

煤燃烧过程中痕量元素 As、Cd、Cr 释放特性实验研究

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摘 要: 主要研究以 As、Cd、Cr 为代表的痕量重金属在煤加热过程中的释放机理, 因其挥发性将直接影响其对大气的排放量。试验表明, 痕量元素的释放不仅与元素的物理化学性质有关, 而且与元素在煤中的浓度和赋予的形态及燃烧工况等因素有关。As 主要以硫化物形态存在, 而且其熔点和沸点较低, 故 As 最易挥发; 而 Cr 主要以无机物形态存在, 熔点和沸点又高, 故最难挥发; 而 Cd 介于二者之间, 故挥发性 $As > Cd > Cr$ 。试验证明随着温度升高, 各元素的挥发率也逐渐升高, 而且 $As >> Cd > Cr$ 。

关 键 词: 痕量元素; 释放; As; Cd; Cr

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1 前 言

煤中痕量元素在燃烧过程中因各痕量元素在煤中的浓度、赋存状态以及燃烧工况的差异所表现的热行为是不同的。目前, 国内外通常根据各元素热行为的不同, 将痕量元素分为 3 类: (1) 高挥发性元素, 如: Hg、Se 和 As; (2) 中等挥发性元素, 如: Pb 和 Cd; (3) 低挥发性元素, 如: Zn、Ni 和 Cr 等。具体分类与煤种、炉型和燃烧工况有很大关系。

已有研究发现, 痕量元素的释放与矿物组分的变化过程是密切相关的, 通常矿物质在煤中的存在形式有以下 3 种: (1) 以自由的矿物质颗粒存在 (常指外来的灰或矿物质); (2) 连结在碳骨架上的矿物质; (3) 分散于煤晶格上的无机质并以共价键和离子键结合在煤的结构上。在煤粒燃烧过程中, 矿物组分会发生熔融和合并, 根据破碎机理和汽化凝结机理, 大多数的矿物质将形成不同粒径的飞灰颗粒, 其中小颗粒主要是由煤中矿物组分的汽化凝结生成, 而大颗粒则是由焦炭的爆裂而生成, 所以矿物组分 Fe、Si、Al、Na、Ca 和碱土元素等是飞灰颗粒的主要成份。而煤中大部分的痕量元素以多种形式与矿物组分结合, 如 Hg 和 As 多存在于黄铁矿中; Cd 多存在于闪锌矿和黄铁矿中; Cr 多存在于黏土中或其它无

机物中。在矿物质通过破碎机理和汽化凝结机理形成飞灰颗粒的过程中, 与矿物组分相连接的痕量元素也经历了一系列复杂的物理化学过程, 最终释放到外部气流中, 并与周围的气体发生化学反应。随着温度的降低, 通过均相成核形成很细小的颗粒, 而这些颗粒很快通过碰撞凝聚而长大, 或者通过异相冷凝富集在周围已形成的飞灰颗粒上, 并随之排到大气中。

为了深刻揭示煤中痕量元素的释放规律, 以及它与痕量元素本身的物理化学性质和在煤中赋存形态的关系, 它与煤种及煤中矿物质以及燃烧工况的关系等, 我们进行了专门的实验研究。

2 痕量元素释放特性实验研究

选用我国典型的 3 种煤种: 褐煤、烟煤和无烟煤, 重点研究 As、Cd 和 Cr 3 种代表不同挥发性元素的释放过程。实验在管式炉中进行, 称取一定量煤样置于石英舟中, 并放到炉子恒温区, 控制温度在 $500 \sim 1100$ °C 之间, 为使燃烧完全, 通以 900 mL/min 流量的空气, 使之在充足的空气下燃烧, 燃烧时间 2 h, 然后取出石英舟去干燥器内冷却和称重, 各样品痕量元素浓度结果如表 1 所示。

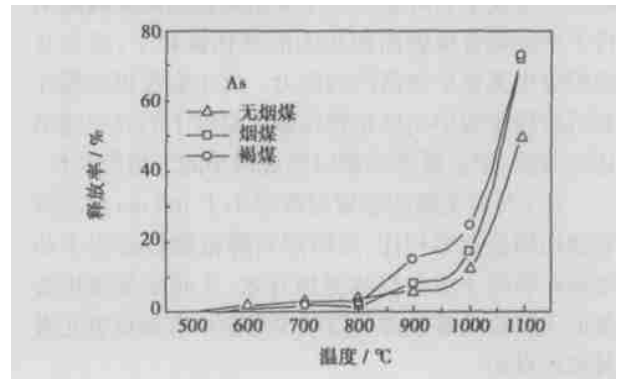


图 1 燃烧过程中 As 的释放

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表 1 不同温度下煤灰内痕量元素浓度

(mg/kg)

温度/℃	As			Cd			Cr		
	无烟煤	烟煤	褐煤	无烟煤	烟煤	褐煤	无烟煤	烟煤	褐煤
500	26.5	23.5	23.8	4.4	1.1	1.6	31.7	5.2	15.6
600	26.3	23.6	23.4	4.3	1.1	1.6	31.5	5.1	15.7
700	26.1	23.1	23.1	4.4	1.0	1.5	31.5	5.1	16.0
800	26.1	22.9	23.7	4.2	1.1	1.6	31.3	5.0	16.4
900	24.8	20.1	23.5	4.0	0.9	1.4	31.3	4.6	15.0
1 000	24.8	17.8	21.0	4.1	0.9	1.5	31.5	4.3	14.5
1 100	7.8	6.6	12.2	3.7	0.8	1.4	31.5	4.2	15.4

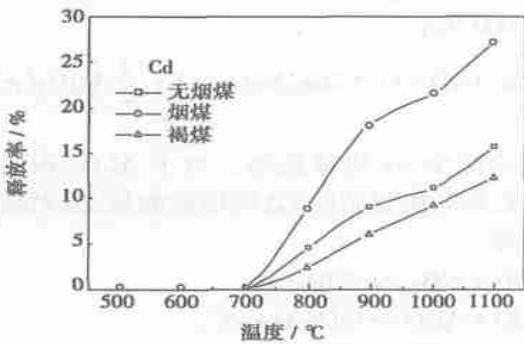


图 2 燃烧过程中 Cd 的释放

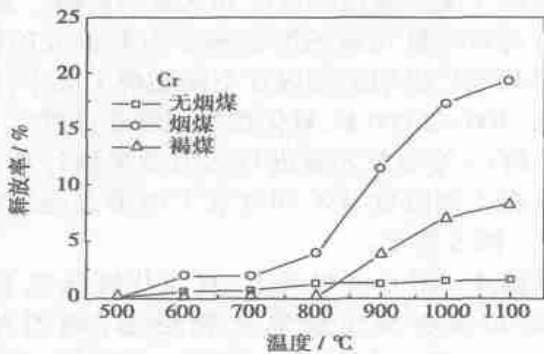


图 3 燃烧过程中 Cr 的释放

图 1~图 3 分别给出了不同煤种 As、Cd 和 Cr 的释放率随温度的变化关系。可以看出, 这些元素的释放率均随温度升高而增加, 但是不同煤种不同元素的释放程度是不同的, 具体与各元素的物理化学性质及赋存形态、煤种及煤中矿物质以及燃烧工况等因素有关。

3 影响因素分析

3.1 痕量元素本身的物理化学性质及煤中赋存形

态的影响

燃烧过程中大部分痕量元素的汽化是在焦炭燃烧阶段开始的, 熔点和沸点低的痕量元素更容易汽化, As 的熔点和沸点低, 故相对于 Cd 容易汽化, 而 Cr 最难汽化, 所以随温度增加, Cr 变化平缓。各元素及其化合物的熔点和沸点如表 2 所示。

表 2 痕量元素的熔点和沸点

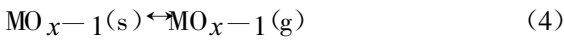
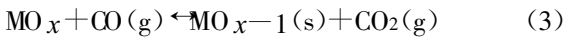
(°C)

元素	单质	氧化物	硫酸盐	硫化物	氯化物
As	615 升华	300/707	57/193	/	315/461
Cd	321/769	568/964	1 135	1 328	1 560 升华
Cr	1 890/2 680	150/1 300	/	1 550	> 2 335

挥发性还与各元素在煤中的赋存形态有很大的关系。不同形态痕量元素的挥发性是各不相同的。煤中的痕量元素已如前述, 有的与煤中的有机物结合, 有的与煤中的矿物质结合, 如与硫化物、硫酸盐、碳酸盐和铝硅酸盐等矿物质, 有的则在有机物和矿物质中都存在。As、Cd、Cu、Pb、Hg、Se 和 Zn 等为亲硫元素; Cr、Co 和 Ni 等在有机质和无机质中均存在。通常认为, 与硫化物和有机物结合的元素容易挥发, 因为这些亲硫元素在高温还原性条件下容易分解, 硫与金属元素发生分离, 所以这些元素在燃烧时很容易部分汽化, 存在于有机物中的元素在燃烧时更容易挥发。As 在煤中主要存在于黄铁矿中(占总砷的 73%~83%)有机态仅占 8%左右, 故释放机理为:



Cd 多存在于闪锌矿和黄铁矿中, 即以硫化物形态存在, 部分以无机态存在, 其熔点和沸点比 As 高, 所以释放较 As 慢。而 Cr 多存在于黏土或其它无机物中^[1~2], 主要是以硫酸盐存在, 其挥发性很低, 甚至不挥发, 在加热过程中, 硫酸盐首先会发生分解形成氧化物, 然后被还原生成易挥发的次氧化物, 但挥发性还是要低于硫化物, 所以挥发率低。



式(2)~式(4)中 A 代表煤中的主量和微量元素,如 C、N、Si、Al、P、Ti 和 Mn 等,MO_{x-1}是痕量元素的次氧化物或单质态形式,它们比氧化物形态 MO_x 更容易汽化,氧化物态通常是煤中其它的一些金属化合物(如硫酸盐、碳酸盐和硝酸盐等)在高温下分解得到的,如式(2)所示。Quann 等人认为,式(3)是煤中难溶性氧化物释放的主要机理(还原机理),焦炭矿物组分内处于还原性气氛,以难熔氧化物形态存在的痕量元素被还原成更容易挥发的次氧化物或单质态,然后发生式(4)的挥发汽化过程^[3~4]。

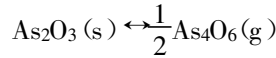
根据以上所述,由于痕量元素自身不同的沸点和熔点,以及不同的存在形态,因此在加热过程中的挥发性是不同的,As 主要以硫化物形态存在,而且其熔点和沸点较低,As 最易挥发,而 Cr 主要以无机物形态存在,熔点和沸点又高,最难挥发,而 Cd 介于二者之间,挥发性 As > Cd > Cr。

3.2 煤种及煤中矿物质的影响

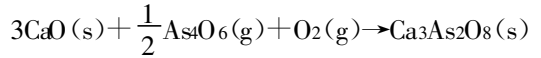
从图1~图3可以看出,不同煤种各元素所表现的行为各不相同。对无烟煤来说,As 和 Cd 元素随温度的变化趋势均较 Cr 大,从 600~700 °C 之间开始汽化,As 在 1000 °C 释放急剧增大,到 1100 °C 大部分 As 都释放出来,而 Cd 的变化趋势要平缓一些,Cr 几乎没有什么变化。对于烟煤和褐煤,各元素随温度的变化趋势基本一致,其中 As 变化很剧烈,与无烟煤相同,而 Cd 和 Cr 的释放率不大,在 1100 °C 均低于 30%。这是因为煤种之间存在着差异,一方面是由于各元素在不同煤中的浓度各不相同(见表1),一般来说浓度越大则释放量也越大,如无烟煤中 Cd 的浓度最高,释放量最大,烟煤中 Cr 和 Cd 的浓度很低,所以释放量很少。对3种煤 As 的浓度相近,所以释放量亦相近。而另一方面,痕量元素在煤中赋存形态不同,也会影响释放规律,例如 Cd 在煤中各种赋存形态都有,在烟煤中 Cd 以硫化物存在,而在褐煤中以无机物和硫化物态存在,在无烟煤中以无机物存在,所以烟煤中 Cd 释放剧烈。对于 Cr 在3种煤中都以无机物存在,所以几乎没有什么变化。

由于煤粒本身含有一些矿物组分,如 SiO₂、Al₂O₃、MgO 和 CaO,褐煤中 CaO 和 Fe₂O₃ 含量很高,

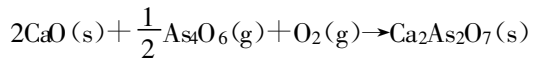
烟煤中 SiO₂ 和 Al₂O₃ 较高。这些矿物质对不同的痕量元素提供了可能的化学吸附位,例如 CaO 化学吸附 As 而生成砷酸钙^[5]:



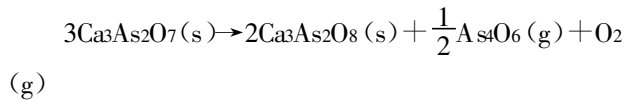
低于 600 °C;



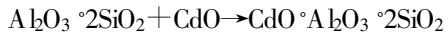
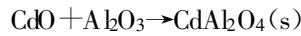
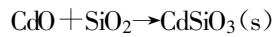
700~900 °C;



> 900 °C;



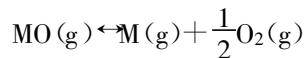
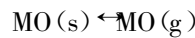
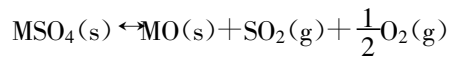
这会减少 As 的释放率。对于 Al₂O₃ 和 SiO₂ 会吸附 Cd,并形成复杂的 Cd 的铝硅酸盐,因而减少 Cd 的释放率。



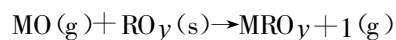
3.3 燃烧工况的影响

燃烧工况主要是指温度和气氛的影响。温度和气氛首先对痕量元素的形态和分布有很大的影响,我们对某电厂燃用的烟煤在不同燃烧工况下,(标准大气压,400~2000 K,氧化性气氛和还原性气氛)对 As、Cd 和 Cr 等痕量元素进行热力学平衡计算,得到各元素在不同温度及不同气氛下的形态变化规律,如图4~图6所示。

从图4~图6可以看出,在氧化性气氛下大多数痕量元素容易生成氧化物形态,例如对 As: As₂O₅、As₄O₆ 和 AsO;对 Cd: CdSO₄、Cd(OH)₂ 和 CdO;对 Cr: Cr₂O₃、FeCr₂O₄、CrO₂(OH) 和 CrO(OH)₂ 等;对于以硫酸盐形态存在的 Cr 和 Cd 元素,其形态变化可以以下式表述:



有些元素虽然在低温下以硫酸盐存在,但在高温下发生分解并同其它元素发生反应,如对 Co、Cu、Mn、Ni 和 Zn 等会与一些痕量元素和微量元素(Si、Al、Fe 等)发生反应:



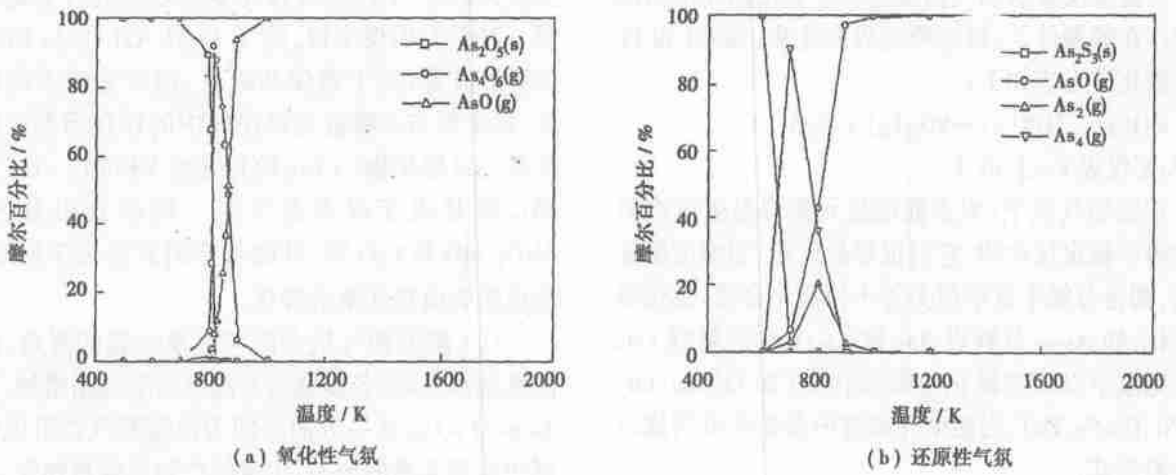


图 4 As 的热力学平衡计算

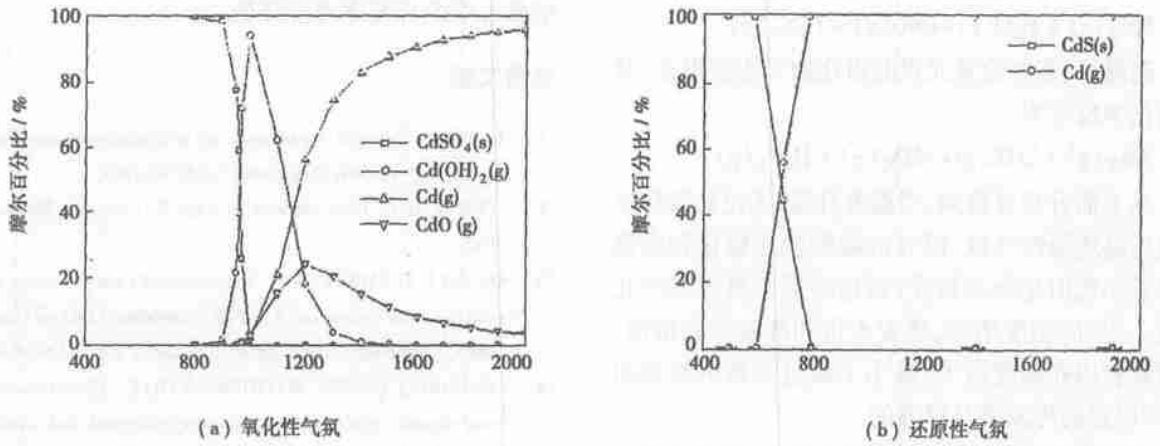


图 5 Cd 的热力学平衡计算

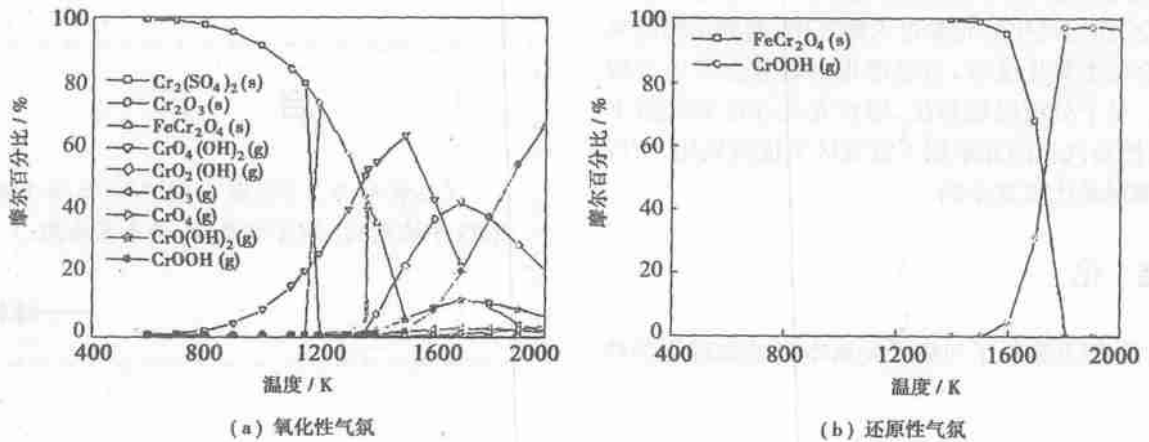
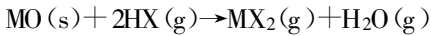


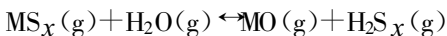
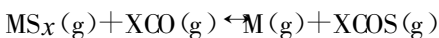
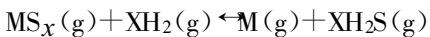
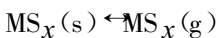
图 6 Cr 的热力学平衡计算

在温度没有达到气相痕量元素氧化物和单质能稳定存在的条件下,很容易生成卤化物,如 Cd 和 Pb 等平衡化学反应如下:

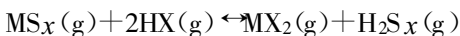


式中: X 代表 F、Cl、Br、I。

在还原气氛下,大多数痕量元素容易生成次氧化物等不稳定化合物,它们很容易汽化,当温度继续升高,则会分解生成单质类等不稳定化合物,也很容易汽化,如 As_2S_3 分解成 As_2 和 As_4 ; CdS 分解成 Cd; 对于低温下以固态硫化物形态存在(如 Cd、Co、Cu、Hg、Ni、Pb、Se、Zn),当温度升高时形态变化可写成以下一般形式:



高温下,有些痕量元素的卤化物为主要形态,其平衡化学反应为:



从上面分析可得知,当温度升高,无论是氧化性气氛还是还原性气氛,原有的硫酸盐或硫化物态都向单质态或卤化物态转变,而这些形态更容易汽化释放。另外,温度增加,随着水份和挥发份的析出,焦炭颗粒内孔隙度增大,减小了痕量元素的扩散阻力,所以总的挥发率是增加的。

必须指出的是,在实际燃煤条件下,痕量元素所处的环境气氛往往是变化的,因为当痕量元素从煤粒内部汽化时,外部的氧气很难扩散进入颗粒内部,所以此时痕量元素所处的是还原性气氛,这样很容易汽化,而当汽化的元素进入烟气中,遇到足够的氧气时会发生氧化反应,当温度很高时还会发生分解反应。对于分级燃烧系统,煤粒先是在还原气氛下汽化,然后汽化的元素到了富氧区又重新氧化,所以实际情况是比较复杂的。

4 结 论

(1) 挥发率除了与痕量元素本身的物理化学性

质有关系外,不同煤种各元素所表现的行为也不相同。对于无烟煤来说,除了 Cr 外, Cd 和 As 的变化趋势最显著;对于烟煤和褐煤,相对变化不是那么大,这主要与各痕量元素在煤中的存在形态有很大关系, As(硫化物) > Cd(硫化物或无机物) > Cr(无机物),而且由于煤本身含有一些矿物组分 SiO_2 、 Al_2O_3 、MO 和 CaO 等,可能与它们发生化学反应,因而也影响痕量元素的释放。

(2) 温度和气氛会影响痕量元素的释放,随着温度逐渐升高,各痕量元素的挥发率逐渐增加,而且 $\text{As} \gg \text{Cd} > \text{Cr}$,这一方面是因为温度和气氛可以改变煤中痕量元素的形态,生成的产物更容易挥发,另一方面温度升高会增大颗粒内孔隙度,减小痕量元素扩散阻力,所以总的挥发率是增加的,如果温度增加过高使有些矿物质熔融烧结,堵塞小孔的情况下,则痕量元素的挥发率可能降低。

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启 示

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——编辑部

S element is present there exists at the same time the Na element. After a comprehensive consideration of various factors it is concluded that the entry of Na element of a modified desulfurization agent into the crystal structure of sulfidation product can lead to a vacancy defect in the sulfidation product layer. This is the root cause of solid-state ion diffusion in the product layer being made possible to happen. Meanwhile, a concept of “potential” of SO₂ is introduced to explain the cause of the formation of directional ion diffusion flow in the sulfidation product layer. **Key words:** modified desulfurization agent, SEM product layer, ion diffusion

废液水煤浆和精煤水煤浆煤灰熔融特性试验研究 = Experimental Study of the Coal-ash Fusion Characteristics of Waste-liquid Coal Water Slurry (CWS) and Refined Coal CWS [刊, 汉] / SUN Fen-mei, ZHAO Xiang, XIE Yong-gang, et al (Education Ministry Key Laboratory of Energy Clean Utilization and Environmental Engineering under the Institute of Thermal Power Engineering of Zhejiang University, Hangzhou, China, Post Code: 310027) // Journal of Engineering for Thermal Energy & Power. — 2004, 19(5). — 471 ~ 473

An in-depth study was conducted concerning the fusion temperature and fusion process dynamic characteristics of three representative pairs of ash samples taken from two units of coal water slurry (CWS)-fired boilers. It was discovered that due to the presence of inorganic constituents, such as Na₂SO₄, NaOH and NaCl, etc in waste liquid CWS the latter's coal ash fusion characteristics are distinguished by some uniqueness as compared with refined coal CWS and raw coal slurries. **Key words:** waste-liquid coal water slurry, refined coal water slurry, fusion temperature, fusion characteristics

煤燃烧超细颗粒物控制的实验研究 = Experimental Research on Submicron-sized Particulate Control during the Combustion of Pulverized Coal [刊, 汉] / ZHOU Ying-biao, WANG Chun-mei, ZHANG Jun-ying, et al (National Key Laboratory on Coal Combustion under the Huazhong University of Science & Technology, Wuhan, China, Post Code: 430074) // Journal of Engineering for Thermal Energy & Power. — 2004, 19(5). — 474 ~ 477

The control of the formation of submicron-sized particulates during the combustion of pulverized coal by using a sorbent is of major theoretical and practical significance. Titanium sorbent was mainly used to regulate and control the combustion of Xiaolongtan brown coal. An experimental investigation was carried out at three temperatures (850, 1100 and 1125 °C) in a drop-tube furnace reactor to identify the influence of additives on the distribution of submicron-sized particulates along with an in-depth study and discussion of the particulate morphology and function mechanism. The results of the study have shown that the injection of additives can effectively suppress the formation of submicron-sized particulates and within a certain range of temperatures the effectiveness of a proper sorbent can be brought to a maximum value as verified by the experiments. **Key words:** pulverized coal combustion, submicron-sized particulate, sorbent, temperature

煤燃烧过程中痕量元素 As、Cd、Cr 释放特性实验研究 = Experimental Investigation of the Release Characteristics of Trace Elements As, Cd and Cr During the Combustion of Coal [刊, 汉] / XU Lu-si, CHEN Jun-feng, ZENG Han-cai (National Key Laboratory on Coal Combustion under the Huazhong University of Science & Technology, Wuhan, China, Post Code: 430074) // Journal of Engineering for Thermal Energy & Power. — 2004, 19(5). — 478 ~ 482

With As, Cd and Cr serving as representative elements the release mechanism of trace heavy metals was mainly studied during the heating process of coal. The study is of great significance, because the volatility of these elements will directly affect their emission to the atmosphere. Tests have shown that the release of trace elements is related not only to their physical and chemical properties, but also to such factors as their concentration in coal as well as their acquired morphology and combustion conditions, etc. The element As mainly exists in the form of a sulfide and has a relatively low fusion and boiling point, thus exhibiting the greatest tendency to volatilize. On the other hand, Cr mainly assumes the form of an inorganic matter with a high fusion and boiling point, thus making it the most difficult to volatilize. The element Cd

occupies a middle position between the above-cited two elements, resulting in a volatility expressed as $As > Cd > Cr$. Tests have proved that with a rise in temperature the volatility of these elements also gradually increase, and $As \gg Cd > Cr$. **Key words:** trace element; release; As; Cd; Cr

高温低氧燃烧过程中 NO_x 排放规律研究 = **A Study of NO_x Emission Mechanism during a High-temperature and Low-oxygen Combustion Process** [刊, 汉] / ZHONG Shui-ku, MA Xian-guo (Power Engineering Institute under the Shanghai University of Science & Technology, Shanghai, China, Post Code: 200093), ZHAO Wu-fei, SHUI Xiang-rong (Shanghai No. 711 Research Institute, Shanghai, China, Post Code: 200011) // Journal of Engineering for Thermal Energy & Power. — 2004, 19(5). — 483 ~ 486

An experimental investigation was conducted of the NO_x emission mechanism during the process of high-temperature and low-oxygen combustion. The NO_x emission mechanism was identified under various air-preheating temperatures and different oxygen-contents of preheated air. Meanwhile, CFD (computational fluid dynamics) general software has been employed to perform a numerical calculation of the NO_x emission concentration during the high-temperature and low-oxygen combustion process, resulting in the acquisition of some general law-conforming relationships. **Key words:** high-temperature air combustion, NO_x emission, experimental investigation, numerical calculation

木屑在固定床焚烧中 HCl 的控制研究 = **Research on the Control of HCl during the Incineration of Sawdust in a Fixed Bed** [刊, 汉] / JIANG Xu-guang, LI Xiang-pai, CHI Yong, et al (Education Ministry Key Laboratory on Energy Clean Utilization and Environmental Engineering under the Thermal Energy Engineering Institute of Zhejiang University, Hangzhou, China, Post Code: 310027) // Journal of Engineering for Thermal Energy & Power. — 2004, 19(5) — 487 ~ 490

Through tube-furnace tests the dechlorination effectiveness of various dechlorinating agents was investigated. By comparing the dechlorination results of the one and the same dechlorinating agent under various operating conditions the optimum dechlorination conditions were determined. The results of tests indicate that the dechlorination efficiency of calcium-based absorbents is higher than that of magnesium-based absorbents. The optimum dechlorination conditions of CaO can be given as follows: combustion temperature 500 - 600 °C, residence time 5 - 15 min. At a high temperature section the dechlorination efficiency of CaO is reduced drastically due to the high-temperature hydrolysis of dechlorination product $CaCl_2$. **Key words:** HCl, sawdust, combustion, CaO, absorbent, combustion dechlorination, pollution control

基于模糊方法的垃圾焚烧炉燃烧控制系统 = **Combustion Control System of a Fuzzy Logic-based Municipal Solid Waste (MSW) Incinerator** [刊, 汉] / SHEN Kai, LU Ji-dong, LIU Gang, et al (National Key Laboratory on Coal Combustion under the Huazhong University of Science & Technology, Wuhan, China, Post Code: 430074) // Journal of Engineering for Thermal Energy & Power. — 2004, 19(5). — 491 ~ 494

As an item of mature technology for refuse waste-heat utilization refuse incineration systems have found increasing applications in China. The combustion process control of a refuse incinerator constitutes the basis for the stable operation of such incinerators. The authors have conducted a study of the refuse incineration process by making use of a fuzzy method-based control strategy. The fuzzy control algorithm of refuse incineration is briefly described and compared with conventional PID (proportional, integral and differential) control algorithm. The continuous operation of a specific unit based on the recommended algorithm has been realized with a relatively high effectiveness. **Key words:** refuse incineration, fuzzy control, incinerator, fuzzy method

改变进气流量实现可调回流区位置的研究 = **A Study of the Realization of an Adjustable Recirculation-zone Location through the Change of Inlet Airflow Rates** [刊, 汉] / FU Wei-biao, GONG Jing-song (Department of Engineering Mechanics, Tsinghua University, Beijing, China, Post Code: 100084) // Journal of Engineering for Thermal En-