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何沁源, 刘霄龙, 李彬, 等. 钢铁烧结烟气二噁英生成机理及控制技术研究进展 [J]. 能源环境保护, 2025, 39(5): 44-56.

HE Qinyuan, LIU Xiaolong, LI Bin, et al. Research Progress on Formation Mechanism and Control Technology of Dioxins in Iron and Steel Sintering Flue Gas[J]. Energy Environmental Protection, 2025, 39(5): 44-56.

钢铁烧结烟气二噁英生成机理 及控制技术研究进展

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摘要: 钢铁烧结烟气中二噁英(PCDD/Fs)的排放对区域空气质量和人体健康构成严重威胁。近年来,随着国家对二噁英污染控制的日益重视,钢铁烧结工序作为二噁英的重要排放源,其控制需求愈发迫切。因此,选择经济可行、环保高效的PCDD/Fs控制技术至关重要。基于现有文献,首先分析总结了烧结过程中二噁英的生成机理,指出其生成过程和机理较为复杂。其次,阐明了烧结烟气中二噁英及其同系物的分布特征,发现其主要以多氯二苯并呋喃(PCDFs)为主。随后,综述了当前烧结工序中二噁英的控制技术,并强调在实际应用中需要重点关注各技术的优缺点,结合实际条件合理采用多技术联用策略。同时,提出了“以废治废、协同治理”的技术路线。最后,对二噁英控制的研究方向进行了展望,以期对烧结烟气中二噁英的有效控制提供参考。

关键词: 烧结烟气; 二噁英; 生成机理; 同系物分布; 多技术联用; 协同治理

中图分类号: X701

文献标识码: A

文章编号: 2097-4183(2025)05-0044-13

Research Progress on Formation Mechanism and Control Technology of Dioxins in Iron and Steel Sintering Flue Gas

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Abstract: The emission of dioxins (PCDD/Fs) from iron and steel sintering flue gas poses a serious threat to regional air quality and human health. The process is considered a major source of dioxins. Therefore, it is necessary to select a cost-effective, environmentally friendly, and efficient control technology for enterprises. To control the formation and emission of sintered dioxins, it is essential to clarify the formation mechanisms of dioxins during the sintering process. Additionally, understanding the formation and distribution of sintered dioxins and their homologues is crucial for regulating emissions at the source, during the process, and at the end-of-pipe. The complexity of the sintering process makes it difficult to study the formation mechanisms of sintered dioxins. However, current research indicates that the formation mechanisms of sintered dioxins mainly include the *de novo*

收稿日期: 2024-12-31

修回日期: 2025-02-24

接受日期: 2025-02-26

DOI: 10.20078/j.eep.20250313

基金项目: 国家自然科学基金资助项目(52230002)

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synthesis mechanism and precursor synthesis mechanism. Since the sintering process meets the basic conditions for the *de novo* synthesis of dioxins: a carbon source, a chlorine source, and a metal catalyst, a consensus suggests that the primary formation mechanism of sintered dioxins is the *de novo* synthesis mechanism. Concerning the generation and distribution of PCDD/Fs and their homologues, researchers have sampled and analyzed iron and steel sintering plants worldwide. The results indicate that the products of sintered dioxins are primarily PCDFs, with a smaller proportion of PCDDs, which further supports the conclusion that the *de novo* synthesis mechanism is the dominant formation pathway for sintered dioxins. For the control of already-formed dioxins, strategies can be categorized into source control, process control, and end-of-pipe treatment. Source control is the most effective approach for reducing dioxin formation and includes measures such as raw material screening and the addition of inhibitors. Process control involves optimizing the sintering process, controlling the sintering temperature zone, and implementing synergistic solid waste treatment. Among these, the synergistic treatment of solid waste is a promising area for future research due to its significant potential. End-of-pipe treatments include high-efficiency dust removal systems, activated carbon adsorption technology, and selective catalytic oxidation technology. However, the application of high-efficiency dust removal and activated carbon adsorption technologies is limited due to economic limitations and technical constraints. Selective catalytic oxidation, on the other hand, has strong potential owing to its operational simplicity and lack of secondary pollution. The selection of an appropriate catalyst is crucial for the successful application of selective catalytic oxidation technology. Future research should focus on developing catalysts with high efficiency, stability, and cost-effectiveness, since no single solution is sufficient for dioxin control. Each control technology has its own limitations. Only by integrating multiple control technologies, methods, and processes adapted to specific conditions can optimal results be achieved. The control paradigm of waste treatment, solid waste co-treatment, and collaborative treatment is likely to become a major focus in future research on dioxin control in sintering processes.

Keywords: Sintering flue gas; Dioxins (PCDD/Fs); Formation mechanism; Homologous distribution; Multi-technology integration; Synergistic treatment

0 引言

钢铁工业的烧结过程被认为是二噁英排放的主要来源。据统计,我国烧结工艺的二噁英排放占总量 15.0%^[1], 欧洲为 19.6%^[2], 日本为 8.4%^[3], 澳大利亚为 6.4%, 美国为 1.9%^[4]。二噁英是指含有 1 个或 2 个—O—连接 2 个苯环的含氯有机化合物, 是一种持久性有机污染物(POPs), 包括多氯二苯并对二噁英(PCDDs)、多氯二苯并呋喃(PCDFs)和二噁英类多氯联苯(dl-PCBs)^[5-9]。二噁英的毒性因氯原子的取代数量和取代位置不同而有所差异, 含 1~3 个氯原子的被认为无明显毒性, 含 4~8 个氯原子的具有毒性, 其中 2,3,7,8-四氯代二苯并对二噁英(2,3,7,8-TCDD)是目前已知毒性最强的二噁英类污染物^[10-11]。二噁英具有毒性、生物累积性, 渗入到环境中难以自然降解, 对环境 and 人类有着较大的危害^[12-16]。PCDDs/PCDFs

和多氯联苯可导致生殖障碍、皮肤损伤、发育问题、免疫系统受损和癌症风险增加等问题^[17-18]。因此二噁英被《斯德哥尔摩公约》列入受控名单^[19-22]。

由于二噁英的危害性, 在工业生产过程中采用了一系列的措施来控制二噁英的排放, 例如选择性催化还原(SCR)的催化分解^[23-25]、活性炭喷射(ACI)^[26]、安装固定床吸附系统^[27]和静电除尘器。其中 ACI 因其操作简单且效率高, 被认为是最方便的二噁英控制策略^[28-30]。末端治理只能作为二噁英排放的补充控制手段。研究二噁英的形成机理是从源头控制和过程控制削减二噁英排放的根本途径^[4]。金属催化剂参与催化反应可直接将二噁英降解为 CO₂、H₂O 和 HCl, 减弱甚至消除二噁英的毒性, 因为该方法操作简单、去除效率高被广泛应用。然而, 催化剂在实际应用中常因工况复杂导致失活, 因此, 催化剂的选择已成为催化降解控制技术的关键, 而协同治理也逐渐成为催

化降解未来的趋势^[31-33]。

针对钢铁烧结工艺过程中二噁英排放所带来的危害,有必要厘清烧结工序中二噁英的生成机理以及分布情况,为烧结工艺二噁英排放控制提供参考。本文通过整理和分析钢铁烧结过程中二噁英合成机理的相关研究,更深层次地分析了烧结过程中二噁英的来源、生成机理,其次揭示了烧结过程二噁英及其同系物的生成规律与分布情况。最后总结了目前烧结过程二噁英控制技术,并提出了“以废治废、协同治理”的烧结二噁英控制策略,为未来控制二噁英技术提供新的方向。

1 钢铁烧结工序二噁英生成机理

目前垃圾焚烧过程中二噁英的生成机理被广泛研究,其生成机理主要分为以下 3 种:从头合成、前驱体合成以及热分解反应^[34-37]。与垃圾焚烧过程不同的是,钢铁烧结工序二噁英的合成机理主要包括以下 2 种:从头合成和前驱体合成。

1.1 从头合成机理

从头合成是指在 250~450 °C 的较低温度条件下,C、H、O 和 Cl 等元素在含有金属及其氧化物的飞灰催化作用下,通过氧化、环化和氯化等一系列基元反应生成二噁英的过程(图 1)^[38]。XHROUET 等^[39]通过分析烧结厂静电除尘器捕获的飞灰,研究了二噁英的生成特性。结果显示,二噁英及其同系物的分布情况与反应时长及温度关联性较弱。这一发现证实了二噁英及其同系物在生成过程中的分布受热力学调控。据此推断,PCDDs 与 PCDFs 在烧结环境下的生成路径可能存在差异:PCDFs 遵循从头合成机理,而 PCDDs 可能遵循前驱体合成的路径。此外,二噁英的浓度随着烧结区域的不同而不同。BUEKENS 等^[40]采用固定床流体反应器,对烧结机不同区域(包括布料器、点火区、烧结区、冷却区)的原料及静电除尘器(ESP)收集的除尘灰进行了二噁英从头合成的模拟实验。结果表明,布料器和点火区样品的二噁英浓度在实验前后变化较小,而烧结区和冷却区样品中的二噁英浓度略有上升,ESP 除尘灰中的二噁英浓度增幅最为显著。这一现象表明,这些样品中的二噁英主要通过从头合成途径生成,推测烧结区、冷却区以及废气进入静电除尘器前的管道可能是二噁英从头合成的主要区域。工艺的不同可能导致二噁英的生成量不同,KASAI 等^[41]

针对烧结干燥袋中的二噁英生成行为进行了从头合成的模拟实验。实验结果与 BUEKENS 的研究结果相似,表明在干燥带及烧结混合料中能够发生二噁英从头合成反应,但其生成量显著低于相同实验条件下垃圾焚烧炉飞灰的反应量。这一发现进一步证实了不同原料及工艺条件下二噁英生成潜力的差异性。龙红明等^[42]研究发现氯元素是导致二噁英排放量增加的关键因素。从二噁英生成机理的角度来看,氯元素不仅是从头合成反应的必要条件,还会直接参与反应过程。氯元素在二噁英生成过程中既是反应物又是催化剂的重要载体。

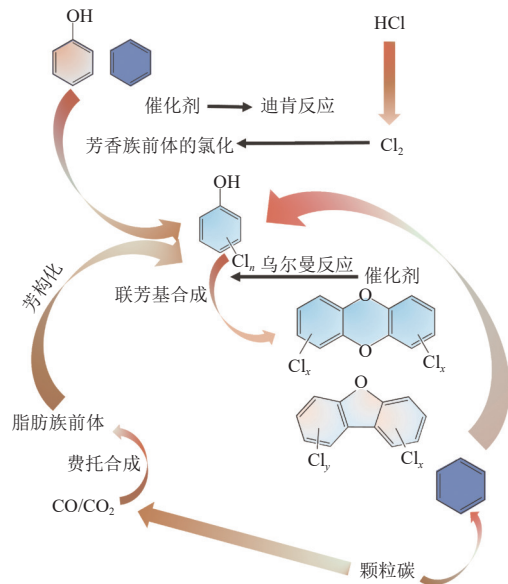


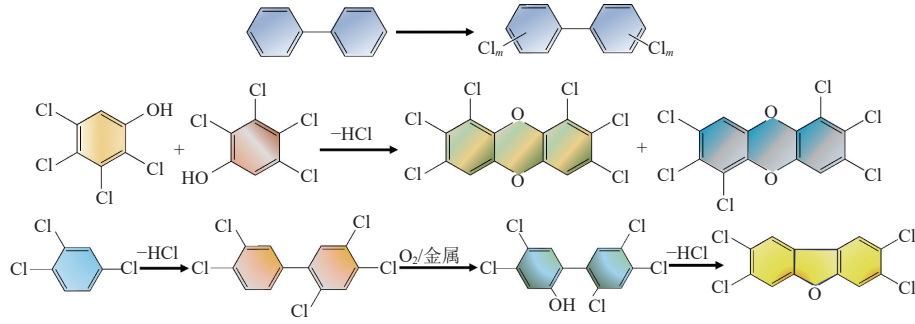
图 1 二噁英从头合成示意图^[43]

Fig. 1 Schematic diagram of *de novo* synthesis of dioxins^[43]

1.2 前驱体合成机理

前驱体合成机理是指 200~500 °C 内,在催化剂的参与下,废弃物的不完全燃烧产物转化为二噁英的前驱体。这些前驱体在催化剂的催化作用下,经历缩合等一系列复杂的有机化学反应,最终生成二噁英^[44]。在二噁英的前驱物合成过程中,PCDDs 和 PCDFs 2 类物质的形成过程有所区别,如图 2 所示^[43,45]。

ANDERSON 等^[34]在探究烧结机点火位置与二噁英生成量的相关性时发现,二噁英的产生量与烧结烟气温度的变化趋势相吻合。他们认为,二噁英前驱物最初在烧结料层的顶部区域形成,随后向下迁移至生料区域。在此迁移过程中,这些前驱物会经历一系列复杂的化学反应。据此推

图2 PCDDs 和 PCDFs 形成过程中的有机氯化反应、缩合反应及氧化反应^[43]Fig. 2 Organic chlorination reaction, condensation reaction and oxidation reaction during the formation of PCDDs and PCDFs^[43]

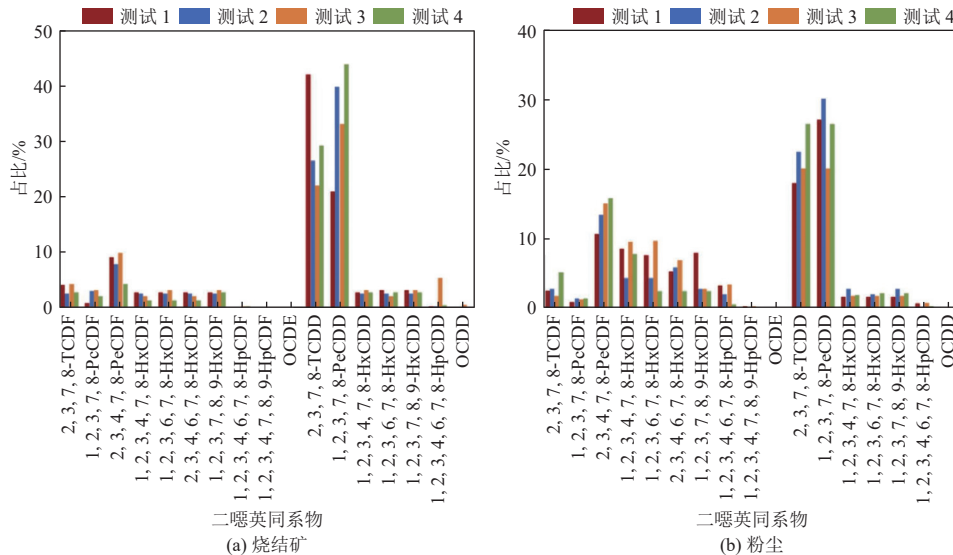
测, 烧结过程中二噁英的生成机制很可能涉及前驱物的合成过程。此外, 龙红明等^[42] 研究发现, 原料中的氯元素在燃烧过程中能够与气相中的有机物相互作用, 进而形成含氯的有机化合物或前驱体。在 200~800 °C、含氧条件下, 这些化合物会发生分子异构、重排以及氯化反应等化学变化, 最终生成二噁英。

总的来说, 在烧结工序开始时温度较低, 反应气含有碳源、氯源, 符合从头合成的条件。此外, 有研究表明在烧结过程中二噁英主要生成产物是 PCDFs, 而 PCDFs 是从头合成的产物。因此, 更多学者认为在钢铁生产过程中, 从头合成机理是烧

结二噁英生成的主要机理^[46]。

2 烧结二噁英及其同系物分布

烧结过程中二噁英及其同系物的生成分布也值得关注, 厘清烧结过程二噁英的排放特征对于烧结二噁英的排放控制具有指导意义。ZHOU 等^[4] 通过调查烧结产品和排放粉尘样品中 PCDDs、PCDFs 和 dl-PCBs 的浓度(图 3), 发现烧结产品中 PCDDs 浓度高于 PCDFs, 而在粉尘中 PCDDs 浓度小于 PCDFs, 虽然烧结产品和粉尘样品中的多氯二苯并对二噁英/呋喃(PCDD/Fs)的分布情况明显不同, 但多氯联苯同系物的比例相似。

图3 烧结矿和粉尘样品中各同系物对 PCDD/Fs 总量的相对贡献率^[4]Fig. 3 Relative contribution rates of each homologue to the total amount of PCDD/Fs in sinter and dust samples^[4]

LIU 等^[47] 以北方某铁矿烧结厂为研究对象, 研究了烧结循环流化床入口处的 PCDD/Fs 的排放特征(图 4)。结果发现, 在气相中丰度最高的 3 个同系物分别是 2,3,4,7,8-PeCDF(2,3,4,7,8-五氯

二苯并呋喃)、1,2,3,7,8-PeCDF、1,2,3,4,7,8-HxCDF(1,2,3,4,7,8-六氯二苯并呋喃)。颗粒相中, 丰度最高的 3 个同系物分别是 1,2,3,4,6,7,8-HpCDF(1,2,3,4,6,7,8-七氯二苯并呋喃)、2,3,4,6,7,8-HxCDF、1,2,

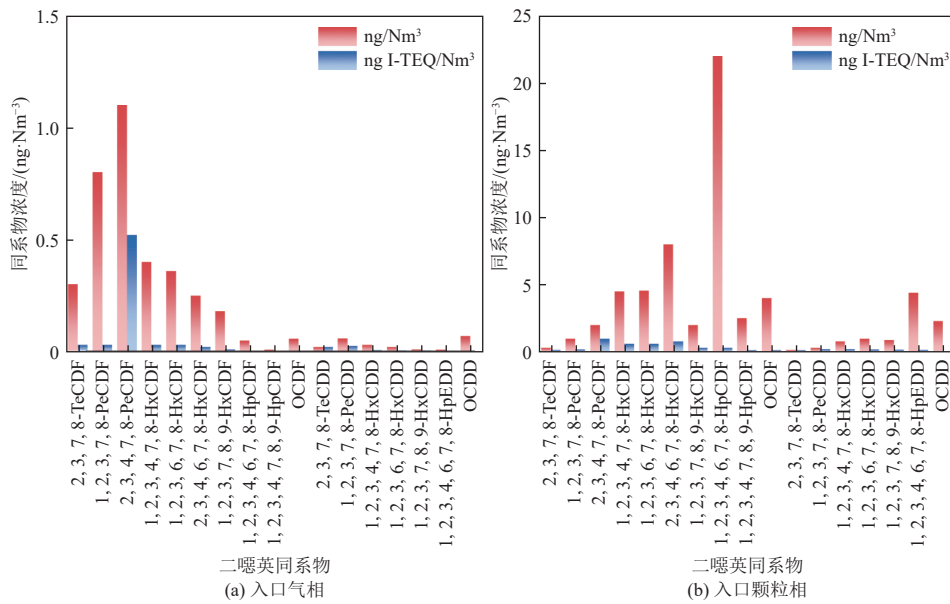


图 4 入口处气相和颗粒相 PCDDs 和 PCDFs 的同系物分布，无活性炭样品^[47]

Fig. 4 Congener profiles of PCDD/Fs for gas phase and particle phase of inlet without ACI samples^[47]

3,6,7,8-HxCDF。PCDFs 在气相和颗粒相中明显占据主导地位。另外，对喷吹活性炭-循环流化床-袋式除尘器耦合工艺进行了研究，发现投加活性炭后二噁英的去除率由 91.61% 增加到 97.36%。

WANG 等^[48]通过分析静电除尘器的灰尘样品和英国某烧结厂的烟囱排放物，同样发现在粉尘和烟囱排放物中 PCDFs 的含量最高。LONG 等^[49]对二噁英及其同系物的组分浓度和毒性当量换算浓度分析发现，在 3 家烧结厂排放的二噁英类同系物中，PCDFs 占比最大，毒性最强。

钱立新等^[50]对国内某钢铁厂 3 台烧结机静电

除尘灰、脱硫灰和脱硫装置进出口烟气中二噁英及其同系物排放情况进行了检测分析，脱硫前后气相中的二噁英同系物主要以五氯二苯并呋喃 (PeCDFs) 为主，电场除尘灰和脱硫灰中的 PeCDFs 和六氯二苯并呋喃 (HxCDFs) 含量之和分别占总排放量的 84% 和 85% (图 5)。另外，烧结机静电除尘灰、脱硫灰和脱硫装置进出口烟气中 PCDFs/PCDDs 比值分别为 9.88、9.14 和 6.29，证明烧结过程二噁英的合成机理以从头合成为主。研究表明，国内烧结厂二噁英主要是以 PCDFs 为主，仅含有少量的 PCDDs。

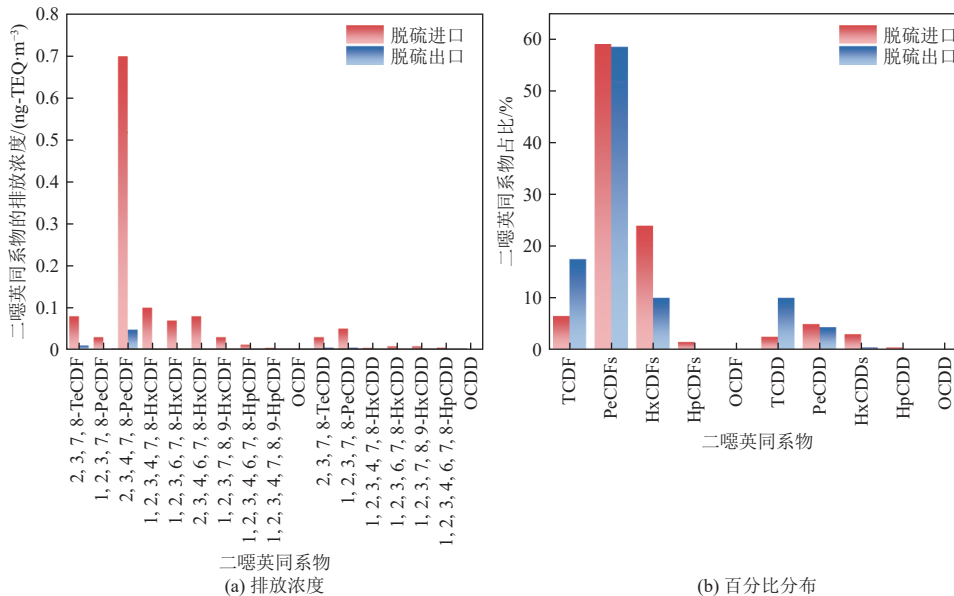


图 5 烧结烟气脱硫进出口二噁英同系物的排放浓度及百分比分布^[50]

Fig. 5 Influence of desulfurization on PCDD/Fs homolog concentration and percentage distribution^[50]

对于国外钢铁厂烧结工艺二噁英及其同系物的分布, KASAI 等^[41] 对日本 2 个钢铁厂烧结工艺干式除尘过程中的烟气采样分析, 对四至八氯二苯并对二噁英和二苯并呋喃的形成特征分析得出: PCDD/Fs 倾向于在烧结后期排放, 与 SO_x 、 HCl 相似, 在 PCDD/Fs 同系物中, 高氯化同系物的排放时间早于低氯化同系物。在干式除尘烟气中, 八氯二苯并对二噁英(O8CDD)和 1,2,3,4,6,7,8-七氯二苯并呋喃含量最高。PCDFs 的总浓度是 PCDDs 的 10 倍以上并且 PCDDs 中高氯化同系物

的浓度更高; 此外还指出, PCDDs 和 PCDFs 可能在风箱、静电除尘器以及烧结床中形成。

ANDERSON 等^[34] 指出英国烧结烟气中最丰富的同系物是 1,2,3,4,6,7,8-七氯二苯并呋喃和 2,3,4,7,8-五氯二苯并呋喃, 分别占目标化合物总浓度的 16.5% 和 16.0%, PCDFs 在排放中占主导地位, 约占目标化合物总浓度的 85%(图 6)。尽管烟气中 PCDD/Fs 的实际浓度存在差异, 但烧结厂的排放物中的同系物分布基本相同。

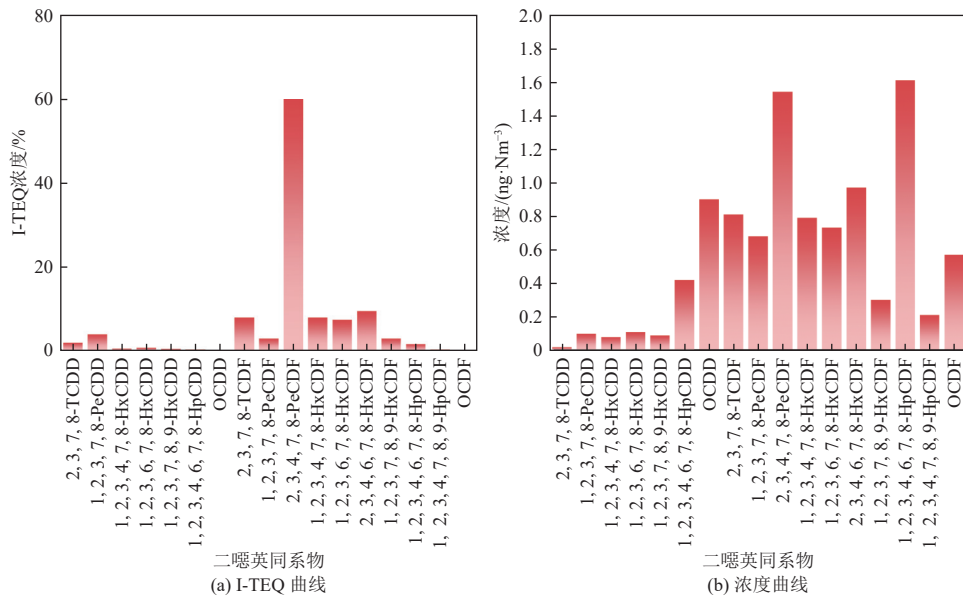


图 6 Corus UK 烧结厂主烟囱排放的典型 PCDD/Fs 和 I-TEQ 以及同系物浓度曲线^[34]

Fig. 6 Typical PCDD/Fs and I-TEQ and concentration congener profiles for a Corus UK sinter plant main stack emission^[34]

总的来说, 无论是国内还是国外, 关于烧结二噁英及其同系物的排放分布均与废弃物焚烧等高温过程大致相似, 其二噁英类排放呈现出典型的高温热过程特征, 即二噁英同类物以 PCDFs 为主, PCDDs 占比较低^[34]。因此, 关于烧结二噁英的控制研究, 需要更多关注的是 PCDFs。

3 钢铁烧结工序二噁英控制

鉴于二噁英对烧结生产和环境造成的巨大危害, 以及为了响应国家政策和相关国际公约的要求, 控制烧结过程的二噁英便尤为重要。目前二噁英的控制方法主要分为源头控制、过程控制和末端治理^[51]。

3.1 源头控制

3.1.1 烧结原料的筛选及优化

由于二噁英生成的关键因素主要是氯、铜等元素的存在, 因此在实际的钢铁烧结生产过程中

应减少高氯含量原料的使用量或者采用预处理减少烧结原料中氯元素和铜元素的含量^[52]。刘晶晶等^[53] 提出源头减少氯源和含铜催化剂等过渡金属催化剂的措施: 优先选用氯、铜等杂质含量低的高品位铁矿石原料; 选用低氯无烟煤, 或用焦粉替代煤粉; 对厂内回收的含铁尘泥和氧化铁皮等进行除油预处理, 或减少掺用比例; 做好轧钢氧化铁皮控油工作, 如轧机减速机漏油接盘回收、平流池及旋流井外井圈浮油回收机收油等; 选用低氯添加剂, 减少 CaCl_2 溶剂的使用量; 禁止将处理后的碳钢冷轧酸洗废水回用于轧钢冲洗氧化铁皮和矿石料场洒水抑尘。

3.1.2 添加抑制剂

向烧结原料中添加抑制剂能够降低二噁英的生成量, 主要是通过消耗氯源或者使催化剂失活。目前的抑制剂主要包括含磷、含氮、含硫和碱性抑制剂。含磷抑制剂中, $\text{NH}_4\text{H}_2\text{PO}_4$ 和 $(\text{NH}_4)_2\text{HPO}_4$

对二噁英生成具有更好的抑制作用^[33]。WANG 等^[54]通过对比 $\text{NH}_4\text{H}_2\text{PO}_4$ 、 $(\text{NH}_4)_2\text{HPO}_4$ 和 KH_2PO_4 、 K_2HPO_4 对二噁英的抑制效果,结果发现抑制效果主要由 NH_4^+ 决定。含氮抑制剂因为含有孤对电子可抑制二噁英类物质形成,此外还可与催化剂类金属(如 Cu)反应生成稳定的络合物,从而抑制二噁英的生成。含硫抑制剂通过 2 种方式抑制二噁英的产生,一是和催化剂 CuO 反应抑制从头合成反应,二是与 Cl_2 反应产生较为不活泼的盐酸以抑制二噁英的形成,但会使烟气中的 SO_2 浓度提高,所以使用较少^[52]。碱性抑制剂能与氯元素发生反应,形成稳定的氯盐,减少烟气中的氯含量,从而降低二噁英的生成量,而碱性组分例如 Na 或 K 不利于操作,所以最常用的抑制剂主要是含氮抑制剂,如尿素、氢氧化铵、三聚氰胺、三乙胺和磷酸氢铵^[55]。SCHÜLER 等^[56]在原料中添加碱性吸收剂(如 CaO 、 NaHCO_3),有效吸收了烟气中的

HCl 等,减少了氯源。此外,龙红明等^[57-58]通过烧结杯实验验证了尿素能够减少烧结过程中二噁英的生成量。

3.2 过程控制

过程控制是在现有的工艺条件下,为减少二噁英排放进行的工艺改善,例如烟道气热循环(图 7)、烟道气急冷降温等措施。烧结烟气循环技术是将烧结过程产生的一部分热烟气引入烧结点火器后的台车上,作为助燃空气循环使用,具有减排和节能双重功效^[53]。李咸伟和 YU 等^[59-60]通过烧结杯实验研究表明,循环烟气的温度越高越有利于促成二噁英的产生,减少循环烟气的氧含量能够在不改变烧结质量的情况下减少二噁英的排放。烟道气急冷降温是采用急速降温措施减少烟道气在二噁英的最佳生成温度区间的停留时间,以达到减少二噁英生成的目的。

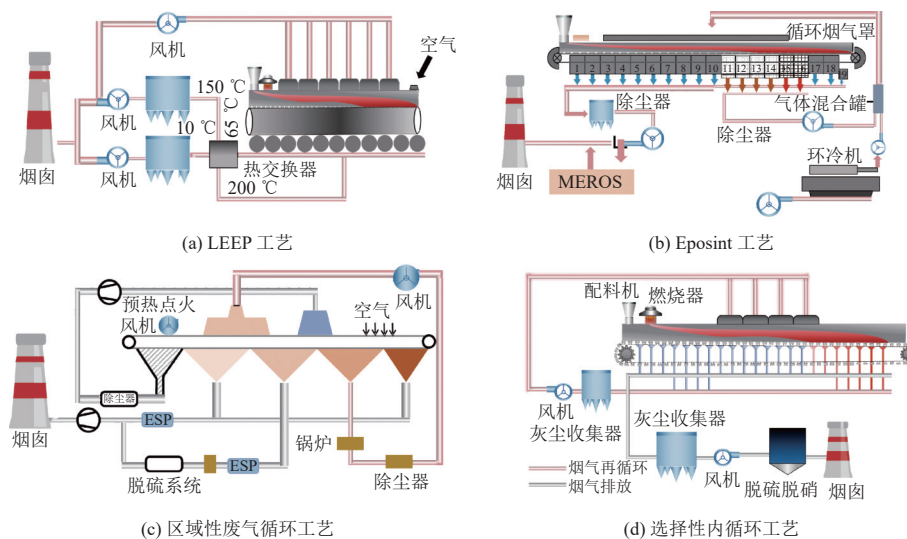


图 7 国外烧结烟气循环工艺示意图^[61]

Fig. 7 Schematic diagram of sintering flue gas circulation process abroad^[61]

3.2.1 烧结工艺的优化

优化烧结工艺可在一定程度上降低二噁英的生成量。通过调节烧结工艺,例如控制烧结终点位置来降低二噁英的排放量^[62]。控制合适的烧结条件,如焦炭量、热风温度、风中含氧量和出口负压均可减少二噁英的生成量^[58, 63]。

刘晶晶等^[53]提出以下措施以优化烧结工艺:保持工况稳定、采用小球烧结、粉尘返料造球技术、控制烧结温度、缩短二噁英生成温度停留时间、保证配料、混合制粒、布料呈稳定态操作。另外, YU 等^[60]提出烧结过程中 O_2 浓度对二噁英的

形成具有重要影响。具体来说,降低 O_2 浓度能够降低从头合成反应的速率,促使二噁英的产量随 O_2 浓度的下降而减少。此外,高温会显著增加烧结过程二噁英的生成量。

3.2.2 固废协同处理

目前,通过二噁英协同城市生活垃圾焚烧飞灰共烧结,能够降低烧结过程二噁英生成量的同时有效处理垃圾焚烧飞灰,实现了一举两得的效果^[64-66]。JI 等^[67]将垃圾焚烧厂的粉煤灰经水洗后得到水洗城市生活垃圾焚烧飞灰(WM-FA),用圆盘制粒机将 WM-FA 制粒成含水率为 9%~12% 的

5~8 mm 球团。在 WM-FA 颗粒上涂覆一层 0.5~1.0 mm 的含 CaO 添加剂,然后干燥至含水率为 5%~9%,再将 WM-FA 球团与铁矿石、助熔剂、焦炭粉和其他烧结原料充分混合。造粒后,通过偏析分布涂有含 CaO 添加剂的球团到烧结原料的

中下层,进行点火和烧结。研究发现 PCDD/Fs 的浓度从 1.042 5 ng I-TEQ/Nm³ 降至 0.624 0 ng I-TEQ/Nm³。最后提出了垃圾焚烧飞灰共烧结过程中抑制二噁英生成的机理(图 8)。

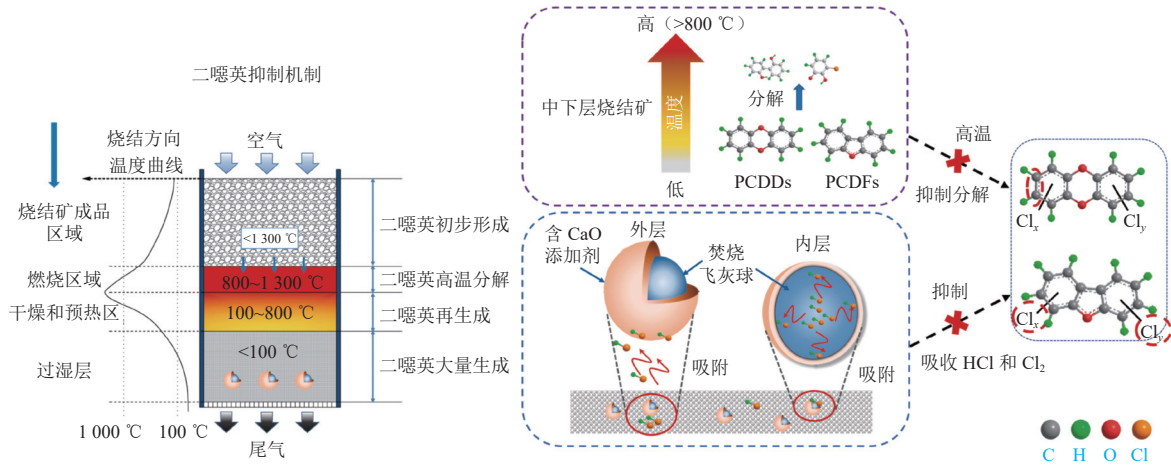


图 8 WM-FA 共烧结过程中二噁英抑制的机制^[67]

Fig. 8 Mechanism of dioxins inhibition in co-sintering process of WM-FA^[67]

GAN 等^[68]在烧结过程中添加固体废物焚烧粉煤灰粉、制粒后粉煤灰球和制粒后含有固体燃料的粉煤灰球,二噁英的降解率分别从 93.03%(粉煤灰粉)提高到 96.10%(粉煤灰球)和 96.61%(含固体燃料的粉煤灰球),烟气中二噁英的浓度分别从 5.61 ng I-TEQ m³(粉煤灰粉)降低到 4.50 ng I-TEQ m³(粉煤灰球)和 4.32 ng I-TEQ m³(含固体燃料的粉煤灰球)。烟气处理后,二噁英的残留浓度分别为 0.083 ng I-TEQ m³(粉煤灰粉)、0.066 ng I-TEQ m³(粉煤灰球)和 0.064 ng I-TEQ m³(含固体燃料的粉煤灰球),均符合我国钢铁行业超低排放限值。除了掺杂废弃焚烧物,HE 等^[69]还研究了生石灰(CaO)和石灰石(CaCO₃)对铁矿石与飞灰共烧结过程中二噁英形成的抑制作用,实验结果表明,当煅烧石灰和石灰石的添加量(质量分数)分别为 5% 和 3% 时,烟气中二噁英的抑制效率最高,可达 92.70%。研究发现低氯二噁英的分布比例增加,而高氯二噁英的分布比例下降,但八氯二苯并二噁英(O8CDD)除外。分析原因是 HCl 的消耗不仅抑制了二噁英从头合成,还通过前体显著促进了冷凝和脱氯,产生更多的四氯二苯并二噁英和 OCDD。

3.3 末端治理

虽然源头控制和过程控制能够有效地减少二噁英的生成,但是仍难以完全杜绝其生成和排

放。对于已经生成的二噁英,主要采用末端治理技术进行控制,主要包括高效除尘技术、活性炭吸附和催化氧化技术。

3.3.1 高效除尘技术

末端治理二噁英控制对象主要包括气相二噁英和颗粒相二噁英。除尘技术主要针对颗粒相二噁英,在 200 °C 下二噁英主要以固态形式吸附在颗粒物表面,可以通过除尘技术去除大部分颗粒相二噁英,但对气相二噁英的去除不是很理想。研究表明,静电除尘器和袋式除尘器对二噁英的减排效率分别为 50%~60% 和 85%~90%,如果将 2 种除尘方式结合,二噁英去除率可以达到 95% 以上^[53]。在国内钢铁厂中,烧结烟气后续处理常采用高效除尘技术,然而,当烟气颗粒物浓度太低时对二噁英的去除效率有限,所以未来高效除尘技术的开发更应该关注于提高低浓度烟气颗粒物中二噁英的去除率。

3.3.2 活性炭吸附

由于二噁英可以被多孔物质吸附,而活性炭因其较大的比表面积常被用作吸附剂,可以采用活性炭喷射的方式物理吸附二噁英。活性炭不仅可以吸附二噁英,还可以同步吸附烟气中的 SO₂ 和 NO_x 等污染物。

目前活性炭吸附法在日本、韩国和中国等钢铁厂使用。活性炭吸附法去除二噁英主要分为固

定床、移动床和注射床过滤器。表1是活性炭的3种吸附方法^[49]。国内许多钢铁厂家如宝钢、鞍钢、日钢等都采用了活性炭烟气吸附技术。虽然活性炭吸附效果好、价格便宜,但是活性炭喷射同样也会导致后续的除尘负荷增加,对除尘设备的性能提出了更高的要求。

表1 不同温度下3种吸收法对二噁英的去除效果^[49]

Table 1 Removal effects of three absorption methods on dioxins at different temperatures^[49]

吸附方法	温度/℃	吸附量/%	应用
移动床	150	98.2	适用于小型焚烧炉
	180	90.4	
固定床	150	97.9~98.8	—
	220	89.9	
注射床袋式过滤器	120	95.8	适用于大型焚烧炉
	160	97.3	
	190	98.3	
	220	89.9	

3.3.3 选择性催化还原

相较于高效除尘技术和活性炭吸附法,SCR具有操作简便、无二次污染的特点而被广泛应用。SCR主要用于去除烟气中氮氧化物,但是对二噁英也有优异的催化降解效果^[70],主要的反应过程如图9所示。

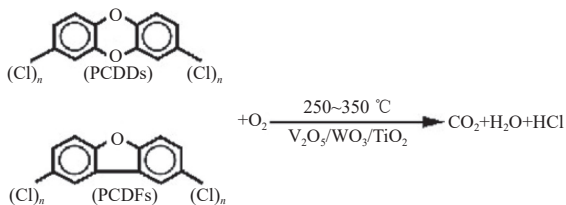


图9 二噁英的SCR脱除反应^[71]

Fig. 9 SCR removal reaction of dioxins^[71]

催化剂的选择是SCR技术去除二噁英的关键。目前,SCR催化剂主要包括贵金属催化剂和过渡金属催化剂^[72]。贵金属催化剂的催化活性虽高于过渡金属催化剂,但是会形成更多的多氯副产物,此外其价格昂贵也限制了应用。在过渡金属氧化物催化剂中, V_2O_5 具有高活性和优异的耐氯性,被用作商业化的 NH_3 -SCR催化剂($V_2O_5-WO_3/TiO_2$)能有效促进氯代芳烃同系物和二噁英的氧化分解^[73-76]。WEBER等^[77]通过研究VW/Ti商业催化剂对PCDD/Fs的催化氧化,发现氧化钒(VO_x)具有足够的活性中心, $V=O$ 基团亲核吸附

PCDD/Fs,对二噁英的催化氧化效果较好。PCDD/Fs被吸附后,便被转化为一类中间化合物,再被氧化为 CO_2 、 CO 、 HCl 、 H_2O 。ZHAN等^[78]比较了 V_2O_5/TiO_2 在不同氯苯类化合物(CBz)和低氯化PCDD/Fs上的催化去除效率,其去除效率的顺序为1,2-DCBz>1,2,3,4-四氯苯(1,2,3,4-TeCBz)>2-MCDD>五氯苯(PeCBz)>2,3-DCDD>六氯苯(HCBz)。除此之外,钒和钨的负载量也影响二噁英的去除效率,YANG等^[15]研究了不同钒负载量的SCR催化剂对二噁英进行催化降解,发现负载1%钒和2%钨的催化剂在280 °C、 $5000 h^{-1}$ 条件下对二噁英的去除率为84%,而钒的负载量提高至3%时,二噁英的去除率达到91%。此外,水蒸气会抑制二噁英的催化降解效率,因为 H_2O 和二噁英会产生竞争吸附,导致二噁英降解效率下降。目前选择性催化还原技术广泛应用于国内外钢铁烧结厂中,用于协同脱除烧结工序污染物。许多研究者正在研制新型的高效SCR催化剂。过渡金属具有良好的低温活性、独特的氧化还原性能、存量大的特点,将成为未来研究的热点^[79-81]。此外,高选择性生成目标产物及催化剂宽温区活性等也是热点研究方向。

4 总结与展望

目前,关于 SO_2 、 NO_x 污染物的控制技术已较为成熟。然而二噁英结构特殊、有毒、同系物种类多的特点,以及烧结工况复杂性,导致烧结工艺二噁英生成机理研究较为困难。亟待开发新的二噁英控制技术。在回顾现有文献的基础上,本文对烧结工艺二噁英的生成机理、二噁英及其同系物分布和控制技术提出了以下结论。

(1) 烧结工艺二噁英生成机理。目前关于烧结工艺过程二噁英的生成机理主要包括:从头合成机理和前驱体合成机理。从头合成机理主要认为,在烧结过程具有二噁英合成的各种条件:碳源、氯源、氧化气氛、温度等。前驱体合成主要是由于烧结配料中的除尘灰含有含氯前驱体,在合适的温度以及铜元素的催化下通过氯化、缩合、氧化反应等生成二噁英。目前来看,认为主要的合成机理是从头合成。

(2) 烧结二噁英及其同系物分布。国内外发现生成的PCDFs浓度总是远远高于PCDDs的浓度,同时也证明了烧结二噁英的生成机理主要是从头合成。

(3) 烧结二噁英控制技术。目前, 二噁英的控制技术包括源头控制、过程控制和末端治理。近年来, SCR 催化剂协同脱除二噁英的能力优异, 且操作简便、无二次污染而被广泛应用。然而由于烧结过程复杂, 催化剂的稳定性、高效性成为了目前研究的瓶颈。此外, 二噁英的生成催化机理尚未明晰, 仍需进一步探明。

目前来说, 源头控制是控制二噁英最经济的选择, 但并不是某一种控制技术就能够一劳永逸, 每种控制技术都存在局限, 只有根据具体生产情况, 选择多种控制技术、方式和工艺联合使用, 才能达到最佳效果。未来烧结二噁英的控制首先需要系统性地研究烧结过程二噁英生成机理; 此外需要研发关于烧结全过程二噁英的检测系统, 关注其产生行为, 以期对二噁英的控制提供依据; 最后, 需要研发高效、便捷的控制技术以减少二噁英排放。催化降解、固废共治、协同治理等技术是未来的研究方向和热点。

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