

燃煤固体产物中元素分布特征

孙俊民¹, 孙志宽², 姚 强¹, 徐旭常¹

(1. 清华大学 热能工程系煤清洁燃烧国家重点实验室, 北京 100084; 2. 河南省电力公司环保办公室, 河南 郑州 450000)

摘 要: 利用中子活化分析、原子发射光谱等元素分析方法研究我国典型低钙和高钙燃煤固体产物中的元素分布。结果表明: 亲硫元素与有机结合态元素(As、Se、Sb、Co、Ni)从底灰—飞灰—结渣—沾污的含量依次增高, 而稀土元素和放射性元素(U、Th)则与之相反。在燃煤飞灰中, 铁质颗粒中多数微量元素的含量高于钙质和硅铝质颗粒。煤中伴生元素在燃烧产物中的分布特征与元素本身的化学性质和赋存状态有关。

关 键 词: 煤中伴生元素; 飞灰; 底灰; 结渣与沾污; 铁质微珠

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1 前言

煤中伴生元素包括常量元素和微量元素, 迄今为止, 煤中已发现 84 种元素^[1]。伴随煤粉的燃烧过程, 这些元素主要转入飞灰、底灰、锅炉结渣与沾污中。在这些元素中, 有些是有毒有害元素(如 Hg、As、Se、Cd、Pb、Cr 等); 有些为稀有分散元素(如 Ga、Ge 等), 具有较高的经济价值; 而有些元素(如 Fe、Sr、Cu 等)对飞灰的利用或脱硫反应(作为脱硫剂载

体)具有催化效应。

20 世纪 70 年代以来, 随着世界燃煤吨位的增加, 煤中伴生元素在燃烧产物中的分布赋存特征及其对环境的影响等方面的研究, 日益受到人们的重视。从过去的研究看, 主要集中在煤中有害微量元素在燃烧过程中的挥发行为及其在不同粒度飞灰和底灰中的分布特征。本文以我国典型的低钙灰(河南省姚孟电厂)与高钙灰(云南小龙潭电厂)为对象, 系统研究煤中伴生常量和微量元素在飞灰、底灰、结渣与沾污中以及不同飞灰结构类型中分布的差异性。

2 不同燃烧产物中元素分布特征

2.1 常量元素

对小龙潭与姚孟电厂入炉煤及各类燃烧产物进行化学全分析。根据测试结果, 分别计算出飞灰与入炉煤、底灰、结渣及沾污与飞灰中元素含量的比值, 结果列于表 1。

可见, 常量元素在不同燃烧产物中的分布具有如下特点。

表 1 常量元素在燃烧产物中的分析

(%)

成分	小龙潭电厂					姚孟电厂								
	C	FA	BA	SL	FO	FA/C	BA/FA	SL/FA	FO/FA	C	FA	BA	FA/C	BA/FA
SiO ₂	3.83	27.78	24.01	26.93	17.16	7.25	0.86	0.97	0.62	18.76	56.24	58.24	3.0	1.04
Al ₂ O ₃	1.98	13.05	10.99	12.36	8.13	6.59	0.84	0.95	0.62	9.10	28.70	28.55	3.15	0.99
Fe ₂ O ₃	1.53	9.68	9.60	14.42	19.80	6.33	0.99	1.49	2.05	0.97	3.89	4.06	4.01	1.04
CaO	5.17	35.20	27.24	39.41	25.64	6.81	0.77	1.12	0.73	0.55	2.08	1.58	3.78	0.76
MgO	0.38	2.83	2.05	3.19	1.59	7.45	0.72	1.13	0.56	0.18	0.79	0.77	4.38	0.97
K ₂ O	0.17	0.53	0.28	0.69	1.41	3.12	0.53	1.30	2.66	0.42	1.09	1.02	2.60	0.94
Na ₂ O	0.05	0.29	0.07	0.31	0.35	5.80	0.24	1.06	1.20	0.23	0.61	0.53	2.65	0.86
TiO ₂	0.10	0.77	0.61	0.75	0.47	7.70	0.79	0.97	0.61	0.31	1.11	0.94	3.58	0.85
SO ₃	3.28	5.60	0.24	1.87	23.83	1.71	0.04	0.33	4.25	0.65	0.23	0.09	0.35	0.39
Loss	—	4.23	24.36	—	—	—	5.76	—	—	—	4.80	4.08	—	0.81

注: 1. 小龙潭电厂与姚孟电厂入炉煤灰分分别为 16.78% 和 33.29%。

2. C—入炉煤; FA—飞灰; BA—底灰; SL—结渣; FO—沾污。

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作者简介: 孙俊民(1966—), 男, 河南上蔡人, 清华大学博士后。

2.1.1 飞灰中元素分布特征

伴随有机组分的燃尽,煤中主要伴生元素在燃烧产物中表现出相应的富集。如果按入炉煤的灰分计算,小龙潭与姚孟电厂飞灰中元素正常的富集系数应分别在 6.0 和 3.0 左右。显然,除 S、K、Na 较低外,其它元素的富集系数与之接近。硫在燃烧过程中以气态形式逸出,由于小龙潭电厂飞灰中的钙对其有一定的自脱除作用,因此其富集系数高于姚孟电厂。K、Na 的富集系数较低,主要由于两者趋于在小于 10 μm 的细颗粒中富集,而除尘器对这些颗粒的捕获率较低。另外,这些颗粒容易在锅炉受热面上沉积,如小龙潭电厂沾污内层中 K 的富集,使得该电厂飞灰中 K 的富集系数进一步降低。

2.1.2 飞灰与底灰中元素分布的差异

在飞灰中富集系数较低的元素在底灰中进一步亏损;其它元素的分布特征也有一定差异,姚孟电厂除 Fe、Si 外,飞灰中元素含量高于底灰;虽然小龙潭电厂所有元素都是飞灰大于底灰,但如果扣除底灰中未燃炭的影响,则 Si、Al 和 Fe 在底灰中的含量高于飞灰。底灰中 Fe 的含量偏高可能与磁珠间及与其它颗粒间粘连较多,往往形成较大的颗粒下沉有关。Ghosal(1995)研究飞灰粒度与化学成分的关系发现,Fe 趋向于在粗粒飞灰中富集^[2]。此外,底灰中还可能混入富铁的炉壁沉积;煤粉颗粒中与有机质解离的石英与粘土矿物的下沉,可能会导致 Si、Al 在底灰中相对富集。

2.1.3 结渣与沾污中元素分布特征

结渣中 Si、Al 含量略低于飞灰,S 更低,其它金属氧化物含量均高于飞灰。沾污的成分与结渣及飞灰差异较大,主要由 Ca、Fe 及 S 组成,其它元素含量明显低于结渣和飞灰,这一特征是由飞灰的沉积特性决定的。

2.2 微量元素

利用中子活化分析方法测定小龙潭电厂各种燃烧产物中主要微量元素的含量,并计算出有关比值,结果列于表 2。

从表 2 中可见,微量元素的分布具有如下特点:

(1) 稀土元素化学性质稳定,在飞灰与底灰中比较正常地富集。飞灰中,这些元素的富集系数差异较大,但底灰与飞灰的比值基本一致,可能与它们在煤中含量较低而导致测试误差有关。在结渣与沾污中这些元素含量依次降低,如果扣除底灰中有机

质的影响,总体上表现为:沾污<结渣<飞灰<底灰。

(2) 其它微量元素在飞灰与底灰中的分布情况,可分出三种类型:第一 As、Se、Sb、Mo、Co 在飞灰中的富集系数较小,底灰中含量显著降低,表明这些元素部分被细颗粒携带,进入大气或沉积在锅炉受热面上;第二 Ba、Cr、Ga、Rb、Th、U 在飞灰中的富集系数正常,底灰与飞灰中含量相近,暗示这些元素挥发程度低,主要残留在原灰粒中;第三 Zn 在飞灰中富集系数较高,底灰中含量显著降低。

(3) 除 Th、U、Ni 外,多数元素表现出在结渣中富集,在沾污中进一步高度富集的特点。尤其是 Zn、As、Cr、Ga、Rb、Sb 在沾污中富集程度较高,例如,Zn 与 As 在沾污中的含量分别高达 1 100 mg/kg 和 680 mg/kg。其他学者也已注意到 As 在炉壁沉积中高度富集的现象^[3]。

表 2 小龙潭电厂燃烧产物中微量元素的分布特征(mg/kg)

元素	C	FA	BA	SL	FO	FA/C	BA/FA	SL/FA	FO/FA
La	4.00	35.90	30.80	21.40	20.90	8.98	0.86	0.60	0.58
Ce	12.00	85.50	71.90	54.20	56.00	7.13	0.84	0.63	0.65
Nd	7.00	38.00	34.90	30.80	28.40	5.43	0.92	0.81	0.75
Sm	1.80	6.50	5.80	6.33	6.27	3.61	0.89	0.97	0.96
Eu	0.20	1.20	0.98	0.83	0.76	6.00	0.82	0.69	0.63
Tb	0.20	0.73	0.70	0.77	0.61	3.65	0.96	1.05	0.84
Yb	0.53	2.80	2.60	1.90	1.70	5.28	0.93	0.68	0.61
Lu	0.11	0.70	0.60	0.41	0.44	6.36	0.86	0.59	0.63
As	49.00	144.00	27.40	382.00	680.00	2.94	0.19	2.65	4.72
Ba	69.00	420.00	350.00	360.20	459.00	6.09	0.83	0.86	1.09
Co	3.10	15.10	11.20	16.20	17.50	4.87	0.74	1.07	1.16
Cr	17.50	108.00	82.60	192.50	264.00	6.17	0.76	1.78	2.44
Ga	2.90	26.00	19.80	41.20	46.70	8.97	0.76	1.58	1.80
Mo	35.80	161.00	121.00	168.00	179.00	4.50	0.75	1.06	1.11
Ni	—	68.00	—	43.60	59.00	—	—	0.64	0.87
Rb	9.60	71.30	50.80	82.80	163.00	7.43	0.71	1.16	2.29
Sb	3.00	8.70	2.10	13.90	53.00	2.90	0.24	1.60	6.09
Se	1.06	4.70	2.30	—	—	4.43	0.49	—	—
Si	1.60	4.70	2.30	5.30	—	2.94	0.49	1.13	—
Th	1.70	10.60	8.50	5.80	5.50	6.24	0.80	0.55	0.52
U	23.50	119.80	110.18	102.00	112.00	5.10	0.92	0.85	0.93
Zn	7.90	59.50	19.10	92.77	1 100	7.53	0.32	1.56	18.3

3 不同类型飞灰中元素分布特征

分别从小龙潭与姚孟电厂飞灰中分选出铁质微珠,利用 ICP-AES 法测定铁质、钙质与硅铝质颗粒中主要常量和微量元素的含量,并利用原子荧光法测定 As,激光荧光法测定 U,硅氟酸钾容量法测定 Si。数据处理计算后列于表 3。

表 3 不同类型飞灰中元素分布特征

元素	小龙潭电厂			姚孟电厂		
	钙质	铁质	Fe/Ca	硅铝质	铁质	Fe/SiAl
Si	12.96	7.96	0.61	26.59	16.98	0.64
Al	6.96	4.57	0.66	14.65	9.13	0.62
Fe	6.81	27.98	4.11	1.94	26.86	13.87
Ca	25.57	13.28	0.52	1.09	1.49	1.37
Mg	1.88	1.14	0.61	0.47	0.99	2.11
K	0.63	0.43	0.69	0.86	0.48	0.55
Na	0.36	0.37	1.01	1.11	0.65	0.59
Ti	0.46	0.29	0.63	0.62	0.38	0.62
Mn	0.31	0.03	0.11	0.02	0.18	11.83
As*	283.87	206.33	0.73	4.91	5.80	1.18
Ba	453.57	394.43	0.87	438.90	325.33	0.74
Be	3.60	7.35	2.04	10.49	11.62	1.11
Co	12.34	< 0.000 3		45.81	27.13	0.59
Cr	164.90	156.03	0.95	160.30	180.80	1.13
Cu	157.57	248.73	1.58	151.45	300.33	1.98
Ga	40.10	133.73	3.33	23.53	134.43	5.71
Mo	3.38	3.76	1.11	2.46	2.72	1.10
Ni	70.17	153.60	2.19	87.20	170.53	1.96
Pb	< 0.000 1	9.56		39.94	31.70	0.79
Sc	25.28	66.33	2.62	18.42	67.74	3.68
Sn	5.84	8.91	1.53	8.21	10.66	1.30
Sr	2 010.33	1 272.33	0.63	434.90	317.00	0.73
Th	34.20	60.53	1.77	19.13	55.27	2.89
U*	134.67	101.30	0.75	22.47	10.34	0.46
V	250.20	175.43	0.70	360.37	381.07	1.06
Zn	114.98	146.89	1.28	472.00	139.13	0.29

注: 常量元素(Si~Mn)以%表示; 微量元素以mg/kg表示。

由上表可见, 铁质微珠与钙质或硅铝质颗粒的元素组成有明显差异。常量元素中, 除 Fe 外, 其它元素的含量均低于钙质微珠, 但与硅铝质颗粒相比, 与 Fe 同时富集的元素还有 Mn、Ca 和 Mg; 微量元素中, 除 As、Ba、Sr、U、V 外, 其它元素的含量均高于钙质微珠, 而与硅铝质颗粒相比, 除 Ba、Sr、U 含量较低外, 其它元素的含量普遍较高。

4 讨论

煤中伴生元素在燃烧产物中的分布与元素本身的化学性质和在煤中的赋存状态有关。从小龙潭电厂燃烧产物中元素分布情况看, 与粘土矿物伴生的稀土元素及 U、Th 等在燃烧过程中主要残留在硅酸盐晶格或玻璃体网络结构中, 它们随硅铝质的含量增加而增加, 表现出在底灰或粗粒飞灰中富集, 而在结渣与沾污或细粒飞灰中亏损的特征。

根据对小龙潭褐煤中元素赋存特征的研究, As、Se、Sb 等为亲硫元素, 与黄铁矿伴生, Co、Mo 为有机结合态元素, 与有机质密切结合。在燃烧过程中这些元素挥发性较强, 因此在底灰中缺乏, 在结渣与沾污中富集。而结渣与沾污主要来自于细粒飞灰, 根据飞灰内部结构的研究, 粗粒飞灰往往内部气孔发育, 以空心或子母珠存在的形式较多, 而细粒飞灰多以实心微珠的形式存在, 粗粒微珠在烟气中由于受到浮力的作用, 上升的速度较快, 不易在锅炉受热面形成沉积, 而细粒飞灰则沉积倾向性较强, 因其比表面积较大, 对挥发性气体的物理或化学吸附量较高, 从而富集挥发性元素。

有关不同类型飞灰颗粒中元素分布特征尚未见报导。本次研究表明, 除少数几种与粘土伴生的元素外, 铁质微珠中大多数微量元素的含量高于硅铝质或钙质微珠。这一特征可根据不同成分的硅酸盐熔体的熔点与表面张力的差异进行解释。硅铝质、铁质与钙质微珠的化学成分可分别用 $Al_2O_3-SiO_2$ 、 $Fe_2O_3-Al_2O_3-SiO_2$ 与 $CaO-Al_2O_3-SiO_2$ 系统来表示, Fe 与 Ca 离子在硅酸盐熔体中是变价离子, 尤其 Fe 离子的极化能力较强, 对 Si-O 键的破坏作用较大, 因此, $Fe_2O_3-Al_2O_3-SiO_2$ 系统熔点最低, 表面不饱和电价最高, 表面能最大。前者意味着在飞灰脱离高温区后, 铁质微珠保持液相的时间最长, 而后者意味着铁质微珠对周围环境中细粒子和挥发性气体的吸附作用最强。因此, 除少数不挥发的元素外, 大多数元素在该类微珠中富集。不过, 由于 CaO 对 As 的化学吸附, 导致钙质微珠中 As 的含量高于铁质微珠。

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PFBC 中试电站煤添加和灰排放技术 = **Coal Feeding and Ash Discharge Technology in a PFBC (Pressurized Fluidized Bed Combustion) Pilot Power Plant** [刊, 汉] / XIONG Yuan-quan, SHEN Xiang-lin, ZHANG Ming-yao, ZHENG Shou-zhong, et al (Education Ministry Key Lab of Clean Coal-based Power Generation and Combustion Technology under the Southeastern University, Nanjing, China, Post Code: 210096) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(6) — 591 ~ 593, 597

The specific feature of pressurized fluidized bed combustion (PFBC) technology itself has led to the pneumatic transport technology becoming an effective means of continuous and stable feeding and discharge of solids for the above-cited technology. The authors have under a boiler pressure of 0.6 MPa investigated the effect of the location of gas nozzle in a pneumatic coal transport system injector (without a diffuser tube) and solid/gas ratio on the pneumatic transport stability. Also investigated were the characteristics of continuous pneumatic transport of ash under a boiler pressure of 0.6 MPa. Through the experimental investigation it has been found that in the coal transport system the mass flow rate of materials is closely related to the geometric parameters of the injector and the ash transport system can ensure a continuous and stable operation under a relatively high solid/gas ratio ($\mu \geq 3$). **Key words:** pressurized fluidized bed combustion, pneumatic transport, solid/gas ratio

声空化场下纳米颗粒对沸腾传热影响的实验研究 = **Experimental Study of the Effect of Nanometer Granule on Boiling Heat Transfer in an Acoustic Cavitation Field** [刊, 汉] / ZHOU Ding-wei, LIU Deng-ying (Institute of Engineering thermophysics under the Chinese Academy of Sciences, Beijing, China, Post Code: 100022), MA Chong-fang (College of Environmental and Energy Engineering under the Beijing Polytechnic University, Beijing, China, Post Code: 100022) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(6) — 594 ~ 597

With nanometer granule-added acetone serving as a working fluid an experimental study was performed for the first time to investigate the effect on the boiling heat transfer in a horizontal circular tube of a variety of factors. The factors include orientation and intensity of acoustic cavitation field, fluid subcooling degree, concentration of nanometer material and light irradiation, etc. In addition, the relevant mechanism is also analyzed. **Key words:** acoustic cavitation, nanometer granule, boiling heat transfer, hysteresis

神木煤钙基矿物高温自身脱硫特性的研究 = **A Study of High-temperature Self-desulfurization of Calcium-based Mineral in Shenmu Coal** [刊, 汉] / SONG Yu-bao, ZHANG Ming-chuan, FAN Wei-Dong, et al (Energy Engineering Department, Shanghai Jiaotong University, Shanghai, China, Post Code: 200240) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(6) — 598 ~ 600, 608

The generation and decomposition experiment of high-temperature desulfurization product CaSO_4 on a tubular furnace indicates that at an oxidizing atmospheric condition with a temperature lower than 1250°C a decomposition of CaSO_4 will basically not occur. A reducing gas CO can lower the decomposition temperature of CaSO_4 to about 1060°C . The Shenmu coal combustion experiment performed on a drop tube furnace shows that the calcium-based mineral in the coal can partially remove SO_2 in the flue gases. **Key words:** self-desulfurization, calcium-based mineral, drop tube furnace, reaction temperature, reducing atmosphere

燃煤固体产物中元素分布特征 = **Distribution Characteristics of Elements in Burned Coal Solid Products** [刊, 汉] / SUN Jun-ming, SUN Zhi-kuan, YAO Qiang, et al (Thermal Energy Engineering Department, Tsinghua University, Beijing, China, Post Code: 100084) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(6) — 601 ~ 603

Through the use of element analysis methods, such as neutron activation analysis and atomic emission spectrometry, etc an investigation is conducted of the elements distribution in typical low-calcium and high-calcium burned coal solid products. The results of the investigation indicate that sulfur-affinity element and organically bonded-state elements (As, Se,

Sb, Co, Ni) have their quantity increased consecutively, depending on the content of bottom ash—fly ash—slag—fouling. Meanwhile, rare earth elements and radioactive element (U, Th) on the contrary assume an opposite tendency. In the fly ash of burned coal the content of many trace elements in iron particles happens to be higher than that of calcium and silicon-aluminum particles. The distribution characteristics of in-coal accompanying elements in the combustion products is related to the chemical properties and assigned state of the element itself. **Key words:** accompanying element in coal, fly ash, bottom ash, slag and fouling, iron micro-ball

油水乳化液中长气泡漂移速度的研究 = **A Study on the Drift Velocity of Long Bubbles in Oil-water Emulsion**

[刊, 汉] / WANG Yue-she, LIU Lei, ZHOU Fang-de (National Key Lab of Power Engineering Multi-phase Flow under the Xi'an Jiaotong University, Xi'an, China, Post Code: 710049) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(6)—604~608

Set up was a momentum analysis model of the drift velocity in stagnant liquid of long bubbles in an annular tube. Taylor bubbles drift velocity at various rates of water content in stagnant oil-water emulsion and under a slug flow regime was measured with the use of a high-speed dynamic analyzer. In conjunction with available experimental data and on the basis of Wallis' flow classification criteria put forward is a semi-empirical formula for Taylor bubble drift in oil-water emulsion, which reveals the law of motion of long bubbles in liquids with different hydrodynamic characteristics. **Key words:** oil-water emulsion, Taylor bubble, drift velocity, study

炉内喷钙脱硫技术的工业应用研究 = **Industrial Applied Research of In-furnace Sorbent Injection-based Desulfurization Technology**

[刊, 汉] / WU Shu-zhi, ZHAO Chang-sui, DUAN Yu-feng, et al (Education Ministry Key Lab of Clean Coal-based Power Generation and Combustion Technology under the Southeastern University, Nanjing, China, Post Code: 210096) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(6)—609~611

Presented is a desulfurization project undertaken on two 10 t/h chain grate stokers along with some relevant test results. The desulfurization system comprises two parts: 1. The injection of sorbent into a furnace in conjunction with four-corner vortex firing technology; and 2. The humidification and activation of desulfurization agents for a tail portion through the use of a Venturi nozzle and water-film dust collector. The test results indicate that the introduction of a four-corner vortex and secondary air techniques can markedly improve the mixed calcination of desulfurization agents in the furnace without affecting the boiler operation and is conducive to enhancing the desulfurization efficiency in the furnace. The use of Venturi water nozzle and a dust collector can lead to the activation of those calcium oxide particles, which have not undergone reaction, thus increasing the reaction speed of desulfurization. This makes it possible to realize a higher desulfurization efficiency at a relatively low Ca/S ratio. During the upgrading for environmental protection purposes of industrial boilers originally fitted with Venturi water nozzles and water-film dust collectors the technology of in-furnace sorbent injection with tail portion humidification and calcium oxide activation enjoys a significant technico-economic edge. **Key words:** desulfurization, upgrading, sorbent injection into a furnace, Venturi wet dust collector

烟煤与石油焦掺混燃烧特性研究 = **Research on the Combustion Characteristics of Burning Bituminous Coal Mixed with Petroleum Coke**

[刊, 汉] / YANG Ya-ping, CAI Song (Thermal Energy Engineering Research Institute under the Southeastern University, Nanjing, China, Post Code: 210018) // Journal of Engineering for Thermal Energy & Power. — 2001, 16(6)—612~614, 631

Based on a combustion test of burning a mixture of petroleum coke and coal dust on a small-sized test rig an analytical study was conducted of the effect of various factors on the combustion process. These factors include: fuel characteristics of bituminous coal and petroleum coke, ignition performance of mixed fuel dust, combustion characteristics, pulverized coal fineness, air distribution conditions and thermal load intensity. **Key words:** combustion unit, mixed pulverized coal, pyrolytic characteristics, combustion characteristics