Oil Shale, 2008, Vol. 25, No. 1, pp. 17–26
doi: 10.3176/oil.2008.1.03
ISSN 0208-189X

RESEARCH ON RELEASE OF TRACE ELEMENTS AT RETORTING OF HUADIAN OIL SHALE

BAI JINGRU[(a, b)*], WANG QING[(a)], LI SHUYUAN[(b)], LI CHUNYU[(a)], GUAN XIAOHUI[(a)]

[(a)] Northeast China Institute of Electric Power Engineering
132012 Jilin, China
[(b)] China University of Petroleum
102249 Beijing, China

Oil shale is abundant in the world. Today, the industry of oil shale retorting for producing shale oil is developing owing to high price of crude oil in the world. In order to study migratory behavior of trace elements in oil shale at retorting, tests were performed in laboratory with oil shale of the Huadian deposit of China at different temperatures from 360 to 560 °C. Trace elements Ba, Co, Cr, Cu, Mn, Ni, P, Pb, Sr, Ti, V, Y present in oil shale and shale char were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Hg and As were determined by atomic fluorescence spectroscopy (AFS). By comparing the content of trace elements in oil shale and shale char, distribution characteristics of trace elements at retorting were studied. The analysis of trace elements indicates that in comparison with the earth crust averages, oil shale samples are richer in some elements, including Mn (more than 30×), P (more than 6×), and Ti (more than 5×). The amounts of Ti, Ba, Co, Cr, Cu, Mn, and V are increased in shale char at retorting. Pb and Hg start to volatilize at 410 °C. Shale char is enriched with arsenic by about 50% at temperatures from 360 °C to 560 °C. Reducing atmosphere promotes the release of trace elements. The effect of heating rate on different elements was also studied in these experiments. For most of the elements, their release from oil shale can be promoted by higher heating rate and nitrogen atmosphere.

Introduction

In China, oil shale deposits are widespread in many regions. The proved reserves amount to about 32 billion tonnes, presenting a potential energy source. The world's increasing crude oil price and increasing need in liquid fuel stimulate shale oil production in China. More oil shale retorting plants

* Corresponding author: e-mail *jlbjr@163.com*

for producing shale oil will be built [1–2]. Retorting of oil shale generates wastes and effluents, which may contain trace metals, semi-volatiles, sulfides and other pollutants. The impact of oil shale industry development on the environment and health could not be ignored.

Some trace elements are relatively highly concentrated in oil shale. Therefore studies on mobilization of trace elements and their distribution during oil shale retorting are important. Due to the behavior of trace elements during coal combustion these processes have been widely studied in coal [3–7], and a number of studies on trace elements have been carried out on combustion of Estonian oil shale at power plants [8–13]. The trace metal content of Estonian oil shale was found to be in the same order of magnitude as that of coal on average, only the content of Mn was found to be apparently higher in Estonian oil shale than that in coal [8]. The results of the study by Aunela-Tapola *et al.* [8] show remarkably high concentrations of toxic heavy metals in flue gases (e.g., Pb, Zn, Mn and As: >200 $\mu g/m^3$ each) and high concentration of Pb, Cd, Zn, Tl and As in fly ashes.

There are few studies on retorting of oil shale in China. The purpose of this paper is to study the release behavior of some trace elements at oil shale retorting at different final temperatures, in various atmospheres and at different heating rates.

Experimental

Oil shale sample

The material used was oil shale from the Huadian deposit in China. Huadian deposit is characterized by sandstone roof and shale floor. Huadian oil shale is distributed throughout the most Huadian basin that extends from the Huadian downtown north to the northeast, being divided along the line from west to east as the Beitaizi, Dachengzi and Gonglangtou three regions and the south Miaoling, according to the geological structure and natural conditions [14]. The Huadian oil shale deposit, in the Jilin province is of Cenozoic Era, Paleogene Period. Other characteristics are as follows: type of basin – fault, sedimentary environment – inland lake, thickness – 1–4.5 m, oil yield – 8–12%, proven reserve – $3.38 \cdot 10^8$ t [15].

Oil shale sampling, preparing and milling to get grains smaller than 0.2 mm as well as determination of moisture, ashes and volatile matter were done according to the standards. The results of standard analysis of Huadian oil shale are as follows: calorific value – 11914.12 kJ/kg, proximate analysis (wt.%, as received) – M_{ad} 3.06, V_{ad} 33.73, A_{ad} 57.97, FC_{ad} 5,03; oxides (wt.%) – Al_2O_3 54, Fe_2O_3 4.15, CaO 3.86, MgO 0.71.

Retorting procedure

To study behavior of trace elements at oil shale retorting, retort experiments were conducted in the intermission reactor shown schematically in Fig. 1. The retorting furnace is a stainless steel cylinder (l = 1300 mm, Ø = 1500 mm). A fine-mesh steel filter is placed at the bottom and lids attached to the ends. The top lid accommodates the inlet of nitrogen flow, oil shale sampling device and two thermocouples. The resistance coil serves the purpose of maintaining temperature throughout the oil shale sample layer and also improving heat transfer into the middle of the column. Oil shale retorting needs a certain amount of heat – usually 1.26 MJ per kg oil shale. The furnace was heated up at pre-set heating rate until reaching the final retorting temperature. The temperature of the oil shale sample was recorded by a thermocouple embedded in the centre of the sample bed.

Oil shale was heated at linear heating rate of 2 °C/min, 5 °C/min and 20 °C/min to the final temperatures of 360 °C, 410 °C, 460 °C, 510 °C and 560 °C under the nitrogen and air atmospheres, respectively. The inductively coupled plasma atomic emission spectroscopy ICP-AES was used to analyze the content of trace elements Ba, Co, Cr, Cu, Mn, Ni, P, Pb, Sr, Ti, V, Y, Be, Cd, and Mo in oil shale and in shale char. The elements Hg and As were analyzed by atomic fluorescence spectroscopy (AFS).

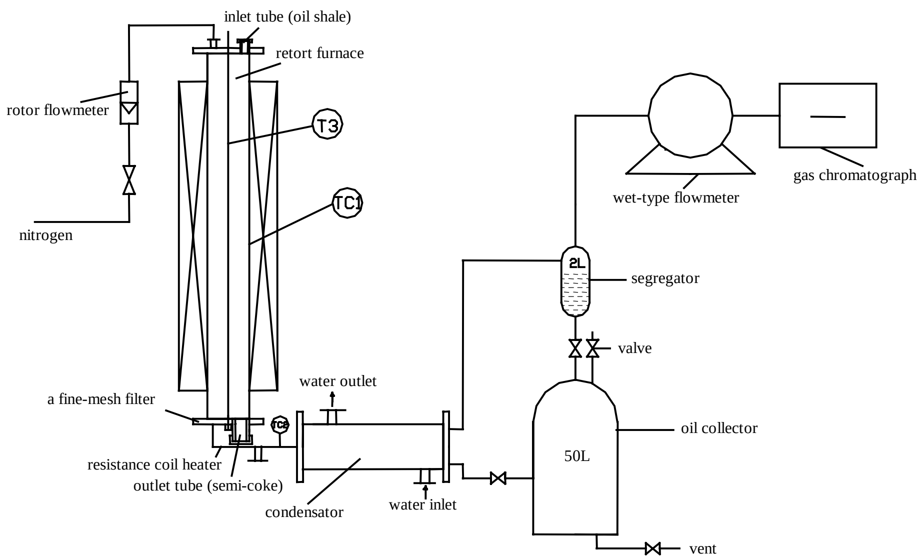

Fig. 1. Schematic diagram of oil shale retorting apparatus.

Trace element analysis

Trace element concentrations in oil shale and shale char were measured by ICP-AES and AFS. The bleeding degree of elements at retorting was determined by measuring the remaining amount of the elements in the solid product – shale char.

In this paper, the bleeding ratio (BR) for each element is defined as:

$$\mathrm{BR} = \left(1 - \frac{\text{concentration in shale char} \times \text{char yield}}{\text{concentration in oil shale}}\right) \times 100\% ,$$

which is used to evaluate the change in the trace element content of oil shale at retorting.

Results and discussion

The concentrations of trace elements in oil shale are listed in Table 1. The concentrations of the elements Be, Cd, and Mo are below the detection limit of the method and consequently are not reported in Table 1.

Concentration levels of most studied trace elements are close to or below the earth's Clarke values. An exception for Huadian oil shale is arsenic on which one has paid particularly much attention; its concentration is eight times higher than the mean value (approximately 17 µg/g). The level of lead is also significantly higher than the earth's Clarke value (more than twice).

Table 1. **Analysis of trace elements in Huadian oil shale of China, µg/g**

Trace element	Huadian oil shale	Earth's Clarke value			Concentration in sedimentary rock	Coal in China		World coal	
		Range	Arithmetic mean	Geometric mean		Range	Mean	Range	Mean
As	17.77	1.9–2.2	2.03	2.03	6.6	0.4–10	5	0.5–80	5
Ba	521	390–600	463	454	800	13–400	160	20–1000	500
Co	14.25	23–26	24.7	24.6	20	1–20	7	0.5–80	5
Cr	47.79	71–200	127	116	100	2–50	16	0.5–60	10
Cu	25.53	45–63	56	55.4	57	1–50	13	0.5–50	15
Hg	0.04	0.057–0.7	0.103	0.0911	0.4	0.01–0.5	0.1	0.02–1.0	0.012
Mn	1513	774–1549	1090	1060	670	4–109	47	5–300	50
Ni	37.59	75–89	81.3	81.1	95	1–60	15	0.5–50	15
P	1237	800–1310	1070	1050	770	10–1000	206	ND	
Pb	29.46	12–16	14	13.9	20	10–47	14	2–80	25
Sr	389.3	215–480	382	359	450	27–300	149	ND	
Ti	2237	540–5590	6520	6070	4500	16–4201	380	ND	
V	61.36	110–180	143	140	130	2–100	25	2–100	25
Y	25.28	19–40	27.7	26.3	30	0.5–22	9	ND	
Zn	96.02	65–94	73.6	75.3	80	1–100	38	5–300	50

ND – no data in literature [19]

In comparison with Chinese coal averages estimated by Zhao Ji-yao and coworkers [18], Huadian oil shale (Table 1) is highly enriched with Mn (more than 30×), P (more than 6×), and Ti (more than 5×); and slightly enriched with other elements. Thus, Chinese oil shale is more rich in studied trace elements than Chinese coals. The concentrations of studied trace elements in Chinese oil shale are compatible with those in the sedimentary rock on average. Aunela-Tapola and coworkers [8] presented the content of some trace elements in Estonian oil shale (μg/g): Pb – 30; Zn – 84; Cu – 7.5; Ni – 15; Cr – 17.0; Co – 3.0; As – 21; Hg – 0.22; Mn – 340; V – 24; Tl – 0.5. They found that Estonian oil shale contains less Mn, Cu, Zn, As, V and Cr than Green River oil shale. Comparison with the values given above shows that the Chinese Huadian oil shale is highly enriched with Cu, Ni, Co, V and Mn. So, Huadian, Estonian and Green River oil shales have one congruent characteristic: they contain noticeably more Mn than coal on average.

There are many factors which control the enrichment of oil shale and coal with trace elements. One of them is geological feature of oil shale deposits. Huadian oil shale is unusually rich in Mn as compared with average values of Chinese and other coals in the world. Manganese is typically associated with carbonates (siderite, dolomite and calcite), but it has also been determined to be present in organic matter of some low-rank coals. Oil shale contains carbonate minerals, generally expressed as CaO. Ash of Huadian oil shale contains more than 10% CaO. So this can explain high Mn content of oil shale. Generally Mn is considered to be a non-volatile element, but it is classified as a hazardous air pollutant due to its potential negative impact on plant growth. No health or environmental problems due to Mn have been reported relative to coal mining and utilization.

Effect of final temperature on release of trace elements

Table 2 shows the data on trace element concentrations in shale char formed at retorting temperatures of 360 °C, 410 °C, 460 °C, 510 °C and 560 °C at heating rate of 5 °C /min.

Resulting from the release of Pb and Hg, their content in the solid retorting product – shale char decreases, and the content of other elements increases when the retorting temperature is increased.

Table 3 presents the bleeding ratios of the studied trace elements at various retorting temperatures. As a rule, bleeding ratios of trace elements tend to increase with incresing retorting temperatures. When comparing the release runs obtained for different elements tested, significant differences in the bleeding ratio may be noticed. At the highest retorting temperature, 560 °C, the highest volatility, over 50%, was found for mercury and arsenic. The volatility of zinc, phosphorus and lead exceeded 40%.

Table 2. **Trace element concentration in Huadian oil shale semi-coke**

Number of semi-coke probe	Final temperature, °C	Solid retorting product, %	Trace element, μg/g														
			Ti	Mn	P	Ba	Sr	Zn	Cr	V	Ni	Y	Cu	Pb	As	Co	Hg
HSC11	360	83.84	2642	1784	1141	612.9	434.5	74	56.7	65.6	37.91	21.14	29.86	33.62	11.87	13.69	0.045
HSC12		82.63	2662	1820	961.6	629.3	456.7	108	56.23	60.86	37.32	23.42	28.31	34.66	11.82	12.85	0.047
HSC21	410	72.85	3055	2012	1085	710.5	508.2	98.65	63.17	65.36	40.13	27.56	31.6	29.98	9.79	13.23	0.042
HSC22		74.12	2968	1991	1363	674.9	420.4	79.26	62.18	71.85	43.74	24.55	31.52	35.62	12.33	15.22	0.035
HSC31	460	68.33	3089	2123	1242	729.7	565.3	84.5	67.64	69.13	41.54	29.35	32.76	35.16	14.71	15.99	0.043
HSC32		68.30	3001	2048	1065	743.4	518.5	84.12	66.49	71.52	39.4	30.59	31.34	28.86	13.3	15.07	0.031
HSC41	510	66.44	2913	2245	1086	763.8	570.1	76.7	64.69	69.45	42.19	29.36	31.33	23.33	12.82	15.16	0.043
HSC42		67.65	3067	2190	1577	708.1	549.6	80.6	65.99	69.61	51.12	27.5	32.87	24.71	15.95	14.87	0.033
HSC43		66.68	2996	2074	1161	750.2	570	80.31	65.36	60.59	41.54	28.06	28.94	26.24	14.74	15.28	0.038
HSC51	560	65.05	3055	1795	1132	750.2	582.7	89.12	67.33	69.15	43.13	29.43	32.06	24.12	14.64	13.34	0.032
HSC52		64.70	3308	1783	1029	730.7	539.5	82.39	66.62	79.58	43.93	31.31	32.81	22.97	13.28	14.12	0.026

Table 3. **Effect of retorting temperature on bleeding ratio of trace elements**

Number of semi-coke probe	Final temperature, °C	Bleeding ratio of trace element, %														
		Ti	Mn	P	Ba	Sr	Zn	Cr	V	Ni	Y	Cu	Pb	As	Co	Hg
HSC11	360	0.98	1.14	22.67	1.37	6.43	35.39	0.53	10.37	15.45	29.89	1.94	4.32	44.00	19.45	5.68
HSC12		1.67	0.60	35.77	0.19	3.06	7.06	2.78	18.04	17.96	23.45	8.37	2.78	45.04	25.49	2.91
HSC21	410	0.51	3.12	36.10	0.65	4.90	25.15	3.71	22.40	22.23	20.58	9.83	25.86	59.86	32.36	23.51
HSC22		1.66	2.46	18.33	3.99	19.96	38.82	3.56	13.21	13.75	28.02	8.49	10.38	48.57	20.83	35.15
HSC31	460	5.65	4.12	31.39	4.30	0.78	39.87	3.29	23.02	24.49	20.67	12.32	18.45	43.44	23.33	26.55
HSC32		8.37	7.55	41.20	2.54	9.03	40.16	4.97	20.39	28.41	17.35	16.16	33.09	48.88	27.77	47.07
HSC41	510	13.48	1.42	41.67	2.60	2.70	46.93	10.06	24.80	25.43	22.84	18.47	47.38	52.07	29.32	28.58
HSC42		7.25	2.08	13.76	8.06	4.49	43.21	6.59	23.25	8.00	26.41	12.90	43.26	39.28	29.41	44.19
HSC43		10.70	8.60	37.42	3.99	2.37	44.23	8.81	34.16	26.31	25.99	24.41	40.61	44.69	28.50	36.65
HSC51	560	11.16	22.83	40.47	6.33	2.63	39.62	8.35	26.69	25.36	24.27	18.31	46.74	46.41	39.10	47.96
HSC52		4.32	23.75	46.18	9.26	10.34	44.48	9.81	16.09	24.39	19.87	16.85	49.55	51.65	35.89	57.95

According to the results in Table 3, Ba, Cr, Sr and Ti do not volatilize, or their volatility at oil shale retorting is low. Release of Ti, Ba, Cr and Sr was lowest, even at the highest temperature.

The bleeding ratio of Mn is low till 510 °C, (1.4–8.6%), but it becomes much higher at 560 °C (22.8–23.7%) It may be explained by the fact that Mn is more associated with oil shale mineral matter and less combined with oil shale kerogen, so that when oil shale is heated to 510 °C, and kerogen decomposes to produce shale oil and retort gas, Mn is not effected; when heated to 560 °C, part of the mineral matter begins to decompose releasing Mn.

Volatility of arsenic was found to be of averge value about 45% at all final temperatures of retorting. V, Ni and Y (BR being about 20%) show moderate bleeding.

Bleeding ratios of Co and P are moderately high. Bleeding ratio of Zn shows a little increase at retorting from 360 °C to 560 °C.

Hg and Pb show an obvious increase in bleeding degree with increasing retorting temperature (both 4–5% at 360 °C, 57% and 44%, respectively at 560 °C).

The release of elements no matter how much, always means their emission along with the emission of volatile matter. The differences in the bleeding ratio indicate that the trace elements investigated are bound with oil shale kerogen and its mineral matter in a different manner.

Effect of the atmosphere on release of trace elements

Figure 2 shows BRs of the trace elements at retorting Huadian oil shale under nitrogen and air atmospheres (retorting temperature 510 °C, heating rates 5 °C/min (Fig. 2a) and 20 °C/min (Fig. 2b)). For all trace elements, except for Zn, values of RB are higher under the nitrogen atmosphere. This suggests that reductive environment promotes release of trace elements, and increases the yield of volatiles. Interaction between trace elements and the reducing environment are the main reasons for increased values of BRs. Higher heating rates obviously promote release of trace elements under the nitrogen atmosphere.

The atmosphere of retorting had no effect on release of Zn (Fig. 2) as shown by the experiments in both atmospheres: BR of Zn at the retorting temperature of 510 °C was the same (45%) under both environments. The main mechanism for Zn release was obviously affected by heating rate.

Effect of heating rate on release of trace elements

Figure 3 shows BRs of trace elements at retorting of Huadian oil shale (heating rate 2 °C/min, 5 °C/min and 20 °C/min, retorting temperature 510 °C) under the nitrogen atmosphere. Various heating rates have different effects on various elements as shown by this experiment.

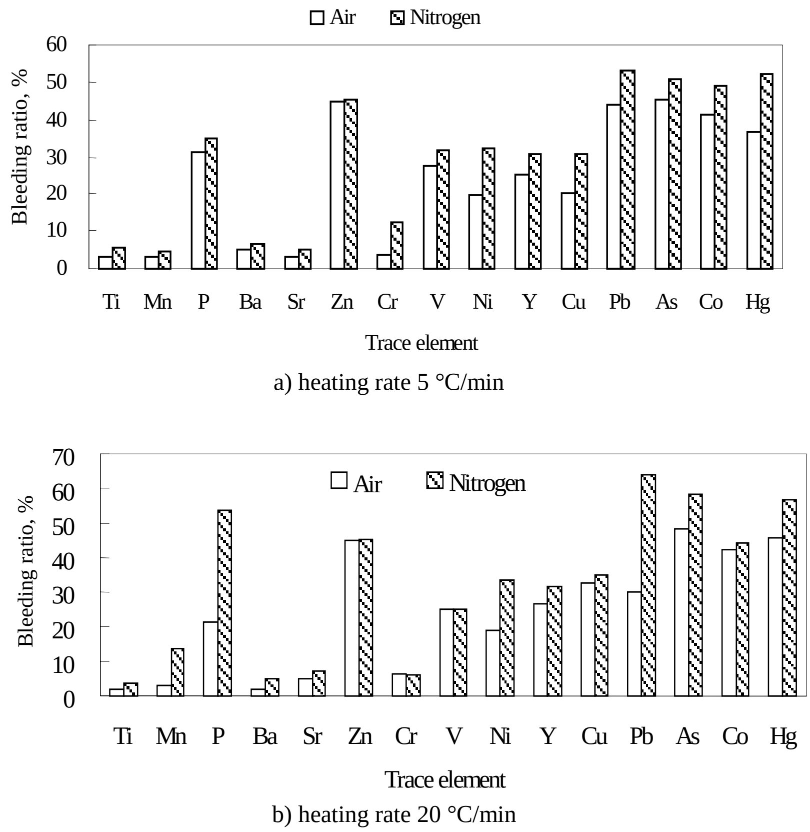

Fig. 2. Effect of the atmosphere on bleeding ratio of trace elements.

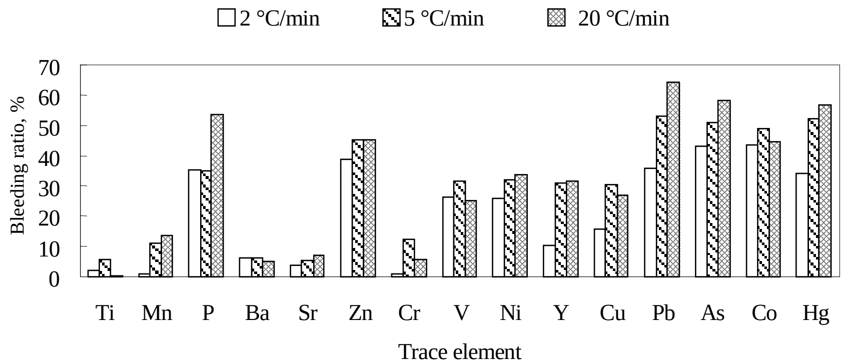

Fig. 3. Effect of the heating rate on bleeding ratio of trace elements.

For most elements, a higher heating rate can promote their release in the nitrogen environment. It can be suggested that some elements may combine with constituents of shale char when heating rate is lower. The elements Cu, Cr, Co and V are all exceptions, as they show the highest BRs at the heating rate of 5 °C/min.

Conclusions

The volatilization behavior of 15 trace elements (Ba, Co, Cr, Cu, Mn, Ni, P, Pb, Sr, Ti, V, Y, Hg, As, Zn) at oil shale retorting was studied.

Huadian oil shale contains more trace elements than Chinese coals. The difference is particularly great concerning content of Mn (more than 30-fold), P (more than 6-fold), and Ti (more than 5-fold). Huadian, Estonian and Green River oil shales are all characterized by high content of Mn as compared with coal on average.

Except for Pb, As and Hg, solid retorting product (shale char) contains more trace elements than raw oil shale. Due to their higher content in shale char and mobility of these trace elements, snowmelt, rainfall, or ground water have the potential to leach toxins and salts from shale char into the environment highly impacting on the environment and causing technological problems during utilization unless proper waste management technology is implemented. Air quality is another environmental concern, and oil shale processing facilities must comply with the provisions of the Clean Air Act.

Barium, chromium, strontium and titanium do not volatilize or their volatility at oil shale retorting is low (volatilization percentage ≤10%). Bleeding ratio is the highest for mercury, lead and arsenic. Bleeding ratio of arsenic is high and invariable (about 45%) at all final retorting temperatures (360–560 °C).

Atmosphere and heating rate have no effect on release of Zn. For most of elements, higher heating rate can promote their release under the nitrogen atmosphere; however, the release of elements Cu, Cr, Co and V is highest at the heating rate of 5 °C/min.

Acknowledgements

Authors are grateful for financial support from the Ministry of Science and technology of the People’s Republic of China (2004BA907A25) and from the Department of Education of Jilin Province (200416).

REFERENCES

1. *Qian, J.* China’s oil shale business is going ahead // Oil Shale. 2006. Vol. 23, No. 4. P. 295.
2. *Qian, J. L., Wang, J. Q., Li, S. Y.* World oil shale utilization and its future // Journal of Jilin University (Earth Science Edition). 2006. Vol. 36, No. 6. P. 877–887 [in Chinese, with English abstract].

3. *Xu, M., Yan, R., Zheng, C. G., Qiao, Y., Han, J., Sheng, C.* Status of trace element emission in a coal combustion process: a review // Fuel Process. Technol. 2004. Vol. 85, No. 2–3, P. 215–237.
4. *Meij, R,, te Winkel, B. H.* The emissions and environmental impact of PM_{10} and trace elements from a modern coal-fired power plant equipped with ESP and wet FGD // Fuel Process. Technol. 2004. Vol. 85, No. 6–7, P. 641–656.
5. *Clemens, A. H., Damiano, L. F., Gong, D., Matheson, T. W.* Partitioning behavior of some toxic volatile elements during stoker and fluidized bed combustion of alkaline sub-bituminous coal // Fuel. 1999. Vol. 78, No. 12. P. 1379–1385.
6. *Senior, C. L., Bool, L. E., Morency, J. R.* Laboratory study of trace element vaporization from combustion of pulverized coal // Fuel Process. Technol. 2000. Vol. 63, No. 2–3. P. 109–124.
7. *Senior, C. L., Bool III, L. E., Srinivasachar, S., Pease, B. R., Porle, K.* Pilot scale study of trace element vaporization and condensation during combustion of a pulverized sub-bituminous coal // Fuel Process. Technol. 2000. Vol. 63, No. 2–3. P. 149–165.
8. *Aunela-Tapola, L. A., Frandsen, F. J., Häsänen, E. K.,* Trace metal emissions from the Estonian oil shale fired power plant // Fuel Process. Technol. 1998. Vol. 57, No. 1. P. 1–24.
9. *Pets, L., Vaganov, P., Zhou, R. S.* A comparative study of remobilization of trace elements during combustion of oil shale and coal at power plants // Oil Shale. 1995. Vol. 12, No. 2. P. 129–138.
10. *Aunela, L., Häsänen, E., Kinnunen, V., Larjava, K., Mehtonen, A., Salmikangas, T., Leskelä, J., Loosaar, J.* Emissions from Estonian oil shale power plants // Oil Shale. 1995. Vol. 12, No. 2. P. 165–177.
11. *Pets, L., Haldna, U.* Microelements in Estonian and Green River (U.S.A.) oil shales: a quantitative comparison // Oil Shale. 1995. Vol. 12, No. 3. P. 239–245.
12. *Häsänen, E., Aunela-Tapola, L., Kinnunen, V.* Emission factors and annual emissions of bulk and trace elements from oil shale fueled power plants // The Science of the Total Environment. 1997. Vol. 198, No. 1. P. 1–12.
13. *Liiv, S., Kaasik, M.* Trace metals in mosses in the Estonian oil shale processing region // J. Atm. Chem. 2004. Vol. 49. No. 1–3. P. 563–578.
14. *Wang, Q., Bai, J. R., Sun, B. Z., Sun, J.* Strategy of Huadian oil shale comprehensive utilization // Oil Shale. 2005. Vol. 22, No. 3. P. 305-316.
15. *Liu, Z. J., Liu, R.* Oil shale resource state and evaluating system // Earth Science Frontiers. 2005. Vol. 12, No. 3. P. 315–323.
16. *Li, T.* The statistical characteristics of the abundance of chemical elements in the Earth's crust // Geology and Prospecting. 1992. Vol. 28, No. 10. P. 1–7.
17. *Mason, B., Moore, C. B.* Principles of Geochemistry. – New York. Wiley, 1982. 344 pp.
18. *Zhao, J. Y., Tang, X. Y., Huang, W. H.* Abundance of trace elements in coal of China // Coal Geology of China. 2002. Vol. 14, No. 7. P. 5–13, 17.
19. *Zhang, J. Y., Ren, D., Zhu, Y. M., Chou, C.-L., Zeng, R., Zheng, B.* Mineral matter and potentially hazardous trace elements in coals from Qianxi Fault Depression Area in southwestern Guizhou, China // International Journal of Coal Geology. 2004. Vol. 57, No. 1. P. 49–61.

Presented by Jialin Qian
Received June 4, 2007