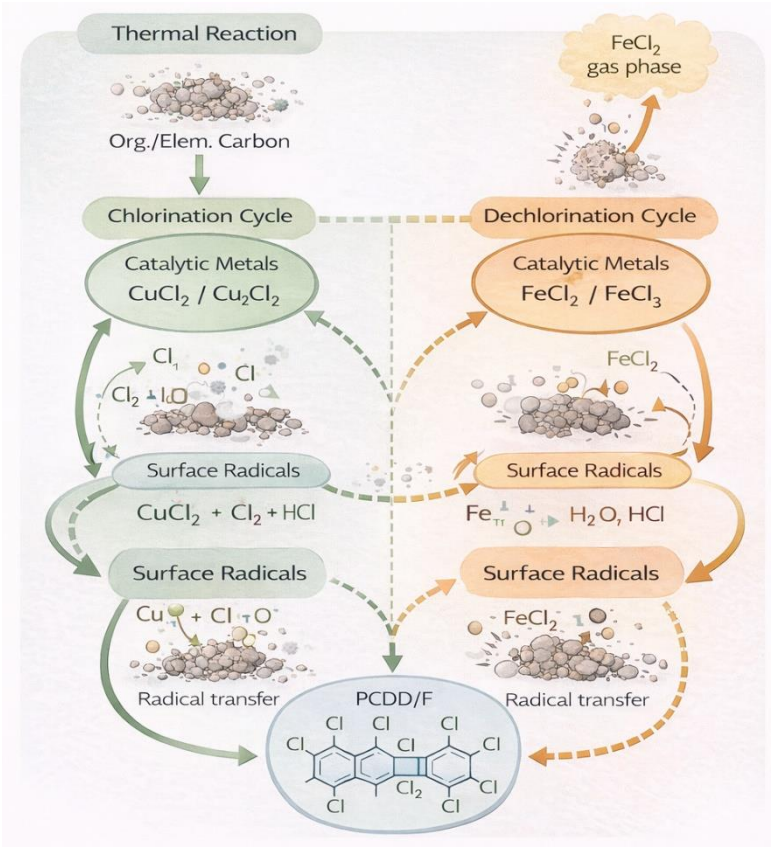


Figure 9. Catalytic role of transition metals in heterogeneous PCDD/F formation, highlighting chloride-mediated activation cycles. Adapted from Weidlich (2021) and Zhang, Fujimori, Lin, et al. (2023).

Catalyst redistribution explains why formation often peaks downstream of the reactor.

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5.4. Gas cooling and the “Critical Temperature Window.”

PCDD/F formation rarely occurs in the hot calcination zone. It is concentrated in the cooling section, where temperature, residence time, and surface availability converge (Palmer et al., 2021).

The 200–450 °C window defines this zone. Slow cooling increases the residence time in this range. Reactive surfaces remain available, and chlorine activity remains sufficient. Together, these factors create ideal conditions for net formation (Wang et al., 2023).

Rapid quenching reduces formation by bypassing this window. Conversely, extended ductwork, heat recovery units, and hot filters may inadvertently act as reactors. Although advanced off-gas technologies, such as electron-beam treatment, demonstrate that post-formation destruction is possible, they also underscore the complexity and cost of relying on downstream solutions rather than prevention (Zwolińska et al., 2020).

Industrial observations indicate that baghouse and heat exchanger sections often account for the majority of total emissions (Xiong et al., 2021). Similar trends are observed across incineration, pyrolysis, and gasification environments, underscoring the transferability of the cooling-driven formation concept (Lin, X., Qian et al., 2025).

Figure 10 translates thermodynamic and catalytic concepts into a process sequence. It is necessary to consider how gas cooling, surface contact, and residence time interact along the off-gas path.

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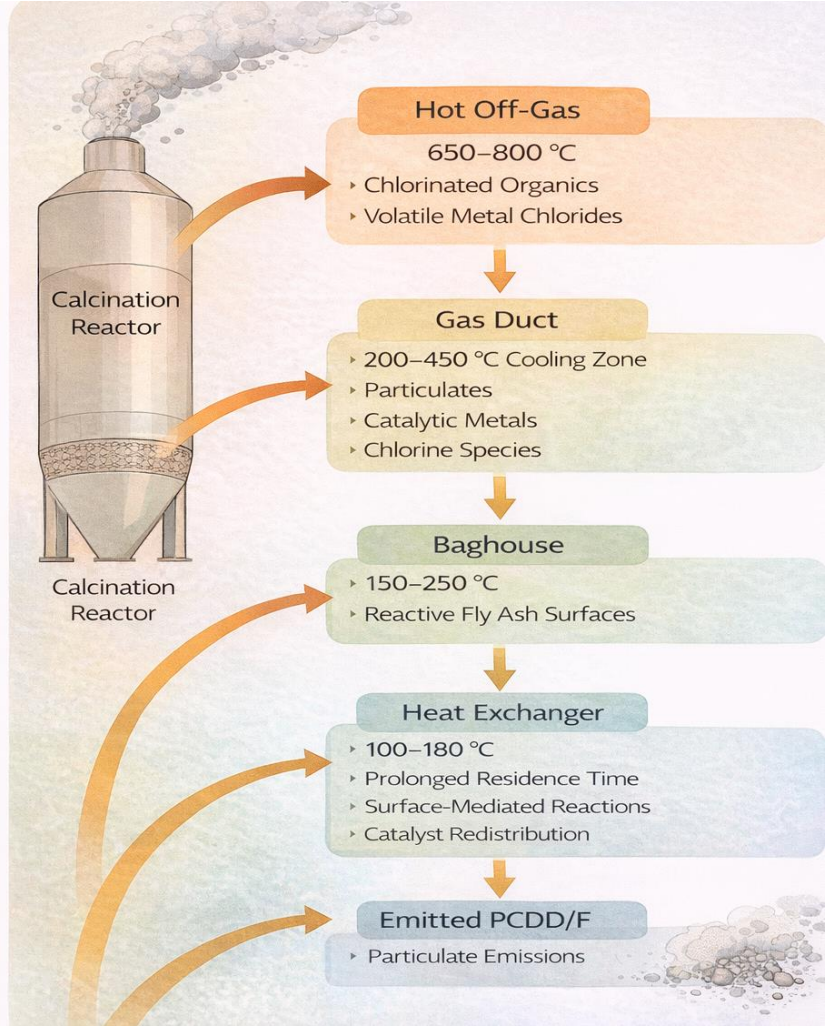


Figure 10. Sequence of PCDD/F formation during gas cooling in metal chloride–based calcination systems. Adapted from Palmer et al. (2021) and Xiong et al. (2021).

This sequence identifies the dominant formation zone outside the primary calcination reactor.

In chloride-assisted calcination systems, evidence shows that net PCDD/F formation mainly occurs during gas cooling, not in the high-temperature calcination zone, as confirmed by lab, pilot, and industrial data. However, much understanding of formation kinetics is still based on incineration studies, where feed and environmental conditions differ from metallurgical systems dominated by metal chlorides. Consequently, uncertainties remain about the thermodynamic stability and kinetic rates of PCDD/F formation in chloride-rich conditions, mainly due to the lack of specific ΔG–T diagrams and reaction data for relevant metal chlorides. From an engineering view, effective mitigation depends on rapid quenching, reducing reactive surface

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exposure, and controlling catalyst redistribution, rather than altering the primary calcination process.

These mechanisms explain why PCDD/Fs form during chloride-assisted calcination. The next section examines process variables that affect PCDD/F formation and translates these mechanisms into controllable design and operating parameters.

6. Process variables affecting PCDD/F formation

PCDD/F formation in metal chloride–based calcination depends on temperature, atmosphere, chloride chemistry, and mineralogy. Similar complexity exists in other chloride systems needing tight control, highlighting the importance of integrated process analysis (Hur et al., 2023).23).

6.1. Temperature profile and residence time

The temperature profile is the primary determinant of where PCDD/F formation occurs. During high-temperature calcination, most PCDD/F congeners are thermally unstable. Net formation is therefore unlikely inside the reactor. Risk increases sharply during gas cooling, where temperatures cross the **200–450 °C** range (Wang et al., 2024).

Residence time amplifies this effect. Continuous furnaces with long ducts, heat exchangers, or hot filtration units may extend exposure within the critical window. Batch systems often cool more slowly, increasing formation potential even at small scales (Zhou et al., 2023). Studies of off-gas systems in high-temperature chloride environments show that residence time in downstream equipment usually dominates overall reaction, regardless of reactor temperature (McFarlane et al., 2022).

Figure 11 shows that PCDD/F formation is governed by thermal history rather than peak operating temperature alone, so comparing temperature–time profiles provides direct insight into formation risk under different calcination modes.

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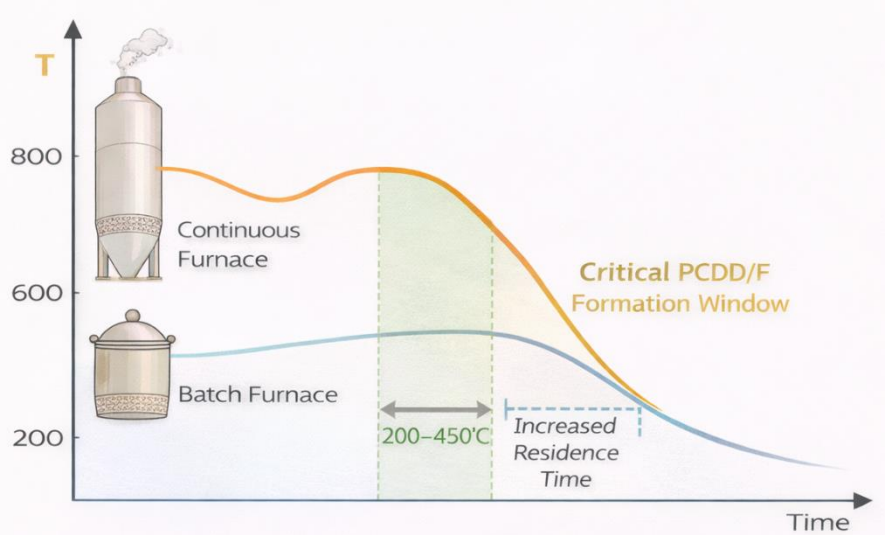


Figure 11. Comparison of temperature–time profiles in continuous and batch calcination systems and their overlap with the critical PCDD/F formation window. Adapted from Wang et al. (2024).

Extended residence time during cooling is often more critical than peak calcination temperature, particularly in systems with long ducts, heat-recovery units, or hot-gas filtration.

6.2. Atmosphere composition

Atmospheric composition governs both chlorine chemistry and surface reactions. Residual oxygen promotes oxidative coupling reactions and stabilizes surface radicals. Even low oxygen levels can sustain PCDD/F formation (Hsu et al., 2021).

Water vapor influences chlorine speciation by promoting HCl formation and affecting metal chloride volatility. Steam also alters surface hydroxylation, changing catalytic activity (Huang & Jin, 2024). Minor moisture variations greatly impact downstream chemistry in chloride-rich off-gas systems (McFarlane et al., 2020).

The combined effect is best indicated by redox potential, not individual gas levels. Oscillating systems show more variability in formation (Tang et al., 2024). Control strategies emphasize the need to stabilize redox conditions during chloride cycling and dechlorination to prevent undesired reactions (Riley et al., 2021).

Table 4 assesses the role of gas composition. The main atmospheric components influencing chlorine chemistry and surface reactions are summarized below.

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Table 4. Influence of atmosphere composition on key reactions involved in PCDD/F formation. Adapted from Hsu et al. (2021) and Huang & Jin (2024).

Atmospheric component	Typical source in calcination systems	Primary chemical effects	Impact on PCDD/F formation
Residual O_2	Air ingress, excess combustion air	Promotes oxidative coupling; stabilizes surface radicals	Increases precursor-route and *de novo* formation potential
H_2O (steam)	Feed moisture, hydrated chlorides, combustion products	Shifts Cl_2/HCl equilibrium toward HCl; modifies surface hydroxylation	Alters chlorine availability and catalytic activity
Cl_2	Direct injection; in situ release from chlorides	Strong electrophilic chlorination agent	Enhances aromatic chlorination and surface-mediated pathways
HCl	Chloride hydrolysis; gas–solid reactions	Acid–base chlorination moderates chlorine activity	Sustains chlorination under milder conditions
Reducing species (CO, H_2)	Carbon oxidation; incomplete combustion	Limits oxidation; modifies redox balance	May suppress precursor formation but sustain *de novo* routes
Fluctuating redox conditions	Transient operation; batch heating cycles	Alternating oxidation and reduction	Increases the variability and unpredictability of formation

Even modest variations in oxygen or steam content can shift dominant reaction pathways, underscoring the need for stable, well-controlled atmospheres. Small changes in oxygen or steam content can also shift dominant reaction pathways.

6.3. Type and dosage of metal chlorides

The type of metal chloride strongly influences chlorine release and catalyst distribution. $MgCl_2$ and $CaCl_2$ are less volatile yet highly hygroscopic. They release HCl upon heating and during hydration–dehydration cycles (Ying et al., 2025).

$FeCl_3$ decomposes and volatilizes more readily, serving as a chlorine source and a catalyst precursor. NaCl, though less reactive, can still participate through molten-salt formation and chloride transport (Lin, Qian, et al., 2025). Similar control challenges arise in other chloride-rich processes, where limiting chloride mobility is essential for stability (Hur et al., 2023).

Dosage is critical. Low doses may be sufficient to activate surfaces. High doses increase chlorine availability and moisture retention, thereby amplifying the risk of formation (Ying et al., 2025).

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Figure 12 shows that Chloride-assisted calcination systems differ markedly in how chlorine is released and transported, depending on the physicochemical properties of the metal chlorides used.

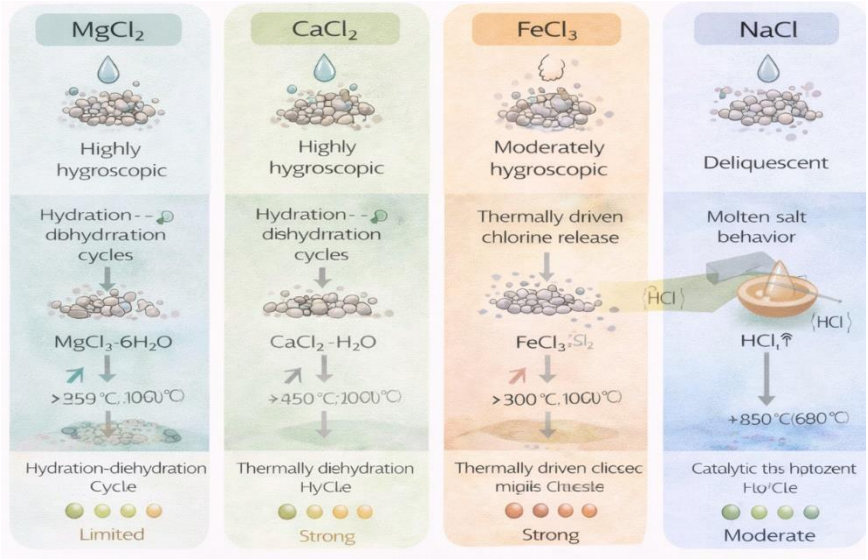


Figure 12. Comparative behavior of common metal chlorides used in calcination, highlighting hygroscopicity and chlorine release pathways. Adapted from Lin, Qian, et al. (2025).

These differences explain why chloride selection influences not only reaction efficiency but also downstream chlorine activity and PCDD/F formation potential. The choice of chloride also affects downstream emission chemistry.

6.4. Mineralogical composition of ores

Feed mineralogy defines the baseline susceptibility to PCDD/F formation. Ores with elevated Cu or Fe content introduce catalytic centers even without intentional additives. These metals may redistribute as chlorides during processing (Yang et al., 2020).

Carbonate-rich feeds release CO_2 during decomposition, altering gas composition and residence time. Silicate-rich feeds tend to produce fine particulates that provide reactive surfaces (Zhou et al., 2021).

Natural organic matter often goes unnoticed, even at trace levels providing carbon for heterogeneous formation with chlorine and metals (Zhu & Huang, 2025). While advanced sensors for organic and toxic species exist, most are unsuitable for harsh, high-temperature environments, limiting real-time feedback in calcination systems (Verma & Rani, 2021).

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Figure 13 illustrates how feed characteristics and operating parameters interact to control PCDD/F formation. A conceptual overview is presented that links ore mineralogy, chloride chemistry, and thermal history within chloride-assisted calcination systems.

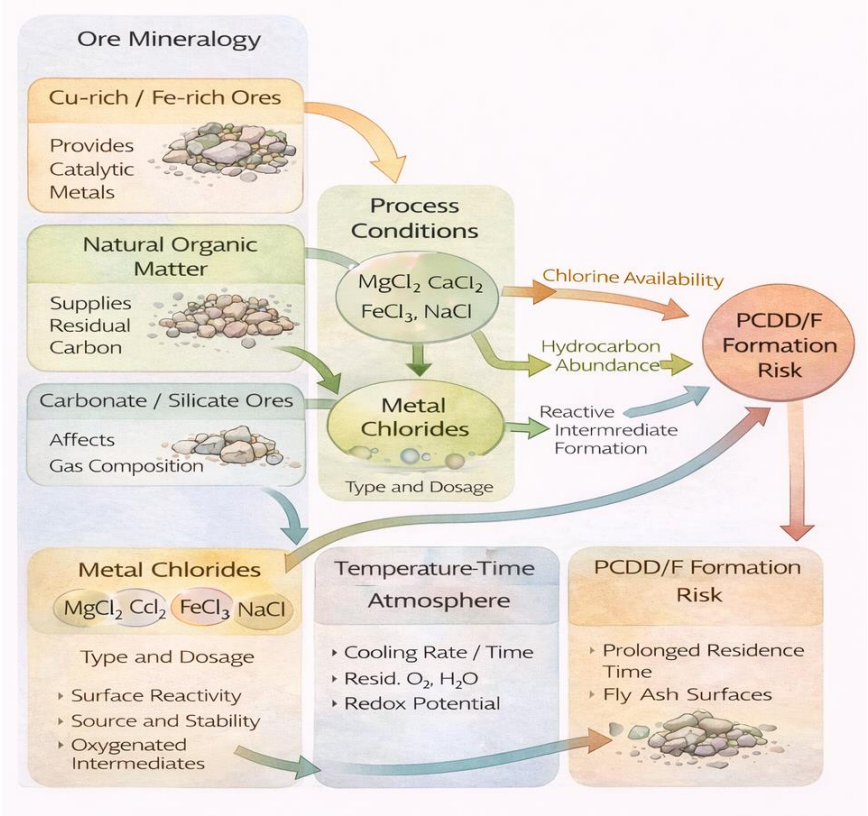


Figure 13. Interaction between ore mineralogy, process conditions, and PCDD/F formation risk in chloride-assisted calcination. Adapted from Yang et al. (2020) and Zhou et al. (2021).

Mineralogy determines whether process conditions lead to actual formation. These variables determine how and why PCDD/Fs form under specific operating conditions.

The literature consistently identifies temperature history and residence time as the main factors controlling PCDD/F formation in chloride-assisted calcination systems, supported across various thermal sectors and scales. However, most studies assess these variables separately, despite their strong links with atmosphere composition, chloride chemistry, and feed mineralogy under industrial conditions. This limits the predictive power of single-parameter analyses, as the combined effects governing real-world formation are poorly understood. Engineering-wise, effective risk

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mitigation requires integrated control of feed, gas atmosphere, and thermal profiles rather than optimizing individual parameters.

The next section focuses on prevention strategies, translating this analysis into engineering and chemical approaches that minimize formation rather than relying on downstream mitigation.

7. Prevention strategies: Engineering and chemical approaches

Effective prevention of PCDD/F formation during metal chloride–based calcination depends on process-first decisions. Upstream and reactor design measures are more effective than downstream controls alone. This section summarizes successful engineering and chemical strategies.ess.

7.1. Upstream measures: Feed preparation

Oxidative precalcination reduces organic carbon prior to chlorine introduction. This step limits precursor availability and suppresses heterogeneous pathways. Controlled oxidation is especially effective for feeds containing natural organic matter (Ju et al., 2020).

Carbon removal can also be achieved through washing, thermal desorption, or controlled low-temperature oxidation. Even partial removal results in measurable reductions in formation potential (Fu et al., 2022).

Control of catalytic impurities is critical. Copper- and iron-rich fines can be removed by classification or magnetic separation prior to calcination. Reducing the catalytic inventory upstream shifts formation risk downstream. (Peng et al., 2020).

Table 5 shows that, because the formation potential of PCDD/Fs is strongly influenced by feed characteristics, upstream preparation measures are the first and most robust line of prevention.

Table 5. Upstream feed preparation measures and their impact on PCDD/F formation potential. Adapted from Ju et al. (2020) and Fu et al. (2022).

Upstream measure	Main objective	Typical implementation	Impact on PCDD/F formation potential
Oxidative pre-calcination	Decompose organic matter	Low-temperature oxidation (300–500 °C) before chlorination	Strong reduction of precursor availability
Thermal desorption	Remove volatile organics	Controlled heating under inert or mildly oxidizing atmosphere	Reduces surface-bound chlorinatable species

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Feed washing	Remove soluble organics and salts	Water or mild chemical washing	Moderate reduction of chlorine–carbon interaction
Carbon burnout control	Minimize residual carbon	Staged oxidation with limited O_2	Suppresses *de novo* synthesis pathways
Magnetic separation	Remove catalytic metals	Removal of Fe- and Cu-rich fines	Reduces heterogeneous catalytic activity
Particle size classification	Reduce reactive surface area	Removal of ultrafine fractions	Limits surface-mediated formation
Binder and additive control	Avoid organic residues	Use of inorganic binders or reduced dosages	Pre

By removing reactive carbon and catalytic impurities prior to chlorination, these measures significantly reduce the risk of downstream formation. Upstream actions reduce the need for aggressive downstream controls.

7.2. Process design strategies

Operating the calcination reactor above 800–900 °C induces thermal instability in PCDD/F congeners. High temperatures alone do not eliminate risk, but they prevent in-reactor formation (Yang et al., 2021).

Minimizing free oxygen reduces oxidative coupling reactions. Slightly reducing or tightly controlling the inert atmosphere limits radical stabilization without compromising chlorination efficiency (Hur et al., 2023).

Atmosphere control is most effective when paired with real-time monitoring. Stable redox conditions reduce transient formation events commonly observed during start-up or load changes (He, F. et al., 2025).

Figure 14 shows the combined influence of reactor temperature and atmosphere composition, defining the intrinsic envelope within which PCDD/F formation is either suppressed or promoted.

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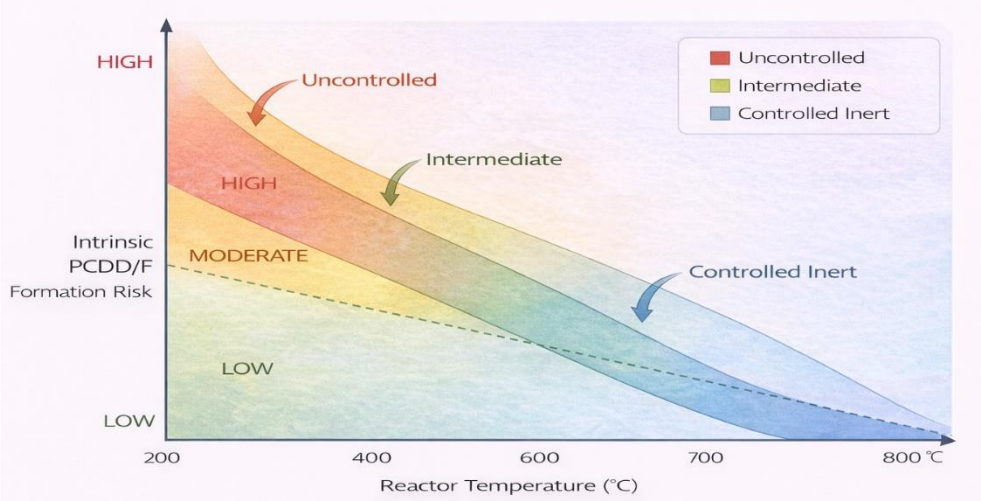


Figure 14. Effect of reactor temperature and atmosphere control on intrinsic PCDD/F formation risk. Adapted from Yang et al. (2021).

Design choices at the reactor level, therefore, establish the baseline formation risk before any downstream mitigation is considered. These choices define the baseline formation envelope.

7.3. Rapid gas quenching and cooling design

Gas cooling design is crucial; direct quenching reduces residence time in the 200–450 °C range and outperforms gradual cooling (Zwolińska et al., 2020).

Slow heat exchangers should be avoided whenever possible. Extended surface contact promotes heterogeneous reactions. When heat recovery is required, compact designs with minimal surface residence are preferred (McFarlane et al., 2022).

Inert construction materials reduce catalytic activity. Replacing metal-rich surfaces with ceramics or coated steels lowers formation rates in ducts and filters (McFarlane et al., 2020).

Figure 15 shows that because PCDD/F formation is strongly controlled by residence time within the critical temperature window, the cooling strategy is one of the most decisive design variables in a chloride-assisted calcination system.

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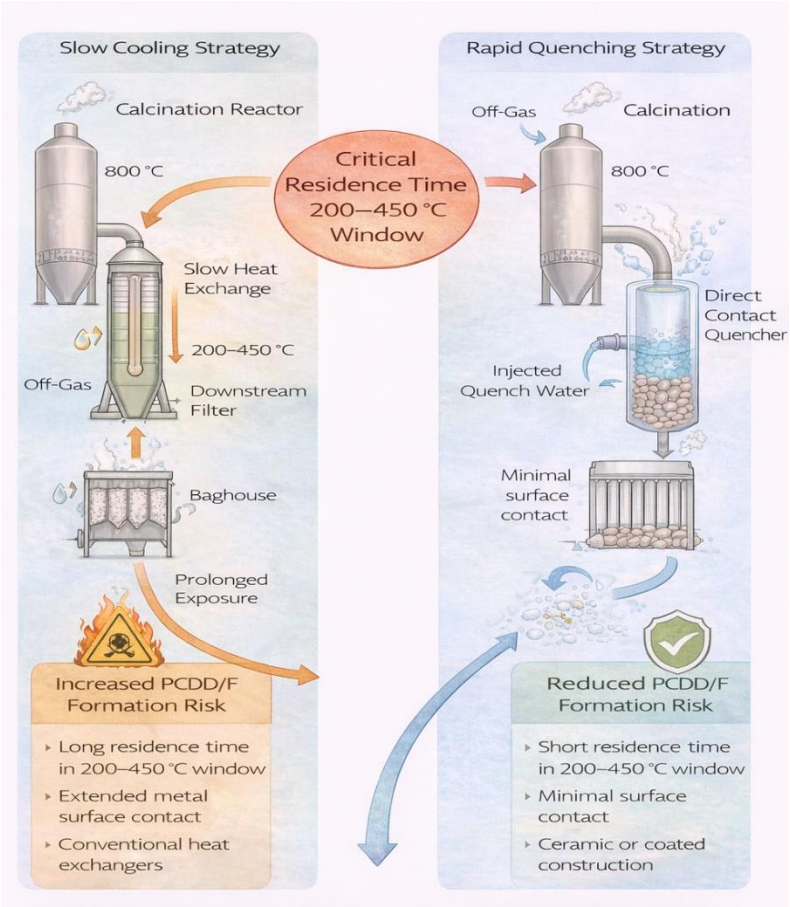


Figure 15. Comparison of slow cooling versus rapid quenching strategies in chloride-assisted calcination systems. Adapted from Zwolińska et al. (2020).

The comparison shows that slow cooling unintentionally prolongs exposure to formation-prone conditions, whereas rapid quenching minimizes surface contact and residence time, thereby reducing PCDD/F formation at the system level. Cooling design often determines whether prevention succeeds or fails.

7.4. Chemical inhibition strategies

Sulfur and sulfur-containing compounds deactivate catalytic metals by forming stable sulfides, thereby suppressing both precursor and de novo pathways (Lu et al., 2021). Ammonia and urea act via radical scavenging and surface passivation. Their effectiveness depends on injection location and temperature (Wu et al., 2024).

Copper capture strategies, including phosphate-based additives, immobilize the most active catalyst in PCDD/F formation. This reduces catalytic cycling during cooling. (Wang et al., 2022).

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Table 6 shows that when engineering measures alone are insufficient, chemical inhibition provides an additional layer of control by targeting key formation mechanisms.

Table 6. Chemical inhibitors used for PCDD/F suppression and their dominant mechanisms. Adapted from Lu et al. (2021) and Wang et al. (2022).

Inhibitor type	Typical compounds	Dominant suppression mechanism	Main limitations
Sulfur-based additives	Elemental S, SO_2, sulfates	Formation of stable metal sulfides (CuS, FeS); catalyst deactivation	Risk of SO_2 emissions; possible corrosion
Ammonia-based agents	NH_3, urea	Radical scavenging; surface passivation	Narrow effective temperature window
Phosphorus-based inhibitors	Ammonium phosphates, phosphoric acid	Immobilization of Cu and Fe; inhibition of catalytic cycles	Potential slag modification
Nitrogen–phosphorus compounds	NP-based inhibitors	Combined radical suppression and metal passivation	Limited long-term stability
Alkaline additives	CaO, MgO	Chlorine capture; reduction of Cl activity	Increased solid residue generation
Metal chelating agents	Silicates, aluminates	Reduction of metal chloride volatility	Lower effectiveness at high temperature

Chemical inhibition is most effective when paired with engineering controls. These preventive strategies demonstrate that PCDD/F formation can be minimized through design. However, residual emissions may still occur. The next section addresses off-gas treatment and end-of-pipe solutions, completing the hierarchy from prevention to mitigation.

The reviewed prevention strategies agree that upstream and in-process measures are more effective than downstream mitigation for controlling PCDD/F formation during chloride-assisted calcination. Feed preparation, atmosphere control, thermal management, and rapid quenching all help reduce formation risks at the source. However, most evidence assesses individual strategies under idealized or short-term conditions, limiting insights into long-term stability, operational trade-offs, and costs when multiple measures are combined. Chemical inhibition, effective in controlled settings, adds concerns about reagent use, by-products, and process compatibility. Overall, prevention is best when integrated as a coordinated design—covering feed quality, reactor operation, and cooling—rather than standalone actions.

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8. Off-gas treatment and end-of-pipe solutions

Off-gas treatment is the last line of defense against PCDD/F emissions. These systems are essential for regulatory compliance but do not address root causes. Their effectiveness depends strongly on upstream process stability and gas composition.

8.1. Gas cleaning technologies

Wet scrubbers remove acid gases and soluble chlorine; their impact on PCDD/F is indirect, mainly reducing chlorine but limited in removing particle-bound congeners. Performance improves with upstream quenching (Jin et al., 2022).

Fabric filters (baghouses) are widely used for particulate control and for capturing PCDD/F associated with fly ash. However, they may also serve as sites for formation if operated within the critical temperature window. Filter cake composition is therefore decisive (Lin, Wang, et al., 2023).

Activated carbon injection (ACI) is the most established technology for direct capture of PCDD/Fs. Its high surface area and tailored pore structure enable the adsorption of both gaseous and particulate-bound congeners. This approach is robust across a wide range of processes (Gao et al., 2024).

To place end-of-pipe solutions in context, Table 7 summarizes the primary off-gas treatment technologies for PCDD/F control, highlighting their functional role, typical performance, and inherent limitations.

Table 7. Main off-gas treatment technologies for PCDD/F control and their primary functions. Adapted from Jin et al. (2022) and Gao et al. (2024).

Technology	Primary target	Dominant removal mechanism	Typical effectiveness	Key limitations
Wet scrubbers	Acid gases, soluble chlorinated species	Absorption and neutralization	Low–moderate for PCDD/F	Limited removal of particle-bound congeners; liquid effluent generation
Fabric filters (baghouses)	Particulate-bound PCDD/F	Physical filtration and cake adsorption	Moderate–high	Risk of secondary formation if operated in the 200–450 °C range
Activated carbon injection (ACI)	Gaseous and particulate PCDD/F	Adsorption on high-surface-area carbon	High (>90% under optimal conditions)	Generates contaminated solid residues; high operating cost
Catalytic filters	PCDD/F and precursors	Oxidative destruction on	High	Catalyst deactivation;

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		catalyst surfaces		narrow temperature window
Dry sorbent injection	Chlorine species, partial PCDD/F	Chemical capture and adsorption	Moderate	Efficiency is sensitive to dosage and mixing
Hybrid systems	Multiple pollutants	Combined filtration and adsorption	High	Increased complexity and CAPEX

End-of-pipe systems are effective for compliance, but their performance is highly sensitive to operating conditions and cannot compensate for insufficient upstream process control.

8.2. Performance and limitations

Reported removal efficiencies often exceed 90%. However, these values reflect controlled conditions. In practice, efficiency varies with gas temperature, dust loading, and chlorine chemistry (Zhao et al., 2022).

Activated carbon systems produce secondary solid residues enriched in PCDD/F. These residues require careful handling and disposal. Regeneration is possible but costly (Xiao et al., 2020).

Wet scrubbers produce liquid effluents containing chlorinated species. Treatment and disposal add operational complexity (Silva et al., 2025).

Baghouse filters may promote secondary formation if temperature control is inadequate. This risk is well documented in systems with long gas residence times (Xiong et al., 2021).

Economic assessments show that off-gas systems often dominate operating costs when used as the primary mitigation strategy. Prevention-oriented designs reduce long-term expenditures (Cao et al., 2025).

Figure 16 compares the practical effectiveness of end-of-pipe technologies. It is necessary to consider not only nominal removal efficiencies but also operational limitations and secondary impacts associated with each option.

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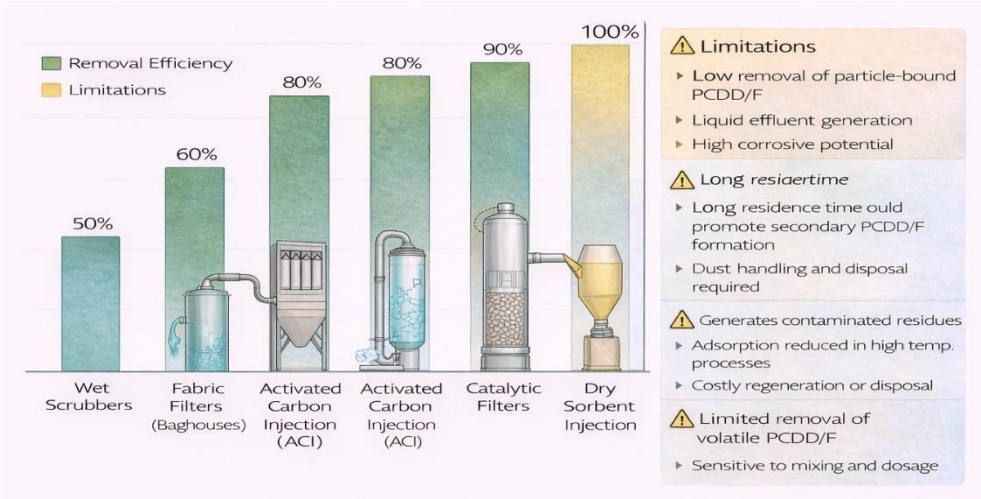


Figure 16. Comparative performance and limitations of major off-gas treatment options for PCDD/F control. Adapted from Zhao et al. (2022) and Cao et al. (2025).

The comparison shows that high apparent removal efficiency doesn't guarantee robustness, as technologies with strong adsorption or catalytic performance can cause secondary residues, corrosion, or sensitivity to temperature and mixing, highlighting the need for prevention-focused process design.

Off-gas treatment is indispensable, but it should serve as a barrier, not a substitute for sound process design. The next section situates these technologies within regulatory frameworks and Best Available Techniques (BAT), clarifying how prevention and end-of-pipe measures are integrated into modern compliance strategies.

Off-gas treatment technologies are vital final barriers for controlling PCDD/F emissions, with their effectiveness proven under controlled conditions. Techniques like fabric filters, activated carbon, and catalytic systems achieve high removal efficiencies when well-designed and operated. However, these are reactive solutions, addressing PCDD/Fs after formation, and pose secondary challenges such as contaminated residues, operational complexity, temperature sensitivity, and higher costs. Thus, off-gas treatment should be seen as a complementary safeguard, with overall emissions primarily determined by upstream design factors like feed composition, thermal profiles, and cooling dynamics.

9. Regulatory framework and best available techniques (BAT)

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Regulatory frameworks treat PCDD/F as priority pollutants with stringent emission limits. Compliance is mandatory across waste treatment and metallurgical sectors. Although chloride-assisted calcination is not always named explicitly, its operations fall within existing categories governed by BAT principles.

9.1. European Union

In the European Union, the Industrial Emissions Directive (IED) sets binding requirements for installations with thermal processes. PCDD/F emission limits are defined using TEQ-based metrics and enforced through BAT conclusions. The BAT Reference Documents (BREFs) emphasize prevention, stable operation, and minimizing residence time within critical temperature windows (HUI & PU, 2020).

Non-ferrous metallurgy provides relevant precedents. Copper and secondary smelting operations are subject to strict PCDD/F limits and continuous improvement requirements. These sectors demonstrate that prevention-oriented design is preferred over reliance on end-of-pipe solutions (Yang, Wu, et al., 2020).

To contextualize prevention and control strategies within current regulatory practice, Table 8 summarizes typical PCDD/F emission limits and compliance frameworks applied across major industrial sectors under European BAT guidance.

Table 8. Typical PCDD/F emission limit values and regulatory scope under EU frameworks. Adapted from HUI & PU (2020) and Yang, Wu, et al. (2020)

Industrial sector	Regulatory instrument	Typical emission limit (stack gas)	Basis of regulation	Key compliance focus
Municipal solid waste incineration	IED / BAT Conclusions (WI BREF)	≤ 0.1 ng TEQ Nm^{-3}	Continuous or periodic averaging	Stable high-temperature operation and rapid cooling
Hazardous waste incineration	IED / BAT Conclusions	≤ 0.1 ng TEQ Nm^{-3}	TEQ-based congener weighting	Strict control during start-up and shutdown
Secondary non-ferrous metallurgy (Cu, Zn, Pb)	IED / NFM BREF	≤ 0.1 ng TEQ Nm^{-3}	Periodic stack measurements	Dust handling and off-gas cooling design
Iron ore sintering	Sectoral BAT guidance	0.1–0.4 ng TEQ Nm^{-3}	Averaged operating conditions	Raw mix control and gas-cleaning efficiency
Thermal treatment of residues	Case-by-case permitting under IED	Typically ≤ 0.1 ng TEQ Nm^{-3}	Risk-based assessment	Demonstration of BAT equivalence

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The comparison shows that similar emission limits are enforced across different thermal sectors, reinforcing that compliance is achieved primarily through process stability, feed control, and cooling design rather than through reliance on end-of-pipe measures alone.

Current regulatory frameworks and BAT guidance show that strict PCDD/F emission limits are technically achievable across many thermal industries. However, these frameworks are mainly sector-specific, focusing on incineration and metallurgical operations. Chloride-assisted calcination processes are often regulated by analogy rather than tailored criteria, which can obscure their unique formation pathways and operational differences. This highlights the need to see BAT as a performance-based framework emphasizing source prevention, integrated design, and equivalent emission control for new or hybrid calcination methods.

9.2. United States (USEPA)

In the United States, PCDD/F regulation is enforced under the Clean Air Act and sector-specific standards. The USEPA sets emission limits and work practice standards for incinerators and metallurgical units. Performance-based compliance is paired with monitoring and reporting requirements (Dat et al., 2020).

Secondary non-ferrous smelting offers important lessons. Studies report that compliance is achieved through integrated strategies that combine temperature control, rapid quenching, and sorbent injection. This reinforces the hierarchy of prevention over mitigation (Yang et al., 2021).

Figure 17 shows that regulatory frameworks consistently emphasize a hierarchical approach to PCDD/F control, favoring source prevention over downstream mitigation.

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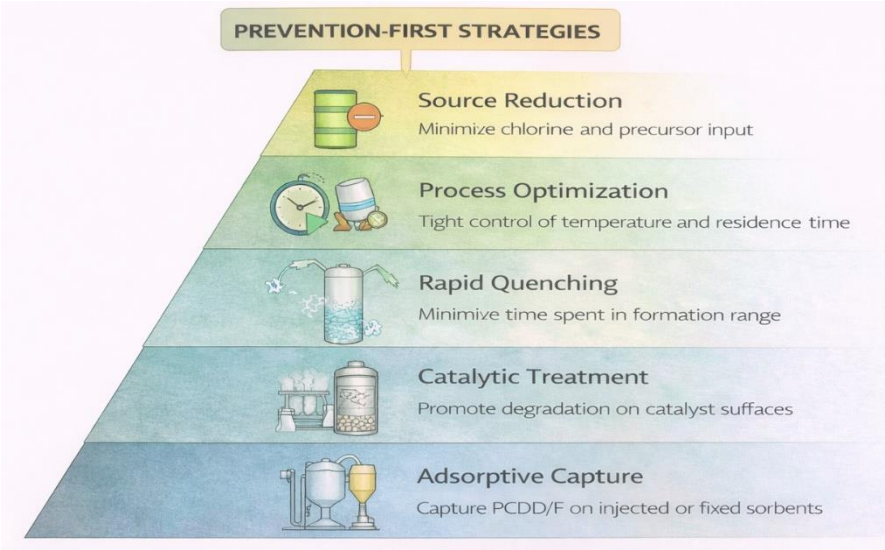


Figure 17. Hierarchy of PCDD/F control measures emphasized in regulatory guidance, from prevention to end-of-pipe treatment. Adapted from Yang et al. (2021).

The hierarchy indicates that measures addressing feed composition, process conditions, and cooling design are fundamentally more robust than end-of-pipe adsorptive or catalytic solutions, which primarily serve as complementary safeguards for residual emissions.

9.3. Typical emission limit values

Across jurisdictions, typical stack gas limits for PCDD/F are 0.1 ng TEQ Nm^{-3}. These values apply to incineration and are increasingly applied to metallurgical processes with comparable risk profiles (Zhang, L. H. et al., 2020).

Compliance is evaluated using averaged measurements during steady-state operation. Transient conditions, such as start-up and shutdown, are recognized as critical risk periods. Regulatory frameworks increasingly require specific management plans for these phases (Wang et al., 2024).

9.4. Lessons learned from incineration and non-ferrous metallurgy

Incineration has a mature regulatory framework. Long-term experience shows that stable, high-temperature operation, rapid cooling, and catalyst management are decisive. Systems relying primarily on downstream capture incur higher operational costs (Zhao et al., 2022).

Non-ferrous metallurgy shows similar patterns. PCDD/F formation is often associated with dust-handling and off-gas cooling sections rather than the primary

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reactor. Regulatory compliance has driven design changes in heat-recovery and filtration systems (Lin et al., 2022).

These lessons are directly applicable to chloride-assisted calcination. Regulatory acceptance will likely depend on demonstrating equivalent control performance and adherence to BAT principles (Stanmore, 2021).

Regulatory frameworks define what must be achieved but not always how. The next section provides a critical assessment and identifies research gaps, highlighting where current knowledge is insufficient to fully support safe and optimized chloride-assisted calcination.

10. Critical assessment and research gaps

Despite extensive literature on PCDD/F formation in thermal systems, significant gaps remain in applying these mechanisms to metal chloride–based calcination. Much of the current understanding relies on indirect analogies rather than process-specific evidence.

10.1. Limited evidence for solid metal chlorides

Most mechanistic studies focus on gaseous chlorination or incineration environments. Solid metal chlorides (e.g., $CaCl_2$, $MgCl_2$, $FeCl_3$) are rarely treated as independent variables. Their hydration–dehydration cycles, molten-salt behavior, and local chlorine activity are poorly quantified under calcination conditions (Lin, Qian, et al., 2025).

Experimental work shows that chloride phase transitions can strongly affect surface chemistry, yet their direct link to PCDD/F formation remains speculative. (Ying et al., 2025). This lack of targeted studies limits reliable risk assessment for solid–solid chlorination routes. (Ge et al., 2022).

10.2. Natural ores versus synthetic feeds

Another major gap concerns natural mineral feeds. Many laboratory studies rely on simplified or synthetic matrices. These systems lack the complexity of real ores, which contain variable amounts of copper, iron, carbonates, silicates, and natural organic matter (Yang, Q. et al., 2020).

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Field data from non-ferrous metallurgy indicate that trace metals and mineral associations can dominate PCDD/F behavior. These effects are not captured by surrogate materials (Yang, Y. et al., 2021). Extrapolating results from simplified systems therefore introduces systematic uncertainty (Zhou, X. et al., 2023).

10.3. Overreliance on incineration-Derived models

A recurring issue is the direct extrapolation of incineration data to metallurgical calcination. Although temperature windows and general pathways are transferable, process dynamics differ substantially. Gas composition, solid residence time, and chloride speciation are not equivalent (Themba et al., 2023).

Models for waste incineration often assume continuous oxidation and homogeneous feeds. These assumptions break down in chloride-assisted calcination, where redox conditions and chlorine sources fluctuate (Tang et al., 2024).

10.4. Need for dedicated kinetic studies

There is a clear need for dedicated kinetic data under chloride-rich conditions. Reaction rates for de novo synthesis and precursor conversion are typically inferred from incineration studies (Stanmore, 2021).

The coupled effects of temperature, chlorine activity, and catalytic metal redistribution remain unresolved. Without kinetic constants derived from relevant systems, predictive modeling remains qualitative (Palmer et al., 2021).

10.5. In Situ monitoring and advanced diagnostics

Most available data are based on ex situ sampling. In situ monitoring of chlorine species, surface radicals, and metal chlorides during cooling is rare, limiting understanding of transient formation events (Xiong et al., 2021).

Emerging diagnostic approaches, including online sensors and real-time emission-prediction tools, show promise but are not yet widely applied to chloride-based processes (Xiong et al., 2021).

10.6. Coupled thermal–Chemical modeling

Current models often decouple heat transfer from surface chemistry. This separation obscures critical interactions during gas cooling and dust contact. (Stanmore, 2021).

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Integrated thermal–chemical–transport models are required to capture residence-time effects, catalyst migration, and local equilibrium shifts. These tools are still in an early stage for metallurgical systems (Tang et al., 2024).

These gaps indicate that prevention strategies are constrained by insufficient process-specific knowledge. The next section discusses future perspectives, focusing on how targeted research, improved monitoring, and advanced modeling can support safer, more efficient chloride-assisted calcination.

11. Future perspectives

Future development of chloride-assisted calcination must reconcile process efficiency with increasingly stringent controls on unintentional pollutants. The path forward is not incremental optimization alone, but **conceptual redesign** of how chlorine is introduced, managed, and monitored.

11.1. Low-chlorine process concepts

One clear direction is the development of **low-chlorine or chlorine-lean processes**. These routes aim to minimize total chlorine inventory while preserving selectivity. Examples include staged chlorination, localized chlorine release, and hybrid chlorination–oxidation sequences. (Bruffey et al., 2021).

Electrothermal and flash-based concepts further reduce residence time and chlorine exposure. Such approaches decouple reaction intensity from chlorine dosage and may inherently suppress secondary formation pathways. (Deng et al., 2024).

11.2. Alternative chloride sources and media

Another perspective involves alternative chloride carriers. Molten-salt systems, mixed-halide media, and controlled solid chlorides offer opportunities to stabilize chlorine activity. By constraining chlorine speciation, these systems may reduce uncontrolled release during cooling (Riley et al., 2021).

Research on selective chlorination in molten or semi-molten environments suggests that chloride activity can be engineered rather than imposed. This represents a shift from “chlorine excess” toward “chlorine precision.” (Hur et al., 2023).

11.3. Integration with circular economy strategies

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Circular economy principles provide additional leverage. Residue valorization, internal recycling of dusts, and controlled reuse of chlorinated by-products can reduce the net chlorine footprint of a plant. Such integration also limits repeated exposure of reactive fines to critical temperature windows. (Cao et al., 2025).

Closed-loop concepts, where off-gas solids are reintroduced under controlled conditions, are particularly promising. However, they require careful assessment to avoid reactivation of catalytic species. (Zwolińska et al., 2020).

11.4. Digital twins and advanced process control

Digitalization will likely play a decisive role. **Digital twins** that couple thermal profiles, gas composition, and surface chemistry can support predictive control of PCDD/F risk. These tools enable real-time assessment of residence time in critical temperature zones. (Xiong et al., 2021).

Integration of online diagnostics with dynamic models allows early intervention before formation conditions are fully established. Such approaches move control strategies from reactive to preventive. (Stanmore, 2021).

11.5. From compliance to design philosophy

Looking ahead, regulatory compliance should no longer be treated as an external constraint. It can be embedded in process design philosophy. Processes that inherently avoid formation-prone conditions are more robust, easier to permit, and economically resilient (Zhao et al., 2022).

Future research should therefore prioritize demonstrator-scale studies that integrate advanced monitoring, alternative chlorination concepts, and digital control. This integration is essential to advance chloride-assisted calcination toward safe, scalable, and socially acceptable industrial deployment (Themba et al., 2023).

These perspectives outline how chloride-assisted calcination may evolve beyond current limitations. The final section consolidates the main findings, discusses the conclusions and industrial implications, and emphasizes design-oriented prevention as the central outcome of this review.

12. Conclusions and industrial implications

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This review shows that PCDD/F formation during metal chloride–based calcination is governed by process configuration and operating history rather than by chlorination chemistry itself. From thermodynamic, kinetic, and surface-chemistry perspectives, PCDD/F formation is a secondary phenomenon linked to cooling conditions, reactive surfaces, and residual carbon.

The central technical message of this work is clear:

PCDD/F formation during chloride-assisted calcination is primarily a cooling and feed-preparation issue, not an intrinsic limitation of chlorination chemistry.

High-temperature chlorination and calcination do not favor PCDD/F stability; formation occurs as gases cool and solids remain active. Long residence times (200–450 °C), catalytic metals, and carbon residues govern formation. Focus shifts from the reactor core to upstream preparation and downstream cooling.

In industrial plant design, feed preparation is a risk-control step that manages residual carbon and impurities. Reactor operation should prioritize thermal stability and controlled atmospheres, avoiding oxygen ingress. Gas systems should minimize residence time in critical zones, favoring rapid quenching and inert surfaces over prolonged heat recovery.

End-of-pipe solutions are vital for compliance but should serve as safeguards, not primary tools. Prevention-by-design plants are more robust, easier to permit, less affected by operational changes, and have lower long-term costs by reducing consumables and waste handling.

More broadly, these conclusions support a design philosophy in which chlorination–calcination is constrained not by environmental inevitability but by engineering choices. When cooling profiles, feed composition, and catalyst management are explicitly addressed, chloride-assisted calcination can be implemented as a selective, efficient, and environmentally defensible industrial route.

This perspective provides a practical foundation for future plant designs and for regulatory discussions focused on equivalence with established best available techniques, reinforcing that the safe deployment of chlorination-based processes is achievable through informed engineering rather than chemistry avoidance.

Declarations

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Ethics Approval and Consent to Participate

Not applicable. This study is a critical review of published literature and does not involve human participants, animals, or confidential data.

Consent for Publication

Not applicable.

Data Availability

No new data were generated or analyzed in this study. All data discussed in this review are derived from previously published literature cited in the reference list

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Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors' Contributions

Conceptualization, literature analysis, and manuscript preparation were performed by the authors. All authors contributed to the critical interpretation of the literature, reviewed the final manuscript, and approved it for submission.

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