电弧炉炼钢多氯萘的排放及影响因素

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摘要 多氯萘(PCNs)是新持久性有机污染物(POPs), 于2015年被列入《斯德哥尔摩公约》. 电弧炉炼钢是PCNs的排放源之一, 然而目前对电弧炉炼钢厂PCNs排放的研究相对较少, 且当前关于电弧炉炼钢中PCNs等POPs的研究也主要集中于冶炼过程, 而忽略了原料预热过程中PCNs的排放. 电弧炉炼钢行业近年来使用高温废气在废钢入炉前对其进行预热, 以减少入炉后的升温时间, 从而降低能耗. 然而预热阶段的温度、原料、气氛等条件适宜PCNs等POPs的生成, 因此废钢预热阶段可能是电弧炉炼钢过程中POPs排放控制的重要工艺段. 随着我国废钢产量的增加, 电弧炉炼钢的市场份额将逐步增加, 深入认识电弧炉炼钢过程中PCNs等POPs的排放水平、影响因素, 控制电弧炉炼钢过程中PCNs等的生成和排放是我国履行国际公约、降低POPs健康风险有待解决的问题. 本研究针对我国典型电弧炉炼钢厂预热阶段展开研究, 阐明了电弧炉炼钢厂预热阶段排放的烟道气中PCNs这类新POPs的排放水平和特征, 提出电弧炉原料预热过程是PCNs的重要排放源, 发现原料净化对预热过程生成PCNs影响显著. 为电弧炉炼钢过程POPs的管控提供理论依据, 为实现电弧炉炼钢行业绿色可持续发展提供重要信息.

关键词 多氯萘, 电弧炉炼钢, 预热阶段, 非故意排放, 持久性有机污染物控制

多氯萘(PCNs)于2015年5月被列入《斯德哥尔摩公约》受控名单, 成为广受关注的新持久性有机污染物(persistent organic pollutants, POPs)^[1]. PCNs的人工合成始于20世纪初, 被广泛应用于变压器和电容器绝缘油和电缆绝缘体等^[2]. PCNs具有化学惰性, 在环境中很难降解, 可在全球范围内传输, 且其具有生物累积性, 能够造成机体肝脏、免疫系统损伤^[3]. PCNs的结构和毒性作用机制与二噁英较为相似, 因此当前科学界将PCNs等新POPs的毒性表征为2,4,7,8-四氯代二噁英(2,3,7,8-TeCDD)的相对毒性, 即毒性当量因子(TEF值, toxic equivalent factors)^[4-6]. PCNs的商品化生产于20世

纪80年代停止, 目前某些有机氯化学品生产和废弃物焚烧、金属冶炼等工业热过程的非故意产生和排放是环境中PCNs的主要输入源^[7-10]. 有研究对比了铁矿石烧结、电弧炉炼钢、焦化、转炉炼钢和铁铸造等不同工业过程烟道气中PCNs的浓度水平, 发现电弧炉过程排放PCNs浓度低于再生锌冶炼、导线焚烧过程, 与再生铜冶炼过程排放PCNs浓度水平相当, 远高于铁矿石烧结、转炉炼钢、铸铁、炼焦等过程^[11-16]. 且研究发现原料组成是影响铁矿石烧结等工业过程排放PCNs浓度水平的关键因素^[13]. 目前对电弧炉炼钢厂PCNs排放的研究相对较少, 有关电弧炉炼钢过程中PCNs等新

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POPs排放现状的研究有待开展。

电弧炉钢在世界粗钢年总产量中占30%^[17]，我国11.6%的粗钢是电弧炉工艺生产的，该工艺的主要原料是废钢和铁水^[18]。相较于其他炼钢工艺，如碱性氧气转炉最多可以使用30%的废钢^[19]，电弧炉炼钢能够使用100%的废钢，废钢循环使用节约了大量的能源和原料。然而与此同时，回收废钢中含有胶皮、塑料等杂质，能够引入高浓度的含氯化合物，导致PCNs等POPs的无意产生和排放^[20]。随着我国废钢产量的增加，电弧炉炼钢的市场份额将逐步增加，深入认识电弧炉炼钢过程中PCNs等POPs的排放水平、影响因素，控制电弧炉炼钢过程中PCNs等的生成和排放是我国履行国际公约、降低POPs健康风险亟待解决的问题。

目前对于电弧炉炼钢工业过程排放PCNs的相关研究较少^[12,14]，且当前关于电弧炉炼钢中POPs的研究也主要集中于冶炼过程，而忽略了原料预热过程中POPs的排放。为减少废钢进入熔炼炉的升温时间，降低能耗，电弧炉炼钢行业近年来使用高温废气在废钢入炉前对其进行预热，使废钢入炉前温度达到600℃，具有非常明显的节能效果。此前关于电弧炉炼钢的研究多集中于冶炼温度非常高的熔炼阶段(1500℃)，报道的PCNs等POPs浓度水平较铁矿石烧结等工业过程相对较低^[15]，然而预热阶段的温度、原料、气氛等条件非常适宜PCNs等POPs的生成^[21]，因此电弧炉炼钢的预热阶段可能是电弧炉炼钢过程中POPs排放控制的重要工艺段。本研究针对我国三家典型电弧炉炼钢厂预热阶段展开研究，阐明了电弧炉炼钢厂预热阶段排放的烟道气中PCNs这类新POPs的排放水平和特征，提出电弧炉炼钢过程中POPs生成的关键影响因素，为电弧炉炼钢过程POPs的管控提供理论依据，从而实现电弧炉炼钢行业绿色可持续发展。

1 实验

(i) 烟道气样品采集。选取了我国具有代表性的3个电弧炉炼钢厂作为研究对象，3个工厂分别代表了我国不同冶炼规模的电弧炉炼钢厂，且其具有3种不同的电炉炉型，选取的工厂均具备废钢预热设备，且预热设备稳定、正常运行，其基本信息见表1。于2019年11~12月期间采集了3个工厂原料预热阶段的烟道气样品，均采于电弧炉炼钢开机后各项参数均稳定以后的生产阶段。采集方法主要参考EN1948方法，应用等速采样技术进行样品采集。采样设备为意大利TECORA公司生产

表1 电弧炉炼钢厂基本信息

Table 1 Basic information for the electric arc furnace plants

电炉厂编号	P1	P2	P3
日投料量(t/d)	2000	3200	4020
年产量(万吨)	60	100	100
原料	废钢	钢切削料	废钢
空气污染控制装置	布袋除尘器	布袋除尘器	布袋除尘器
烟道气流量(m ³ /h)	134000	303000	406000
冶炼过程烟道气温度(℃)	1200~1500	1000	- ^{a)}
冶炼周期(min)	78	38	49
烟气氧含量(%)	16	18.5	20
烟气温度(℃)	170	107	86

a) “-”表示未采集到P3厂温度数据

的TCR等速采样器，利用采样器匹配滤筒捕集烟气中的颗粒物，XAD-2树脂吸附烟气中的气态污染物，每个企业采集3个样品。采样过程中所涉及采样枪的金属内衬管和玻璃部件等都经过甲醇、丙酮和二氯甲烷清洗，各个烟气样品都包括滤筒部分、树脂、冲洗液和冷凝液4个部分。采样结束后，所有的样品立刻用铝箔包好(避光)，运到实验室，储存于冰箱中以备后续处理。

(ii) 样品前处理与分析。采用同位素稀释高分辨气相色谱/高分辨磁质谱方法对采集的烟道气样品中PCNs进行分析，主要参照前期研究^[13,22,23]。简要的分析过程如下：样品中加入PCNs ¹³C₁₀同位素标(ECN-5102, tetra-octa PCN Mixture, Cambridge Isotope Laboratories)，采用索氏提取法甲苯溶剂提取24 h，通过旋转蒸发浓缩提取液，并进行柱色谱净化，包括多层硅胶柱、碱性氧化铝柱净化。进一步通过旋转蒸发和氮吹浓缩至20 μL，加入¹³C₁₀同位素标(ECN-5260, Cambridge Isotope Laboratories)用于回收率的计算。

采用气相色谱/高分辨磁质谱(HRGC/DFS, Thermo Fisher Scientific, 美国)对样品中75种PCNs同类物进行定性和定量分析，DB-5ms毛细管柱(60 m×0.25 mm i.d. ×0.25 μm)用于同类物的分离。进样方式为不分流进样，进样量为1 μL，氦气作为载气，流速设为1.2 mL min⁻¹，离子源为EI，离子源轰击能量设定为45 eV，温度为270℃。色谱柱升温程序为：80℃保持2 min，20℃ min⁻¹升至180℃保持1 min，2.5℃ min⁻¹升至280℃，10℃ min⁻¹升至290℃保持5 min。质谱用全氟四丁基铵(PFTBA)进行校正，采用选择离子监测(SIM)模式，调谐使其分辨率大于10000。

目标化合物的保留时间要求在可利用的同位素内标物质保留时间的0.02 s范围内, 两个监测的选择离子的同位素比值在理论比值的15%范围内, 检出限(LOD)定义为3:1信噪比. 所有样品分析过程中 $^{13}\text{C}_{10}$ -PCNs分析回收率为26%~93%, LOD范围为0.23~7.55 pg m^{-3} . 每批样品中都有一个空白样品作为对照, 用以评估分析过程可能引入的污染. 本研究空白样品中PCNs单体的浓度均低于LOD, 满足烟道气中PCNs的准确定性和定量分析要求.

(iii) 数据分析. 由于PCNs具有和二噁英相似的结构和毒性作用机制, 许多研究将多氯联苯、PCNs等POPs的毒性表征为2,3,7,8-TeCDD(毒性当量因子为1)的相似毒性. 本研究采用Noma等人^[5]报道的相对毒性因子值(TEF)以计算PCNs的毒性当量浓度, 阐明毒性当量贡献较高的PCNs同类物. 毒性当量浓度的计算公式如下:

毒性当量浓度(TEQ)

$$= \text{污染物浓度} \times \text{毒性当量因子(TEF)}. \quad (1)$$

排放因子是相对于调查的工业过程生产强度的平均排放水平, 排放因子对于依据有限的现场研究来估算该行业的污染物排放具有重要意义. 目前对于电弧炉炼钢的预热阶段污染物排放的相关研究较少, 因此本研究对我国典型电弧炉炼钢预热过程产生的PCNs排放因子进行估算, 能够为完善我国电弧炉炼钢过程PCNs排放清单提供重要信息. 排放因子和排放量估算公式如下:

排放因子

$$= (\text{烟气流量} \times \text{污染物的排放浓度}) / \text{生产率}, \quad (2)$$

$$\text{排放量} = \text{排放因子} \times \text{生产量}. \quad (3)$$

2 结果与讨论

2.1 电弧炉炼钢预热过程PCNs排放水平和排放因子

三家典型电弧炉炼钢厂原料预热过程PCNs的排放浓度分别为3473、667.7、92.44 ng m^{-3} , TEQ浓度分别为221.8、10.36、0.38 pg TEQ m^{-3} . 不同炼钢厂预热阶段烟道气中所排放的PCNs浓度差异显著(图1(a)), 工厂P1排放的PCNs浓度分别为工厂P2和P3的5和38倍. 可能是因为工厂P1的主要原料为包括导线胶皮、油桶等回收物的废钢, 这些原料中含有高浓度的含氯有机物, 可作为二噁英前驱体在预热阶段适宜温度下生成二噁

英. 此外, 原材料中掺杂的油漆、塑料中可能含有PCNs等POPs, 而废料加热过程能够促使这些污染物的释放^[24]. 因此电弧炉炼钢原料合理配比和预处理是控制PCNs等POPs生成的关键. 电弧炉炼钢预热过程排放的PCNs的浓度显著高于前期研究中电炉炼钢冶炼过程排放的PCNs浓度(458~1099 ng m^{-3})^[12]. 这是因为电弧炉炼钢原材料预热温度为200~700°C, 该温度段涵盖了适于PCNs从头合成和前驱体合成的最佳温度(200~650°C)^[25], 在预热原材料中含有较高浓度含氯有机物的情况下, 相较于温度较高的冶炼过程(熔炼温度1500°C), 电弧炉炼钢预热过程更易于促进PCNs等POPs的生成. 因此, 电弧炉预热阶段能够为PCNs等POPs的非故意生成提供适宜的前驱体、氯源和温度, 预热阶段排放的PCNs等污染物浓度是电弧炉炼钢过程排放污染物总浓度的重要贡献者, 在评估电弧炉炼钢POPs排放清单时不能忽略, 应当引起重视.

根据调查的3个典型电弧炉炼钢厂的PCNs排放数据, 对电弧炉炼钢预热阶段PCNs排放因子进行评估, 分别为346.7、27.05和2.720 ng TEQ t^{-1} . 原料中含明显有机废料时, 其排放因子高于前期所报道的两家电弧炉炼钢冶炼过程PCNs排放因子水平(分别为21.6和30.1 ng TEQ t^{-1})^[12], 高于炼焦行业PCNs排放因子(1.24 ng TEQ t^{-1})^[7]. 由三家电弧炉厂的排放因子可知, 原料净化对PCNs排放水平影响显著, 提出的PCNs排放因子可用于类似规模和原料类型电弧炉行业PCNs的初步估算, 为补充电弧炉炼钢预热过程PCNs排放清单提供数据支撑.

2.2 电弧炉炼钢预热过程PCNs同系物排放特征

图1所示为不同电弧炉炼钢厂PCNs同系物排放水平, 3个工厂的同系物质量浓度和TEQ浓度水平呈现相同的特征. 低氯代同系物的质量浓度高于高氯代同系物, 随着氯取代数的增加, 同系物浓度降低. 工厂P1排放的PCNs同系物浓度显著高于工厂P2和P3, 尤其是对于高氯代同系物, 工厂P1烟气中一至三氯代同系物浓度分别是工厂P2和P3烟气中的4和32倍, 工厂P1烟气中六至八氯代同系物浓度分别是工厂P2和P3烟气中的350和685倍(图1(a)). 这是因为工厂P1原料中含有充足的氯源, 能够促进低氯代PCNs逐级加氯产生毒性当量因子更高的高氯代同系物, 氯代同系物是其毒性当量总浓度的主要贡献者, 五至七氯代同系物的TEQ浓度占总TEQ浓度的93%~97%. 工厂P2和P3预热原料中含

图1 (网络版彩色)电弧炉炼钢厂PCNs同系物排放水平. (a) 质量浓度; (b) TEQ浓度. Mono, di, tri, tetra, penta, hepta, hexa, octa分别表示一至八氯代多氯萘同系物

Figure 1 (Color online) Mass concentrations (a) and TEQ concentrations (b) of PCN homologues in the stack gas from electric arc furnaces. Mono, di, tri, tetra, penta, hexa, hepta, and octa represent one to eight chlorine-substituted CNs, respectively

氯有机物较少, 其主要生成毒性当量因子较低的低氯代同系物(图1(b)). 氯化度能够更直观地指示氯化化合物的氯化程度^[8], 是各同系物浓度所占总浓度的百分比与氯取代数的乘积之和. 本研究中3个电弧炉炼钢厂预热过程烟气中PCNs的氯化度分别为2.3、1.3和1.86, 与焦化厂烟道气中PCNs的氯化度(1.1~3.3)相当^[7], 略高于铁矿石烧结厂烟气中PCNs的氯化度(1.5~2.4)^[13]. 工厂P1排放烟道气中PCNs氯化度显著高于工厂P2和P3, 与其PCNs排放浓度趋势一致, 进一步说明未净化原料中含氯有机物对PCNs的影响显著.

在三家电弧炉炼钢厂预热阶段烟气样品中, 低氯代PCNs同系物是主要的浓度贡献者(图2), 一至四氯代PCNs约占总PCNs浓度的95%, 与之前关于电弧炉炼钢冶炼阶段PCNs排放特征一致^[12,18]. 铁矿石烧结厂烟气中低氯代PCNs同系物占PCNs总量的85%^[13], 转炉炼钢厂排放烟气中低氯代PCNs同系物占PCNs总量的80%以上^[26]. 这是因为低氯代PCNs具有更高的沸点和更低的饱和蒸气压, 因此不同于二噁英等污染物的气固相分配特征^[27,28], PCNs更倾向于在气相中存在, 而空气污染控制措施(布袋除尘)主要去除飞灰颗粒物, 因此布袋除尘对气相中的低氯代PCNs去除效率较低, 导致其在烟气中的占比较高.

前期研究表明相邻氯取代数目同系物间的相关性比非相邻同系物之间的相关性更强^[7]. 本研究对三家工

厂烟气中PCNs同系物聚类分析发现(图2(c)), 8种PCNs同系物可聚类分为4类. 其中二氯代和三氯代同系物相似度较高, 可分为一类, 四氯代和五氯代同系物分为一类, 六至八氯代PCNs同系物分为一类, 与前期研究结果一致, 进一步验证了氯化/脱氯过程是PCNs的主要生成途径之一.

2.3 电弧炉炼钢预热过程PCNs同类物排放特征

图3为我国三家电弧炉炼钢厂预热过程同类物特征. 由于工厂P1原料未经净化, 含有充足的氯源和含氯有机物, 更易于生成高氯代PCNs. 如图3所示, 工厂P1和工厂P2、P3的同类物特征呈现显著差异, 工厂P1排放烟气中, 高氯代同系物123467/123567-HxCN的毒性当量浓度最高, 占总TEQ浓度的39%; 工厂P2和P3排放烟气中低氯代同系物2-MoCN和23-DiCN的毒性当量浓度较高, 分别占总TEQ浓度的58%和44%. 因此, 即使工厂P1的日投料量、飞灰产量、烟气氧含量均小于P2和P3的, 由于P1的生产原料未经净化处理, 其排放烟道气中毒性当量因子更高的高氯代PCNs的浓度高, 导致P1烟道气中PCNs毒性当量浓度高于P2和P3.

图4所示为三家电弧炉炼钢厂预热过程烟道气中PCNs的同类物浓度分布, 对于一氯代PCNs同类物, 2-CN的浓度占比高于1-CN, 该结果与Dat等人^[29]报道的再生铜冶炼过程排放的烟道气中2-CN相较于1-CN的

图2 (网络版彩色)电弧炉炼钢预热过程同系物特征. (a) 分布特征; (b) 样品误差条; (c) 聚类分析. Mono, di, tri, tetra, penta, hepta, hexa, octa分别表示一至八氯代多氯萘同系物

Figure 2 (Color online) Distribution characteristics (a), error bar (b), and cluster analysis (c) of PCNs in the stack gas emitted from preheating process of the electric arc furnaces. Mono, di, tri, tetra, penta, hexa, hepta, and octa represent one to eight chlorine-substituted CNs, respectively

图3 (网络版彩色)不同电弧炉炼钢厂预热过程同类物毒性当量的贡献比例

Figure 3 (Color online) Fraction of TEQ concentrations of PCN congeners in the stack gas emitted from preheating process of the electric arc furnaces

浓度优势相一致. 前期也发现铸铁过程产生烟道气中的五至七氯代PCNs同类物中 β 位的氯原子数目高于 α 位的氯原子数目^[14], 说明工业热过程中氯化反应更易于在 β 位发生. 由同类物浓度特征分布图可知(图4), CN1、CN2、CN3、CN4、CN5/7、CN6/12、CN9、CN11/18等一氯代、二氯代同类物是主要的浓度贡献同类物. 三氯代同类物中, CN13浓度占比最高; 四氯代同类物中, CN39、CN45/36、CN27/30浓度占比最高; 五氯代同类物中, CN51、CN54、CN52/60是主要的浓度贡献者; 六氯代和七氯代同类物中, CN66/67和CN73

浓度最高. 本研究中发现的部分优势同类物也被认为是废弃物焚烧和炼钢等工业过程的特征同类物^[5,8,15]. 在关于废弃物焚烧产生的PCNs特征的研究中, 将CN45/36、CN54、CN66/67以及CN73作为燃烧过程的特征同类物^[30,31]. 已有研究将几种特征同类物的比值用于识别环境中PCNs的不同来源^[13]. 本研究对电弧炉炼钢预热过程75种PCNs同类物进行了聚类分析(图5), 结合图4中浓度较高的同类物信息, 发现同类物CN1和CN2丰度高且差异显著. 同样, CN5/7和CN6/12的丰度也较高且差异显著, 而通常作为特征同类物的CN45/36和CN42、CN54和CN53/55、CN66/67和CN71/72、CN73和CN74的相似度更高. 因此, 本研究采用CN1和CN2的比值、CN5/7和CN6/12的比值作为区分电弧炉炼钢等工业源烟道气、PCNs化学品、母乳等样品中PCNs的特征同类物比值. 图6所示为不同来源PCNs特征同类物的比值分布特征^[2,5,22,32,33], 如图6(a)所示, 工业来源PCNs特征同类物比值范围存在重叠, 而工业过程和母乳中PCNs特征同类物分布存在差异. 如图6(b)所示, PCNs技术化学品(Halowax系列)中CN1与CN2的比值以及CN5/7与CN6/12的比值明显不同. 因此, 由于热过程中PCNs的生成机制和分布特征相似, 特征同类物比值分布并不能完全区分不同工业来源的PCNs, 而对于工业来源、生物体来源和工业化学品来源的PCNs能够较好地区分.

3 总结

电弧炉炼钢等冶金过程是PCNs的重要排放源, 然而目前对电弧炉炼钢厂PCNs排放的研究相对较少, 且当前关于电弧炉炼钢中PCNs等POPs的研究也主要集

图 4 (网络版彩色)电弧炉炼钢厂预热过程烟道气中PCNs的同类物浓度分布

Figure 4 (Color online) Fraction of mass concentrations of PCN congeners in the stack gas emitted from preheating process of the electric arc furnaces

图 5 电弧炉炼钢预热过程烟道气中PCNs同类物聚类分析

Figure 5 Cluster analysis of PCN congeners in the stack gas emitted from preheating process of the electric arc furnaces

中于冶炼过程,而忽略了原料预热过程中PCNs的排放。本研究针对我国三家典型电弧炉炼钢厂预热阶段展开

研究,我国三家典型电弧炉炼钢厂原料预热过程PCNs的排放浓度分别为3473、667.7、92.44 ng m⁻³, TEQ浓

图6 (网络版彩色)不同来源PCNs的特征同类物的比值分布特征。(a)工业来源和母乳中PCNs特征同类物比值分布特征;(b)工业来源、母乳和PCNs技术化学品中PCNs特征同类物比值分布特征。CP, EAF, HM, IOS, CM分别表示炼焦厂烟气、电弧炉炼钢厂烟气、母乳、铁矿石烧结厂烟气、PCNs技术化学品

Figure 6 (Color online) Distribution characteristics of PCN congeners from different sources. (a) Congener characteristics of PCNs from industrial sources and human milk; (b) congener characteristics of PCNs from industrial sources, human milk and technical chemicals. CP, EAF, HM, IOS, and CM represent the coking plants, electric arc furnace, human milk, iron ore sintering plants, and the PCN technical chemicals, respectively

度分别为221.8、10.36、0.38 pg TEQ m^{-3} 。采用含塑料等废钢作为原料的工厂P1烟气中PCNs的浓度显著高于P2和P3,说明原料净化对PCNs等POPs排放量的影响。预热阶段烟气中PCNs的浓度水平显著高于冶炼阶段(458~1099 ng m^{-3})。这是因为电弧炉预热阶段能够为PCNs等POPs的非故意生成提供适宜的前驱体、氯源和温度,预热阶段排放的PCNs等污染物浓度是电弧炉炼钢过程排放污染物总浓度的重要贡献者,在评估电弧炉炼钢POPs排放清单时不应被忽略。本研究阐明了预热阶段PCNs排放特征,低氯代PCNs同系物是主要的浓度贡献者,一至四氯代PCNs约占总PCNs浓度的95%。

提出同类物CN1和CN2的比值、CN5/7和CN6/12的比值可作为特征同类物比值用于区分工业来源、生物体来源和工业化学品来源PCNs。

本研究阐明了电弧炉炼钢原料预热过程对PCNs排放的显著影响,因此针对预热阶段的废气排放有待增强控制技术。且不同于其他钢铁冶炼过程,电弧炉炼钢能够使用100%的废钢,废钢循环使用节约能源的同时可能导致PCNs的无意产生和排放。因此原料合理配比和预处理可能是减少电弧炉炼钢预热过程PCNs排放的关键,对电弧炉炼钢行业的可持续发展有参考意义。

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Summary for “电弧炉炼钢多氯萘的排放及影响因素”

Emissions of polychlorinated naphthalenes during electric arc furnace steelmaking and their influencing factors

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Polychlorinated naphthalenes (PCNs) are emerging persistent organic pollutants (POPs) listed in the Stockholm Convention in 2015. PCNs were commercially produced and widely applied in transformers, capacitor oil and cable insulator in the early 20th century. PCNs are of persistency and can be globally transported. The widespread PCNs were reported to have hepatotoxicity and immunotoxicity, which were comparable to the toxicity of the notorious dioxins because of their similar structure. Currently, the toxicity of PCN congeners was characterized as the relative potency factors compared to 2,3,7,8-tetrachlorinated dioxins. The commercial PCN production was inhibited since the 1980s because of its toxicity. PCNs dominantly acted as byproducts during thermal-related industrial processes, including the chemical production, waste incineration processes and metal smelting processes, and then be unintentionally emitted into the environment. The electric arc furnace steelmaking plants were one of the important sources, which were rarely researched currently on their POP emission. Current-limited data showed that the PCN concentrations from the smelting process of electric arc furnace were relatively lower than that from the secondary zinc smelting process, comparative to that from the secondary copper smelting process, and much higher than that from iron ore sintering, converter smelting and coking process. However, current data on POPs emission from the electric arc furnace steelmaking plants were dominantly focused on the smelting process, ignoring that from the preheating processes. Preheating of the steel scraps has been conducted currently using the furnace off-gas, to reduce the heating time of the scraps during the smelting processes, and therefore can reduce the energy consumption. The preheating temperature of the steel scraps was about 600°C, which was suitable for the formation of POPs. In addition, the raw material of electric arc furnace steelmaking process can provide sufficient chlorines and precursors for POP formation, as the dominant raw materials for electric arc furnace were steel scraps. Different from other steelmaking processes, 100% steel scraps can be used for electric arc furnace steelmaking, which contained plastics, rubber, and some other impurities. Differently, only 30% steel scraps can be used for basic oxygen converter. Therefore, the steel scraps containing impurities coupling with the lower preheating temperature (600°C) during the preheating process can easily result in the formation of PCNs compared with that during the smelting process (1500°C). Understanding the emission levels, influence factors of PCN formation during the preheating process of electric arc furnace steelmaking plants are urgent for the POPs control and convention implementation.

In this study, occurrences, emissions and characteristics of PCNs during the preheating process of electric arc furnace steelmaking plants were investigated. We found that the steel scrap preheating process is an important emission source for PCNs in the environment, while the emission levels were even higher than that from the smelting process. Mass concentrations of PCNs from the stack gas of preheating process in the electric arc furnace ranged from 92.44–3473 ng m⁻³. Lower chlorinated PCN homologues were dominant, while concentrations of mono- to tetra-chlorinated PCNs contribute to 95% of the total emission. Constitutes of the steel scraps were critical influence factor for PCN emission. The steel scraps containing wires and oil drum used in plant 1 lead to higher PCN concentration in the stack gas, about 5 and 38 times higher than that from the other two plants. The ratio of CN1/CN2 and CN5/7/CN6/12 can be used to characterize the source of PCNs in the environment. The study clarified the critical influence of the steel scraps on PCN emission, indicating that the POPs emissions during the preheating process of arc furnace steelmaking should be paid more attention.

polychlorinated naphthalenes, electric arc furnace steelmaking, steel scrap preheating, unintentional emission, persistent organic pollutant control

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