煤热解过程中氮分配规律的试验研究

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[摘　要]　利用热重分析仪对煤的热解过程进行试验研究, 考察不同终止温度和试样粒径对烟煤或无烟煤中挥发分氮和焦炭氮转化率的影响。结果发现: 碳化程度深的煤热解时, 氮更多地保留在煤焦中, 反之氮更容易随挥发分析出, 形成气态含氮产物; 高温有利于氮从煤焦中析出; 煤的粒径对挥发分氮析出作用明显, 煤粉越细, 挥发分氮转化率越高。

[关键词]　烟煤; 无烟煤; 热重分析; 热解; 氮转化率; 焦炭氮; 挥发分氮

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煤中的氮来源于植物和细菌中含有的蛋白质、氨基酸、生物碱、叶绿素等。氮在煤中主要以芳香环结构存在。一般煤中的氮含量在 1% ~ 3% 之间。燃煤过程中排放的 NO_x 按其生成途径可以分为热力 NO_x、快速 NO_x 和燃料 NO_x, 其中最主要的是燃料 NO_x, 一般占总量的 80% 左右。在一般的燃烧条件下, 燃料中的氮有机化合物首先被热分解成氰(HCN)、氨(NH_3)和 CN 等中间产物, 它们随挥发分一起从燃料中析出, 称之为挥发分氮。挥发分氮析出后仍残留在焦炭中的氮化合物, 称之为焦炭氮。挥发分氮通过气相均相反应生成 NO, 焦炭氮则通过多相气-固反应生成 NO[1]。研究煤热解过程中挥发分氮和焦炭氮的分配比例, 对于深入了解 NO 的生成机理, 寻找降低 NO 生成量的有效措施都有积极的意义。

1　试验设备、参数及过程

本文选用可方便调节升温速率和加热终温等试验参数的热天平作为试验平台, 对无烟煤和烟煤进行了热解制焦试验, 主要分析加热终止温度和粒径对挥发分氮和焦炭氮比例的影响。

试验采用 TGA/SDTA851^e 热重分析系统, 电子天平。试验参数: 氮气流量 40 mL/min; 升温速率 30 ℃/min; 加热终温分别为 700 ℃、800 ℃、900 ℃、1 000 ℃和 1 200 ℃5 种; 煤样粒径范围, 无烟煤选取 3 种(d < 43 μm, 74 μm< d< 149 μm 和 d> 271 μm), 烟煤选取 1 种(74 μm< d< 149 μm)。试验煤样的燃料特性如表 1 所示。

在高纯 N_2(99.99%)的气氛下, 将 60 mg 煤样由室温 30 ℃加热到设定的终温, 让挥发分在不同条件下析出。失重积分曲线和微分曲线以及相应的数据均由计算机给出, 最后将试验得到的剩余物质送元素分析, 测定其中的氮含量。

表 1　试验煤样的工业分析和元素分析

项目	工业分析				元素分析					
	M_{ad} /%	A_{ad} /%	V_{ad} /%	FC_{ad} /%	C_{ad} /%	H_{ad} /%	N_{ad} /%	S_{ad} /%	O_{ad} /%	$Q_{net,ad,p}$ /kJ·kg^{-1}
贵州无烟煤	2.96	19.63	4.36	73.05	73.89	1.94	0.51	0.21	0.86	26 243
铜川烟煤	1.99	28.80	26.74	42.47	55.33	2.96	0.97	0.72	9.23	22 460

2 试验结果与分析

氮转化率定义为焦炭氮或挥发分氮的总量占参与反应的原煤中氮元素总量的质量百分数,挥发分氮的转化率与焦炭氮转化率的总和等于100%。

2.1 温度对氮转化率的影响

无烟煤和烟煤在不同终止温度条件下的试验数据见表2和表3;无烟煤和烟煤的氮转化率随温度的变化曲线如图1和图2所示。

表2 不同终止温度条件下无烟煤的试验数据

终止温度/℃	原煤的氮含量/%	焦炭氮转化率/%	挥发分氮转化率/%
700	0.51	66.94	33.06
800	0.51	64.70	35.30
900	0.51	64.66	35.34
1 000	0.51	62.58	37.42
1 100	0.51	62.22	37.78
1 200	0.51	60.00	40.00

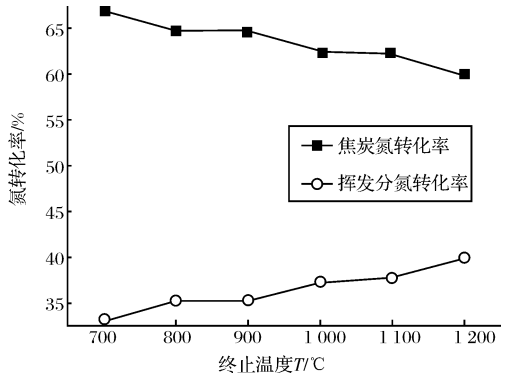

图1 无烟煤焦炭氮转化率和挥发分氮转化率随热解温度的变化

表3 不同终止温度下烟煤的试验数据

终止温度/℃	原煤氮含量/%	焦炭氮转化率/%	挥发分氮转化率/%
700	0.97	75.47	24.53
800	0.97	65.38	34.62
900	0.97	56.90	43.10
1 000	0.97	52.01	47.99

由图1可见,随着热解终止温度的升高,无烟煤的热解程度加深[2],燃料氮转化为挥发分氮的比例(挥发分氮/燃料氮)增加,即挥发分氮转化率增加,相应地焦炭氮的转化率减小[3]。这种变化趋势说明,以热稳定

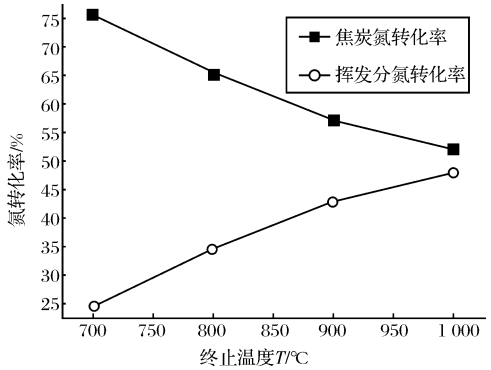

图2 烟煤焦炭氮转化率和挥发分氮转化率随热解温度的变化

性较高的杂环类有机结构存在的氮,温度是影响其析出进入挥发分的重要因素之一。另外由试验结果可见,热解后大部分氮仍残留在焦炭中,这是由无烟煤自身特性决定的,因为吡咯型氮易以焦炭氮的形式留在焦炭中。

由图2可见,烟煤和无烟煤挥发分氮的析出随温度变化的规律相同,都是随热解终止温度的升高而增加。对比图1和图2可以看出,随着热解终止温度的增加,烟煤焦炭氮转化率的变化比无烟煤更加明显,这表明焦炭氮转化率随煤种、温度变化的关系与原煤中氮的有机形态分布有关。一般情况下,挥发分含量越高,其热解也越容易,热解程度越深,相应的挥发分氮转化率也就越高[5]。

吡咯型氮和吡啶型氮是煤中主要的含氮官能团,含氮结构稳定,在1 000 ℃以下时,不会发生明显的裂解。随着煤碳化程度的提高,吡啶氮和吡咯氮的含量均增加,因此无烟煤中这两种含氮官能团的含量要大于烟煤。在无烟煤热解过程中,氮元素更多地留在焦炭中,即试验中无烟煤挥发分氮转化率明显低于烟煤。

2.2 原煤粒径对氮转化率的影响

原煤粒径对氮转化率的影响见表4和图3。

表4 原煤粒径对氮转化率的影响①

原煤粒径/μm	原煤氮含量/%	焦炭氮转化率/%	挥发分氮转化率/%
> 271	0.51	60.80	39.20
149~74	0.51	60.00	40.00
< 43	0.51	55.83	44.17

① 加热终温为1 000 ℃。

由图3可见,煤粉越细,挥发分氮转化率越高,也

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通风量不得小于吹扫风量(大于30%额定风量和小于40%的额定风量),以保证起动和低负荷时有足够的风量将未燃物稀释并排出炉膛外。炉膛吹扫作为点火的必要条件,每次吹扫规定不小于5 min,严禁随意取消吹扫或者缩短炉膛吹扫时间进行短路点火。若锅炉由于烟风系统故障跳闸后,运行人员应严格按照程序进行自然通风和等待时间清扫,禁止用短接信号的办法越过自然通风时间和程序等待时间,以免炉膛内可燃气体聚集,点火时发生爆炸。

(4)加强油枪的检查、使用和维护。燃烧器的起停要用自身的点火器和油枪稳燃,不可用其它燃烧器或炉膛内热烟气引燃。加强点火油系统、点火可燃气系统的维护管理,消除泄漏,防止燃油、可燃气体漏入炉膛发生爆燃。对油枪油阀、点火枪可燃气阀、燃油跳闸阀、可燃气跳闸阀要定期试验,确保动作正确,关闭严密。锅炉停止运行后,应及时关闭油枪和点火枪可燃气的手动门。

(5)严禁随意解除锅炉保护。炉膛压力高低锅炉跳闸保护和火焰故障锅炉跳闸保护在锅炉起动时应投入运行。机组运行期间,若需要临时解除炉膛压力保护进行维护工作时,运行人员必须做好事故预想,根据其它表计综合判断炉膛压力的变化。锅炉运行期间,禁止采用插火焰钥匙的办法模拟火焰扫描器的信号。严禁随意退出火焰探头或联锁装置,因设备缺陷需退出时,应经总工程师批准,并事先做好安全措施。运行中临时解除保护进行维护应尽快恢复。

(6)注意以下运行操作。1)锅炉起动、停运和低负荷运行及煤种改变时,加强对运行工况参数变化的监督,注意燃烧和风煤比的调节;2)锅炉运行期间,运行人员除根据有关表计对燃烧工况进行监视调整外,还应根据火焰扫描器和火焰电视的指示,结合到就地看火对燃烧情况进行综合判断,仔细调整;3)锅炉点火要求用点火器点燃油枪,油枪点燃煤粉。禁止采用隔层或隔角引燃的办法进行油枪点火。投停磨煤机必须按规程规定投助燃油。磨煤机停用时,应将系统内剩余煤粉吹扫干净;4)起动磨煤机时必须进行充分暖磨后再起动,以免冷粉进入炉膛使燃烧不稳定或加剧燃烧恶化;起动跳闸磨煤机必须按运行规程规定进行抽粉。运行中投油助燃时应先投入运行磨煤机相邻的油枪助燃,起动磨煤机时必须投入将要起动的磨煤机相邻的油枪助燃;5)锅炉停止运行后,应及时关闭油枪手动门和点火可燃气手动门,检查制粉系统各挡板、闸板、点火可燃气系统和点火油系统各阀门状态正确,切断全部燃料供给。严禁燃料进入停止运行的锅炉。

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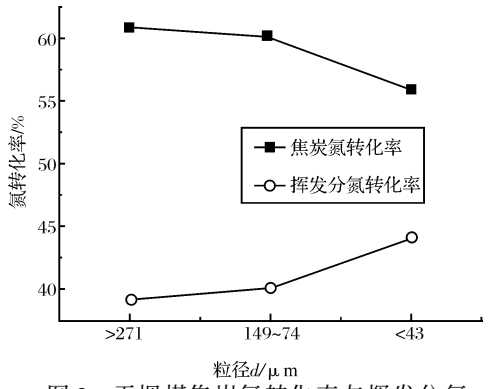

图3 无烟煤焦炭氮转化率与挥发分氮转化率随原煤粒径的变化

即煤粉越细,其在热天平中的加热速度越高,燃料氮转化为挥发分氮的比例越大。

当煤粉颗粒较大时,靠近煤粒中心处产生的热分解产物要向外迁移而逸出。而在迁移过程中,它们可能裂解、凝聚或聚合而发生碳沉积。煤粒越大,沉积量就越大,因而逸出的挥发分就越少。所以煤粉越细,越有利于燃料氮转化为挥发分氮[4]。

3 结 论

随着温度的升高,无烟煤和烟煤的挥发分氮转化率都增加,焦炭氮转化率相应减小,其中烟煤受温度的影响更明显;对于无烟煤,煤粉越细,挥发分氮转化率越高。

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fectiveness of particles' cross-mixing on surface of the bed layer is better than that of particles inside the bed layer, but the effectiveness of particles' cross-mixing is related to the apparent gas velocity. Under high gas velocity, the effectiveness of particles' cross-mixing in central region of the bed layer is better than that in the two side regions; under low gas velocity, the bed layer can only realize partial fluidization, the effectiveness of particles' cross-mixing in the side regions is better than that in central region of the bed layer.

Key words: picture tracking algorithm; fluidized bed; particles; cross-mxing; fluidization

Abstract: The secondary air duct of boilers is a group of large diameter short ducts in parallel connection, having inlet air flow condition with inner positioned resistant pieces. It's resistant coefficient is seriously smaller, and the air damper has strong vortex, thereby, resulting in strong pulsation of the secondary air. Test Data show that the pulsating amplitude of secondary air can reach 40% under some special conditions, affecting more greatly the flame stability. In addtion, analysis shows that the air dampers of same structure installed in different air ducts would have different performance of flow rate adjustment, the secondary air damper with common linear or equal percentage adjusting characteristics isn't existing, unique design with individuality must be made for concrete secondary air duct structure. Increasing original resistan coefficient of the secondary air duct can improve the adjusting performance of air damper, and inhibit pulsation of the flow rate.

Key words: boiler; secondary air duct; air damper; resistant coefficient; pulsation; adjustment of the flow rate

Abstract: At present, the selected catalyst reduction (SCR) denitrification tehnology is comparatively matured one on the world, the said technology can greatly reduce the emission of nitrogen oxides from thermal power plant, but the application of it in our country is fewer. The SCR denitrification technology has been briefly presented, and combined with concrete situation of one power plant in our country, the technical scheme for implementing retrofit project of the original SCR system in said power plant being expounded.

Key words: SCR; denitrification; 100 MW power plant; boiler; NO_x emission

Abstract: Test study on the coal pyrolysis process has been carried out by using thermogravimetric analyser. The influence of different terminated temperature and particle size of the coal sample upon conversion rate of volatile nitrogen and coke nitrogen in bituminous coal or hard coal has been investigated. It is found from the results that the more nitrogen retention existing in the chars when pyrolysis of deeply carbonized coal; on the contrary, the nitrogen is more easily to separate out along with volatile, forming gaseous nitrogen contained products; high temperature is helpful for nitrogen to be separated out from the chars, and the particle size of coal has obvious effect for volatile nitrogen to separate out. The more finely pulverized coal has more higher conversion rate of volatile nitrogen.

Key words: bituminous coal; hard coal; thermogravimetric analysis; conversion rate of nitrogen; coke nitrogen; volatile nitrogen

Abstract: Accident of furnace explosion may be occasionally occurred in operation of utility boilers. The mechanisms of furnace explosion and main causes leading to said explosion have been analysed in detail, and preventive measures, such as furnace has to be ventilated and purged before ignition, preventing the furnace to be outfire, and allocating reliable protection device etc., being put forward, providing certain experiences for reference to prevent furnace explosion.

Key words: thermal power plant; boiler; furnace; preventing explosion

Abstract: Based on practically measured data from several boilers, the real fouling coefficient of different coal quality and of different heating surfaces, as well as real heat transfer coefficient of various heating surfaces have been calculated. Results of calculation show that the influence of different coal quality upon fouling coefficient of the heating surface has comparatively large difference, and affecting more obviously upon the operation performance of boilers. The listed influences of coal quality upon fouling coefficient of heating surfaces have comparatively large difference with recommended values in some standards currently in effect at abroad, needing to accumulate data from boiler test, design, and operation for correcting the said influences.

Key words: Utility boiler; heating surface; fouling coefficient; heat transfer behavior

Abstract: The technical features of fluidized bed incinerator, including structural features, pollutant control, and advantages of co-firing municipal solid waste (MSW) with coal, have been systematically analysed. Co-firing MSW with coal can effectively inhibite and reduce the formation and emissioin of dioxin. Test and analysis of the emission characteristics for a 300 t/d CFB boiler of co-firing MSW with coal have been carried out. Test results show the pollutant emission from cofiring MSW with coal in fluidized bed can meet the requirements to national standard.

Key words: fluidized bed incinerator; MSW; co-firing of MSW with coal; emission characteristics; pollutant control

Abstract: A comparison study on two situations, with and without coal load on a steel plate, has been carried out by using audio and ultrasonic frequency. Results show that the peak amplitude of received signal, signal level, as well as waveform in time domain and amplitude spectrum have very great difference under said two situations. Based on the said difference, judgement of whether coal load exists on the steel plate or not can be made. The ultrasonic attenuation through coal is very great, ultrasonic frequency above 250 kHz is difficult to penetrate through coal layer of 35 mm thickness. This conclusion has certain guiding significance in aspect of applying ultrasonic frequency to detect material level in ball mills.

Key words: ball mill; thin steel plate; coal load; audio-ultrasonic frequency; ultrasonic penetration; material level

Abstract: The calculation method of average fuel detained time in the furnace of circulating fluidized bed (CFB) boilers has been approached, The mutual relationship among three indices, namely average detained time, carbon content in bottom fly ash, and the fuel thickness, being analysed, and suitable fuel layer thickness being determined. Test results for many times show, it is comparatively suitable for selecting fuel layer thichness to be 350~500 mm in operation.

Key words: CFB boiler; fuel layer thickness; average detained time; carbon content in the bottom ash

Abstract: An approach to several problems about the driving turbine of feed-water pumps, such as steam admission mode, lubricating oil and gland seal systems, as well as load switching etc., has been made, and the relationship among them being analysed.

Key words: driving turbine of feed-water pump; steam admission mode; lubricating oil system; gland seal system; load switching

Abstract: The relationship between effects of reheat steam turbine's performance degradation upon power and heat rate has been established, and method of power-correcting calculation for performance degradation being given. When assuming the degradation degree of the intermediate pressure cylinder to be one half of that of the high pressure cylinder, and adopting low pressure cylinder's degradation degree given by ASME PTC 6 Report-1985 to be one half of that of the intermediate pressure cylinder, it is found from calculation for different load conditions and different units that the power-correcting coeffidient of reheat steam turbine's performance degradation to be about -