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钢铁工业排放颗粒物中碳组分的特征

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摘要:为探究钢铁工业排放颗粒物中碳组分的特征,使用荷电低压颗粒物撞击器(ELPI)采样,采集到3组不同载荷和除污设施的烧结炉和1组炼铁高炉排放的颗粒物样品,利用热-光反射法,分析颗粒物中的有机碳(OC)和元素碳(EC)以及按温度划分的7种碳组分物质.结果表明,烧结工艺排放颗粒物中OC的质量分数高于炼铁工艺,OC在PM₁₀和PM_{2.5}质量分数分别是(5.3±2.3)%和(7.1±3.0)%,说明OC易在细粒径段颗粒富集,炼铁工艺排放颗粒物中OC在PM₁₀和PM_{2.5}质量分数分别是2.5%和2.0%;4组样品的7种碳组分相对比例相似,OC2和OC3在7种碳组分中质量分数最高,EC1、EC2、EC3的质量分数依次递减,OC1的质量分数可能与锅炉规模和脱硫设施有关;另外,烧结工艺排放各粒径段的颗粒物中OC和EC表现出较高的相关性,一次排放的PM_{2.5}中的OC/EC为4.7±0.7,远高于受体中估算二次碳组分的指标值。钢铁工业排放颗粒物中碳质组分的深入分析,可以为受体碳质气溶胶的来源解析提供基础数据,也有助于钢铁工业后续的除污管理.

关键词:钢铁工业;烧结工艺;炼铁工艺;颗粒物;碳组分

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Characteristics Research on Carbonaceous Component of Particulate Matter Emitted from Iron and Steel Industry

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Abstract: In order to investigate the carbonaceous characteristics of particles emitted from the iron and steel industry, an electrical low-pressure impactor (ELPI) was used to collect three sets of samples from the sintering process and one set of samples from the ironmaking process emissions of particulate matters. Organic carbon (OC) and elemental carbon (EC), which were divided into seven carbonaceous components based on the temperature of the particulate matter, were analyzed using a thermal-light reflection method. Results show that OC in sintering process particles is higher than that in ironmaking particles and accounts for 5.3% $\pm 2.3\%$ and 7.1% $\pm 3.0\%$ of PM₁₀ and PM_{2.5}, respectively, which reveals that OC tended to be enriched in fine particles. In the ironmaking process particles, OC accounted for 2.5% and 2.0% of PM₁₀ and PM_{2.5}, respectively. The relative proportions of the seven carbonaceous components in the four sets of samples were very similar. OC2 and OC3 accounted for the highest proportion; the EC1, EC2, and EC3 contents decreased in turn; and OC1 may be associated with boiler scale and desulfurization. In addition, the OC and EC of sintering process particles had higher correlation, and the OC/EC value of primary emission particles was 4.7 ± 0.7 , which is much higher than the value of the secondary OC estimation index in environment. Analyzing deeply on the carbonaceous characteristics in particles emitted from the iron and steel industry, which will provide essential data for source apportionment of carbonaceous aerosols in environment and will be conducive to the follow supervisory of pollution cleaning in iron and steel industry.

Key words: iron and steel industry; sintering process; ironmaking process; particulate matter; carbonaceous component

近年来,我国空气污染形势严峻,霾天气频发^[1],对人体健康和大气环境产生不利影响^[2],工业生产是导致霾的一类突出贡献源^[3],尤其是其排放颗粒物中的碳组分危害较大^[4]. 碳组分主要包括有机碳(organic carbon, OC)和元素碳(elemental carbon, EC),OC 含有多环芳烃、醛酮类等多种有毒有害的有机化合物^[5,6],有很多学者指出,钢铁、焚烧等工业是二噁英的重要排放源^[7,8],二噁英也属于 OC 中的一部分; EC 为一种吸光性较强的黑色物质,是大气能见度下降和气候变暖的重要因素^[9,10],所以说,研究钢铁工业排放颗粒物的碳组分特征具

有重要意义.

钢铁工业中的颗粒物排放源包括燃煤发电、烧结、炼铁和焦化等生产工艺,燃煤源与燃煤电厂的排放性质类似,研究较为成熟^[11~13],但是烧结和炼铁源,学者主要对其无机离子和金属元素等进行了研究^[14,15],而针对这两种排放源排放颗粒物中碳组分研究比较缺乏.基于此,本文以钢铁工业的烧结

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源和炼铁源为研究对象,探究这两种排放源所排放 的颗粒物中碳组分的排放特征,以期为受体中碳质 颗粒物的来源解析提供数据参考,并为钢铁工业后 续的除污管理提供实践建议.

1 材料与方法

1.1 样品采集

基于本研究目的"以钢铁工业的烧结源和炼铁源为研究对象,探究这两种排放源所排放的颗粒物中碳组分的排放特征",从锅炉的载荷、除污设施、工况条件等多个角度确定采样点,选取包头市 A 钢铁厂两个烧结机(烧结一和烧结二)、常州市 B 钢铁厂烧结机(烧结三)为烧结采样点(均为机尾),燃料均为无烟煤,选取常州市 C 特钢厂高炉炼铁工艺

(炼铁)为炼铁采样点,炼铁原料来自烧结矿,燃料为焦粉(主要燃料)和煤粉(补充燃料),由于炼铁工艺采样口常散布着高浓度的 CO 气体,采样难度大,只采集一组样品. 4 个采样锅炉基本参数信息见表1,关于采样锅炉的除尘设备,3 个烧结机均采用静电除尘,炼铁采用布袋除尘;关于采样锅炉的脱硫方式,3 个烧结的脱硫方式分别为干法脱硫、石灰石湿法、SDA 半干法,炼铁工艺无脱硫设施;关于采样锅炉的烟气温度和湿度,参数来自烟道在线监测设备,烧结机的排放烟温较高,为55~92℃,其中烧结三的烟气温度最高,炼铁的烟气温度和湿度均比较低. 所选的采样点均为大型的具有完善的除污设备的锅炉,实际采样中,运行工况稳定,样品基本可以代表烧结源和炼铁源的排放颗粒物.

表1 采样点基本参数

Table 1 Basic parameters of the sampling sites 烟气温度/℃ 烟气湿度/% 采样点 锅炉载荷/m² 除尘设备 脱硫方式 烧结一 静电除尘 干法脱硫 180 69 烧结二 500 静电除尘 石灰石湿法 55 92 静电除尘 SDA 半干法 烧结三 550 布袋除尘 炼铁 无

采样仪器为芬兰 Dekati 公司生产的荷电低压 撞击器(electrical low pressure impactor, ELPI),该仪 器在污染源的样品采集中应用广泛^[16,17],可以在 0.006~10 μm 范围内分 14 个粒径段进行采集,并 且全通道加热保温. 如图 1 所示,运用稀释通道法 进行采样(4 组样品均采用 1:8的稀释比),现场可 以得到各粒径段内的包括颗粒数浓度和质量浓度的 在线数据. 采样中根据不同的烟气流速,使用不同 面积的采样嘴,最大程度地实现了等速采样.

采样膜为 25 mm 的铝箔膜和石荚膜:铝膜具有良好的导电性,膜中间涂有耐高温的阿皮松脂可以有效防止颗粒物反弹,本研究将其用于测在线数据,采样时长为 4~6 h;石英滤膜为美国 PALL 公司生产,本研究将其用于碳组分分析,采样时长为 8~12 h.

1.2 样品分析

铝箔膜测在线数据的产生原理:烟气中颗粒物 先在高压电晕室内被荷电,进而被层叠的低压(出口压力保持 40 mbar)撞击器按粒径分离,这样在每一级撞击器中,产生环路感应电流,且每一级都与静电计连接,相邻两个撞击器的电流之差即为该粒径段的电流,最后一级收集盘(蜂窝式超导体材料)对实时测得的电流值进行校正后,得到颗粒物数浓度,

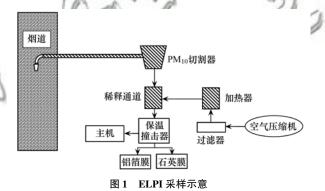


Fig. 1 Schematic of sampling process used by an ELPI

计算如公式(1)所示,再乘以相应粒径段的体积和密度得出质量浓度,如公式(2)所示.

$$N_i = \frac{I}{PneQ} \tag{1}$$

式中, N_i 为颗粒物数浓度(cm⁻³); I 为校正电流; P 为一定粒径范围颗粒在荷电区的带电效率; n 为一定粒径范围颗粒所带的基本电荷数目; e 为每个电子的电荷(1.602 × 10⁻¹⁹C), Q 为 ELPI 的流量(10 L·min⁻¹).

$$m_i = \rho_{\text{eff}} \frac{\pi}{6} d_i^3 N_i \tag{2}$$

式中, m_i 为第 i 粒径段的颗粒物质量浓度; ρ_{eff} 为等效密度,为 1 g·cm⁻³; d_i 为 i 粒径段的 D_{50} 空气动力

学当量直径.

石英滤膜采样前后,在恒温恒湿的环境中平衡 48 h,用百万分之一天平(MX5, Mettler Toledo)进行 称量,循环称量至少两次,每次称量结果相差不得超 过4 µg. 称重后的石英滤膜用于分析碳组分,分析 方法为热光反射法(TOR),仪器为美国沙漠研究所 研发的 Model 2001A 型热/光碳分析仪,进样前用 0.558 cm² 打孔器在样品膜上打一圆孔,前6级的样 品可以将全部颗粒物打出分析,后8级的样品不能 全部打出,需要根据所打的点数比例乘以仪器分析 结果,得出碳组分质量(ELPI 所采集的膜样品呈点 状分布),采用 Improve-A 升温协议,工作原理如下: 在无氧的纯 He 环境下,程序按 120、250、450、 550℃逐步 升温,使颗粒物中有机碳挥发,之后通入 2% O₂/98% He 混合气,继续逐步加热至 550、700、 850℃,使得样品中的元素碳完全氧化成 CO₅. 无氧 加热释放的有机碳经催化氧化炉(镍催化剂)生成 CO,,有氧加热阶段生成的 CO,,按时间顺序在还原 炉中被催化还原(MnO₂),生成甲烷(CH₄),再由火 焰离子化检测器(FID)定量检测,分别检测出有机 碳 OC1、OC2、OC3、OC4 和元素碳 EC1、EC2、 EC3[18~20]. 在仪器分析过程中会产生焦化碳 (OPC),实际上是 OC4 的一部分,样品中的 OPC 量 很少(总碳的5%以下),会产生一定数量的负值(理 论上不应产生负值,负值改为0),且没有发现明显 特征.

1.3 质量控制与质量保证

采样环节,为防止高温烟气冷凝,烟枪、预切割器、收集盘以及每个管路均有加热套件或保温装置;运输和保存环节,使用保温冰袋运输样品,在实验室4℃密闭的冰箱内冷藏;平衡和称重环节,温度控制为(20±1)℃,湿度控制为(50±5)%RH;分析碳组分环节,每天测试前后进行校样,偏差控制在5%以内.

2 结果与讨论

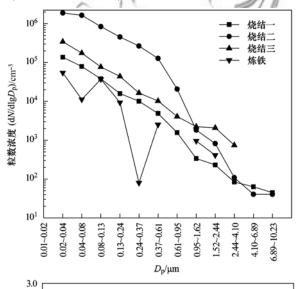
2.1 颗粒物的质量浓度和数浓度特征

为观察低于 10 μm 的颗粒物排放特征,在进样系统中采用旋风式预切割器将烟气中粒径大于 10 μm 的颗粒物去除,通过动力学撞击分级,颗粒物进一步被分粒径采集到滤膜表面^[21]. PM₁₀在线数浓度和质量浓度见表 2,样品的数浓度变化范围是 2.7 × 10⁵ ~ 1.9 × 10⁶ cm ⁻³,与范真真等^[22]观测的炼铁高炉数浓度接近,但是低于李超等^[23]用 ELPI 观测

的燃煤锅炉的排放数浓度, PM_{10} 质量浓度变化范围是 0.45 ~ 7.93 $mg \cdot m^{-3}$, $PM_{2.5}/PM_{10}$ 变 化 范围是 0.10 ~ 0.84,相对炼铁工艺来说,烧结工艺排放的颗粒物质量浓度较高,粒径较粗,尤其是烧结一的粒径 $(PM_{2.5}/PM_{10}$ 是 0.10),可能与其采用的干法脱硫工艺相关.

ELPI 没有明确的 2.5 μ m 和 10 μ m 的粒径切割点,本实验是将前 11 级 (2.44 μ m 以下)的质量加和作为 PM_{2.5}的质量,14 级 (10.23 μ m 以下)总的加和作为 PM₁₀的质量. 另外,在采集炼铁高炉排放颗粒物时,由于仪器故障导致缺失 0.61 ~ 0.95、2.44 ~ 4.10、6.89 ~ 10.23 μ m 粒径段的荷电数据,所以炼铁工艺排放的颗粒物质量和粒数浓度要比测量值高.

进一步观察颗粒物质量浓度和数浓度的粒径分布,由图2可以看出,烧结工艺排放的颗粒物数浓度



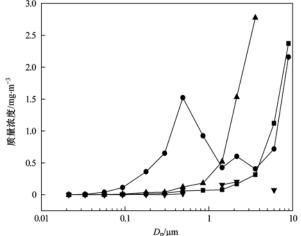


图 2 钢铁工业排放颗粒物的数浓度和质量浓度分布 Fig. 2 Number and mass concentration distributions of particulate matter emitted from the iron and steel industry

表 2 钢铁工艺排放 PM_{10} 的数浓度和质量浓度

Table 2 Number and mass concentrations of ${\rm PM}_{10}$ emitted from the sintering process

锅炉	数浓度/个·cm ⁻³	质量浓度/mg·m ⁻³	$\mathrm{PM}_{2.5}/\mathrm{PM}_{10}$
 烧结一	_	4. 22	0. 10
烧结二	1.9×10^6	7. 93	0. 58
烧结三	3.1×10^5	5. 22	0.46
炼铁	2.7×10^{5}	0.45	0.84

随粒径增大而逐渐减小,曲线平滑,而炼铁工艺排放的颗粒物数浓度下降曲线波动较大;由图 3 可以看出,质量粒径分布方面,烧结工艺的颗粒物在超过 1 μm 后,会迅速上升,而炼铁工艺的颗粒物质量浓度粒径分布均匀.

2.2 颗粒物中 OC 和 EC 特征

样品的碳组分质量分数见表3,PM10和PM2.5碳

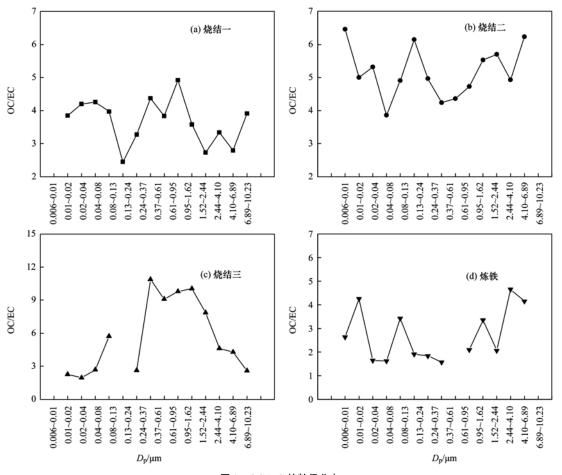


图 3 OC/EC 的粒径分布

Fig. 3 Diameter distributions of OC/EC

组分所占质量分数的计算见式(3)、(4):

$$C_{\text{PM}_{2.5}} = \frac{\sum_{i=1}^{11} m_{ij}}{\sum_{i=1}^{11} m_{i}} \times 100\%$$

$$C_{\text{PM}_{10}} = \frac{\sum_{i=1}^{14} m_{ij}}{\sum_{i=1}^{14} m_{i}} \times 100\%$$
(4)

式中,C 指组分所占质量分数; m_i 指第 i 级粒径段的颗粒物质量; m_{ii} 指第 i 级粒径段内 j 组分的质量.

数据表明,烧结样品中 OC 质量分数明显高于炼铁,在 PM_{10} 的占比为(5.3±2.3)%,在 PM_{25} 中占

表 3 颗粒物中 OC 和 EC 的质量分数

Table	e 3 Mass fra	ction of OC and	l EC in particl	es
锅炉	粒径	OC/%	EC/%	OC/EC
烧结一	PM_{10}	7. 90	2. 11	3. 74
Nr=H	PM _{2.5}	7. 44	1.89	3.94
烧结二	PM_{10}	4. 05	0.79	5. 13
加州一	PM _{2.5}	9. 98	2.06	4. 84
烧结三	PM_{10}	3.82	0.74	5. 16
<i>М</i> С-Н	PM _{2.5}	3.99	0.75	5. 32
炼铁	PM_{10}	2. 51	1. 11	2. 26
NA EX	PM _{2.5}	2. 04	1.06	1. 92

比为(7.1±3.0)%,这与郑玫等^[24]以两组烧结为样品的分析结果不同,其结果显示烧结源 OC 质量分数为(13.0±11.5)%,含量与相对偏差均比本研究

高,较马京华^[25]测得的 OC 质量分数(10.53%)要低,同时,与 Ma 等^[26]用 ELPI 研究的燃煤源颗粒物的碳组分质量分数相比,烧结样品的 OC 质量分数介于煤粉炉和循环流化床炉之间(煤粉炉、循环流化床、格栅炉 PM₁₀的 OC 质量分数分别为 3.0%、7.5%、11.4%);另外,烧结样品 PM_{2.5}中 EC 平均值及相对偏差为(1.56%±0.7%),这与炼铁样品 EC 接近. 炼铁源颗粒物中的 OC 明显小于烧结源颗粒物,这与郑玫的结论一致,且郑玫等^[24]、齐堃等^[27]均认为烧结产生的碳质组分与工艺中的有机添加剂有关. 事实上,颗粒物中的 OC 可能比测量值要高一些,因为 ELPI 的小粒径段中的压强较小,造成颗粒物表面的低沸点有机物挥发.

在很多环境受体的碳质颗粒物研究中,OC/EC大于2左右,被认为发生了二次反应,大于2左右的OC被估算为二次反应生成的有机物^[28~30],但是发现钢铁工业一次排放的颗粒物中,OC/EC近乎都大于2,烧结PM_{2.5}中为3.94~5.32,炼铁PM_{2.5}中OC/EC接近2,为1.92,当然,一次排放的颗粒物的OC可能会和大气中的O₃或者自由基等发生反应,或者挥发等,产生衰减变化.进一步观察OC/EC与粒径的关系,如图3所示,烧结一和烧结二在2.5~7.5

上下波动,都有"翘尾"现象,烧结三样品在 0.24 ~ 1.62 μ m 出现较高峰,而炼铁颗粒物的 OC/EC 是在 1.5 ~ 4.5 之间上下波动.

图 4 和表 4 所示为各粒径段的 OC 与 EC 相关性分析,发现:①烧结源颗粒物 OC 与 EC 表现出较高的线性关系,前两个样品皮尔逊相关系数分别是0.92 和 0.98,相对来说,炼铁源颗粒物 OC 与 EC 表现出较低的线性关系,皮尔逊相关系数为 0.74;②烧结源排放的颗粒,较多粒径段的 OC 质量分数值集中在 9% 左右;③烧结三排放源颗粒物的 OC 与 EC 相关性较低,有可能是烟温较高,部分粒径段 OC 不稳定所致.

图 5 所示为 OC 和 EC 的粒径分布,可以看出,4 个样品都会在 0.05 µm 附近出现一个峰值,烧结源颗粒物在粗粒径(大于 2.5 µm)的碳含量明显小于细粒径,这是由于已蒸发的气相有机物向液相和颗粒相转化中,易形成在细小的颗粒物中所致的富集效应. 欧阳丽华等[31] 对锅炉排放颗粒物的扫描电镜拍摄,颗粒物表面粗糙呈多孔状,推断碳物质一部分会吸附在颗粒物表层,另一部分会吸附在颗粒物中多孔内部,小粒径段的比表面积较大,吸附的碳物质更多.

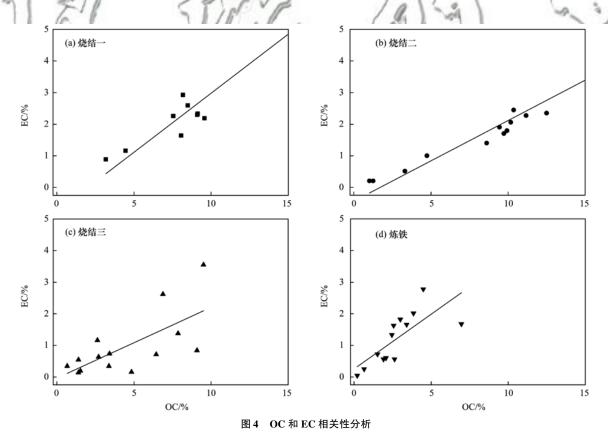


Fig. 4 Correlations analysis of OC and EC

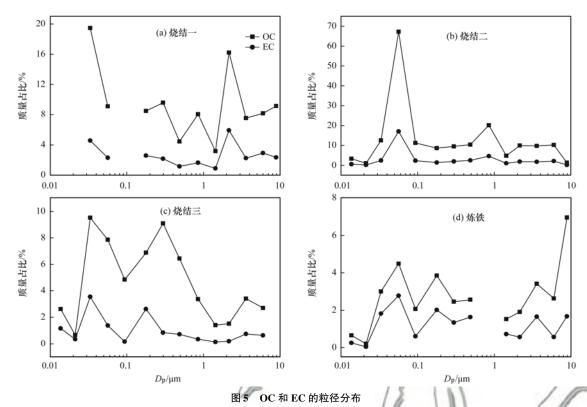


Fig. 5 Particle size distribution of OC and EC

2.3 7种碳组分特征

根据 Improve-A 升温协议,将碳组分按温度划分为7种,图 6 所示为 4 组样品中的 7 种碳组分质

量分数特征,可以看出,烧结一和烧结二样品碳组分结构非常相似,OC3质量分数最高,其次是OC2,EC中,均为EC1>EC2>EC3,可能是烧结一和烧结二

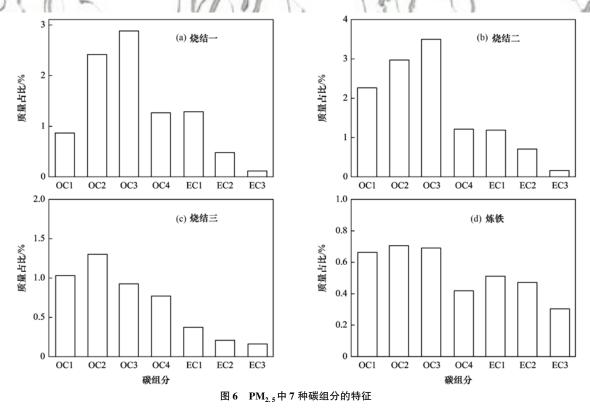


Fig. 6 Characteristics of the even carbonaceous components in $PM_{2.5}$

表 4 OC 和 EC 相关性分析

锅炉	拟合方程	皮尔逊系数
烧结一	y = -0.75 + 0.37x	0. 93
烧结二	y = -0.43 + 0.25x	0. 98
烧结三	y = -0.03 + 0.22x	0. 68
炼铁	y = 0.25 + 0.35x	0. 74

同在 A 公司,煤质和矿石几乎相同造成的,不同处 为,烧结一中 OC1 的质量分数较低,这一原因有可 能与锅炉规模有关,烧结二的锅炉吨位明显高于烧 结一,Wierzbicka等[32]曾发现 OC 的质量分数与锅 炉的载荷相关,但是,本研究认为这可能还与其脱硫 方式有关,烧结一采用干法脱硫,烟气中的气-液相 转化效率低于烧结二的湿法脱硫,且烟温高,造成沸 点较低的部分 OC1 以气体形式存在,并且,采用半 干法的烧结三样品中 OC1 质量分数特征也可作为 这一现象的佐证. 烧结三样品中为 OC2 > OC1 > OC3 > OC4 > EC1 > EC2 > EC3, 与前两个样品略有 不同,可能是由于煤源地和工况均不同造成的. 总 体而言,无论是烧结样品还是炼铁样品,源颗粒物 OC 中突出的组分是 OC2 和 OC3, EC 含量中均为 EC1 > EC2 > EC3,4 组样品碳组分成分谱的两两相 关系数均在 0.73 以上,说明钢铁工艺排放颗粒物中 7种碳组分相对比例相似,指纹特征明显,但炼铁源 排放颗粒物的7种碳组分质量分数相对较少,在 0.3%~0.7%范围内.

- (1)烧结工艺排放的颗粒物粒径较粗,PM_{2.5}/ PM₁₀范围为 0.10~0.46. 颗粒物中的 OC 易在细粒 径段中富集,PM_{2.5}中的 OC 所占质量分数明显高于 PM₁₀. 另外,一次排放的 PM_{2.5}中 OC/EC 为 4.7 ± 0.7,高于受体中估算二次碳组分的指标值.
- (2)炼铁工艺排放的颗粒物粒径较细,OC 所占 质量分数相比烧结工艺要低,但是 EC 所占质量分 数是与烧结工艺接近.
- (3)7种碳组分的指纹特征明显,丰富了钢铁工 业源的成分谱信息,有利于 CMB 等受体模型的进一 步精细化解析.

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