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层燃炉燃煤中9种微量元素的迁移*

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摘要　建立了层燃锅炉底灰、飞灰中Be、Co、Cr、Cu、Mn、Ni、Pb、V、Zr含量与煤中这9种元素含量关系的经验公式，估算了煤中微量元素在底灰、飞灰和排入大气的烟气中的总量分配. 研究了飞灰中元素含量和总量的粒度分布，探讨了煤炭燃烧过程中元素的集散规律. 底灰中多数元素含量高于飞灰，燃煤中9种元素大部分迁移到底灰中. 但飞灰中元素的富集因子高于底灰，元素富集程度随粒径减小而增加，飞灰中元素总量集中于<0.125 mm粒径的粒子上.

关键词　微量元素，迁移，煤炭，层燃炉.

在煤炭燃烧过程中，发生微量元素的迁移和转化[1]. 有关煤炭及其燃烧产物中微量元素含量的资料国内外均有报道[2]，但定量地研究煤中微量元素总量在其燃烧产物中分配规律的工作鲜见报道. 本工作把燃煤产物分为锅炉底灰、除尘器内飞灰和进入大气的烟气3部分，建立了确定燃烧产物中9种微量元素含量的经验公式，进而根据质量平衡原理计算了微量元素在燃烧产物中的总量分配. 研究了燃烧过程中元素的地球化学集散规律. 本文对于表征燃煤中微量元素迁移特征以及确定传输通量具有理论和应用意义.

1　实验部分

选择13台层燃锅炉(往复炉、链条炉)，每台监测4次. 内容包括：在正常工况下同时采集煤、飞灰、底灰样品，并测定煤及其燃烧产物的质量关系. 锅炉燃煤为市售二级烟煤，产自东北和山西. 除尘器为旋风除尘式，平均除尘效率85%. 样品缩分后研磨，过200目筛. 称取0.100 g—0.200 g样品，用$HF-HNO_3-H_2SO_4$在高压消煮罐中消解，制备成溶液. 用电感耦合等离子体发射光谱仪测定微量元素含量，测定精确度用标准粉煤灰环境样品进行检验.

2　结果和讨论

2.1　燃煤产物中微量元素的含量分布

煤中微量元素在燃烧产物中的含量分布是确定元素迁移规律的关键环节. 统计结果见表1. 飞灰和底灰中元素含量是煤中元素含量的1.6—3.1倍. 底灰中Be、Cr、Mn、Ni、Pb、Zr高于飞灰，其余3种元素飞灰高于底灰.

表1　煤及其燃烧产物中微量元素含量/mg·kg⁻¹

样品	统计值	元素								
		Be	Co	Cr	Cu	Mn	Ni	Pb	V	Zr
煤	$\bar{X}$	2.36	6.49	22.05	17.34	226.7	13.50	28.34	35.09	86.03
	S_X	0.78	2.56	11.07	5.94	46.54	6.75	14.50	14.49	37.83
飞灰	$\bar{X}$	5.44	16.06	55.80	51.94	321.6	39.32	46.12	84.81	174.3
	S_X	2.29	4.67	18.79	17.40	142.8	20.04	21.97	38.07	93.88
底灰	$\bar{X}$	6.02	15.12	69.33	49.21	525.7	43.22	51.91	[illegible]	226.7
	S_X	2.12	3.79	31.28	9.92	282.2	22.56	34.57	19.62	73.64

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通过回归分析的方法建立了飞灰和底灰中元素含量与煤中元素含量的关系式，见表 2 和表 3. 式中 x、y 分别为煤和灰中元素含量($mg \cdot kg^{-1}$).

经验公式表明，飞灰、底灰中微量元素与煤中该元素在含量上具有线性关系. 多数元素相关性显著，有的甚至达到极显著的水平，可以用这些公式计算或预测燃煤产物中微量元素的含量.

表 2　飞灰中微量元素含量经验公式

元素	线性方程	相关系数	显著性检验
Be	$y=2.8013x-1.4495$	0.6881	$P<0.005$
Co	$y=1.0203x+8.7520$	0.5363	$P<0.05$
Cr	$y=1.1206x+26.5004$	0.7613	$P<0.0025$
Cu	$y=1.5121x+21.5432$	0.6060	$P<0.025$
Mn	$y=1.5410x+101.68$	0.6698	$P<0.01$
Ni	$y=1.3865x+12.7988$	0.6419	$P<0.01$
Pb	$y=1.0552x+14.9050$	0.5831	$P<0.025$
V	$y=1.7399x+15.9624$	0.6458	$P<0.01$
Zr	$y=1.1856x+62.6883$	0.6207	$P<0.025$

表 3　底灰中微量元素含量的经验公式

元素	线性方程	相关系数	显著性检验
Be	$y=2.0407x+0.9864$	0.5362	$P<0.05$
Co	$y=0.8337x+8.4243$	0.5253	$P<0.05$
Cr	$y=1.1070x+34.0073$	0.5441	$P<0.025$
Cu	$y=1.9927x+13.1676$	0.7728	$P<0.001$
Mn	$y=2.6025x+112.95$	0.6135	$P<0.025$
Ni	$y=2.2082x+9.2928$	0.8031	$P<0.001$
Pb	$y=1.8880x+8.1499$	0.5846	$P<0.025$
V	$y=0.9022x+48.7898$	0.7217	$P<0.005$
Zr	$y=1.3986x+102.6629$	0.6329	$P<0.025$

2.2　燃煤产物中微量元素总量分配

燃煤产物中某元素总量的分配可以根据质量平衡的原理进行计算. 质量平衡式为:

$$M_c = M_f + M_b + M_a$$

式中，M_c 为煤中某元素总量，M_f 为飞灰中该元素量，M_b 为底灰中该元素的量，M_a 为进入大气中该元素的量. 在已知煤中某元素含量的情况下，M_f、M_b 可由经验公式及飞灰和底灰占煤的质量百分数计算得到，M_a 则由差减法得到.

表 4 中列出了层燃炉燃煤中微量元素在燃烧产物中的总量分配情况.

煤中 9 种微量元素燃烧后大部分迁移到底灰中，其比率为 57.56%—83.76%. 迁移到除尘器飞灰中的比率为 12.10%—21.07%，排放到大气中的比率为 1.01%—29.14%. 其中 Pb、V、Co 3 种元素排入大气的量明显高于飞灰中赋存量.

元素总量分配比率随煤中元素含量而变动. 笔者用东北地区长焰煤平均元素含量代入经验公式进行计算，大多数元素的分配比率变动不大，说明微量元素在燃煤产物中分配规律是成立的.

表 4　煤中微量元素在燃烧产物中的分配/%

元素	飞灰中的比率	底灰中的比率	大气中的比率
Be	16.73	66.38	16.89
Co	18.12	57.56	24.32
Cr	17.77	71.53	10.70
Cu	21.07	74.31	4.62
Mn	15.23	83.76	1.01
Ni	17.86	78.20	3.94
Pb	12.10	58.74	29.14
V	16.79	61.92	21.29
Zr	14.64	69.98	15.38

2.3　飞灰中元素的粒度分布

将除尘器中飞灰粒度分为 6 级研究了元素的粒度分布为：<0.038 mm，0.038 mm－0.050 mm，0.050－0.125 mm，0.125 mm－0.250 mm，0.250 mm－0.500 mm，>0.500 mm.

元素的粒度分布类型与锅炉类型及燃烧条件有关[3]，层燃炉占主导地位的分布类型是：随着飞灰粒径减小元素的含量升高(图 1).

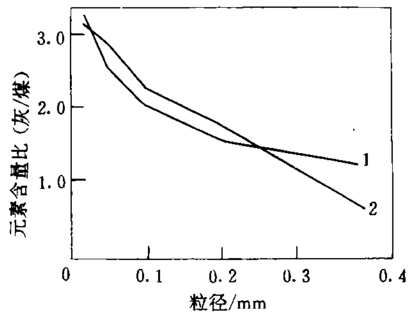

图 1　元素含量比的粒度分布

1. 往复炉　　2. 链条炉

飞灰中微量元素质量的粒度分布也因锅炉类型及燃烧条件而异(图2). 层燃炉一般呈单峰型，峰值出现在0.038 mm—0.050 mm或0.050 mm—0.125 mm粒级，约占飞灰中元素质量的40%—60%，前3个小粒径级分的总和占飞灰中元素质量90%左右，说明飞灰中微量元素绝大部分集中在小于0.125 mm的粒子上.

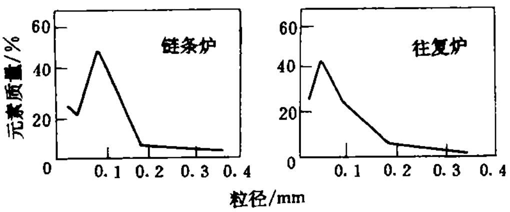

图2 各粒级飞灰中元素质量分布

2.4 微量元素的集散规律

用地球化学富集因子K(灰/煤)来表述元素的集散状态.

$$K=(c_{ia}/c_{Fea})\div(c_{ic}/c_{Fec})$$

式中，c_{ia}、c_{Fea}分别表示灰中i元素及Fe含量，c_{ic}和c_{Fec}分别为煤中i元素及Fe含量.

研究表明，层燃炉飞灰中除Mn以外的微量元素K(飞灰/煤)值大于1.0，而底灰中Be、Co、Pb、V、Zr的K(底灰/煤)值小于1.0，Cr、Cu、Mn、Ni的K值大于1.0. 这说明多数元素在飞灰中被富集，在底灰中约半数元素被富集，半数元素被分散. 除Mn外，飞灰中微量元素K值均高于底灰，即飞灰中元素的富集程度超过底灰.

飞灰中元素富集因子的粒度分布也呈现明显规律性，往复炉绝大多数元素前3级小颗粒粒子K值大于1.0，明显富集. 从K值与粒度的关系看，占绝对优势的分布类型是颗粒越小K值越高.

不同类型锅炉飞灰和底灰的K值范围、各粒级飞灰K值的分布类型都有明显差异. 反映了燃烧方式和条件对集散过程有重要影响.

2.5 经验公式的检验

选择未参与回归分析的往复炉，根据煤中微量元素含量，用经验公式预测飞灰和底灰中元素含量. 飞灰中9种元素预测含量对于实测含量的相对误差范围为−22.8%—29.9%，其中相对误差范围小于±25%的元素有8种，占89%，底灰中元素相对误差范围为−35%～+48.9%，变动略大，相对误差小于±30%的有6种，占66.7%，总体结果令人满意.

3 结论

(1) 层燃炉底灰和飞灰中9种微量元素含量与煤中元素含量具有线性关系. 建立了估算或预测飞灰和底灰中微量元素含量的经验公式，验证效果满意.

(2) 煤中非挥发性微量元素燃烧后大部分迁移到底灰和飞灰中，占元素总量70.86%—98.9%，平均85.86%. 随烟气进入大气的量较小，占总量1.01%—29.14%，平均14.14%.

(3) 占支配地位的飞灰中元素粒度分布类型是元素含量随粒径减小而上升，飞灰中微量元素总量约90%分布在<0.125 mm粒径的粒子上.

(4) 绝大多数微量元素在飞灰中呈地球化学富集状态，在底灰中约半数元素呈富集状态，半数元素呈分散状态.

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Two catalysts were prepared and used for pretreatment of typical dye intermediate wastewater —— tobias acid wastewater by metal oxide catalyzed ozonation. For wastewater with initial COD concentration of 1500 mg/L, when ozonation dose is 0.82 g/L, COD removal efficiency is above 50%. And Ozonation Index (OI) of the two catalysts are 1.44 and 0.7 respectively, while the blank γ-Al_2O_3 is 1.90. The ozonation products of tobias acid identified by gas chromatography-mass spectrography are o-benzendicarboxylic acid, oxalic acid, sulphate ion and nitrate ion, and then the ozonation pathway is proposed. After tobias acid is treated by metal oxide catalyzed ozonation, the biodegradability is improved apparently.

Key words: tobias acid wastewater, catalyst, metal oxide catalyzed ozonation.

Removal of 9 Kinds of Trace Element in Burning Coal in the Layer-Burning Boilers. Wang Qichao et al. (Changchun Institute of Geography, Chinese Academy of Sciences, Changchun 130021), Wang Zhigang et al. (Environmental protection Institute of Northeast Coal Industry): *Chin. J. Environ, Sci.*, **17**(4), 1996, pp. 18—20

An empirical formula on the content of trace elements as Be, Co, Cr, Cu, Mn, Ni, Pb, V, Zr in fly ash and bottom ash of burning coal in layer-burning boilers was developed, by which the distribution and transfer quantity of trace elements from coal into fly ash, bottom ash and atmosphere was calculated. The grain size distribution of content and mass of trace elements in fly ashes was also studied, and the laws of enrichment or dispersion of trace elements in burning process were approached. The content of most of trace elements in bottom ashes is higher than that in fly ashes, most quantity of 9 trace elements in coal is removed into bottom ash after burning, but the enrichment factor of element in fly ashes is higher than that in bottom ashes. The enrichment extent of trace elements in fly ashes increases as grain size decreases. About 90 percent of total quantity of trace elements in fly ashes are distributed in the particles with the diameter less than 0.125 mm.

Key words: layer-burning boiler, burning coal, trace element, removal.

The Application of Surfactants on Treatment of Petroleum-contaminated in Unsaturated Zone. Zhu Mei and Xu Jialin (Institute of Environ. Sci., Beijing Normal University, Beijing 100875), Tian Honghai (Center of Environ. Sci., Peking University, Beijing 100871): *Chin. J. Environ. Sci.*, **17**(4), 1996, pp. 21—24

The paper focused on the application of aqueous surfactant washing for cleaning up petroleum contamination in unsaturated zone. Regional geographical features and contamination characteristics have been investigated. Nine commercial nonionic surfactants were analyzed and tested. Their critical micelle concentrations were measured and their effects on emulsification and solubilization of oil and benzene as well as on soil dispersion were compared. The results showed that the best surfactants are AEO-9 and SA-20, i.e., alcohol polyethoxylated ethers. Their optimum concentrations were also determimed. In batch-washing tests the highest removal efficiency can be as high as 94%. Results of leaching tests for soil columns and lime stone columns were satisfactory as well. From this study, it is clear that the application of surfactants can be included in field experimental research for the treatment of contaminated unsaturated zone of groundwater.

Key words: groundwater, petroleum contamination, surfactant, unsaturated zone.

Studies on Removing Uranium from Digested Solutions of Uranium Bearing Ascharite-Magnetite Syngenetic Mineral by Sulfuric Acid in Wengquegou Liaoning Province. Cao Jiling et al. (School of Chemical Engineering, Dalian University of Technology, Dalian 116012): *Chin. J. Environ. Sci.*, **17**(4), 1966, pp. 25—27

The digested solution of uranium bearing ascharite-magnetite syngenetic mineral in Wengquegou by sulfuric acid contains a large amount of H_3BO_3 and $MgSO_4$ and a little Fe^{3+} (after oxidation with $NaClO_3$)and UO_2^{2+}. The experiments of removing uranium from solutions containing Fe^{3+} and without Fe^{3+}, after adjusting their pH with MgO, were carried out. After precipitation of UO_2^{2+} from solution without Fe^{3+}, the U content is still higher than that in digested solution, whereby it is impossible to remove U. When $Fe(OH)_3$ exists, which can act as coprecipitant, the U content after purification can be depressed,