

Trace Elements Atmospheric Pollution from High Temperature Anthropogenic Processes

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Abstract. Air pollution from coal-fired power plants and from burning coal waste piles is large and varied and contributes to a significant number of negative environmental and health effects. On a global scale, large volumes of green house and toxic gases released from coal combustion may contribute to climate change, alter ecosystems, and affect patterns of disease occurrence.

The aim of this study is to determine the mobility and forms of elements in gas and aerosol phases discharged from high temperature technological processes. In this paper we study in detail: 1) the composition of gas condensate produced in experimental combustion of solid fuel, 2) the composition of gas condensate collected at burning coal dumps and metallurgical slag dumps, 3) the composition of snow (dissolved and particulate fraction) in areas with anthropogenic sources of gas and aerosol pollution. Comparison of the chemical composition of all three objects have shown that the character of elements distribution in the dissolved part of the snow cover near CHP, in condensates sampled on burning coal dumps and condensates obtained by the experiment is the same.

Keywords: Air pollution; coal combustion; heavy metals; coal waste dumps, snow cover.

1. Introduction

Gas pollution is a serious problem in modern environments and is expected to become only more urgent in the next century. Gaseous transfer of chemical elements is very important and promising line of research, since it leads to significant changes of elements content in the environment. It is established that the coal combustion brings into the atmosphere Hg, Mo, Se, As, Cr, Mn and other metals; the petroleum combustion brings V and Ni; the gasoline combustion brings Pb, etc. As, Cr, Cu, Ni and other metals enter in the environment with the city drains; As, Hg and Se come from waste plants; steel-casting produces Cr, Mo, Sb and Zn; melting of non-ferrous ores produces Cd, Ni, Pb, Se, Ba. Especially high concentrations of metals smoke emissions are typical for plants, processing non-ferrous metals and accumulators. An emission of metals with smoke occurs in the form of dust particles, gases and aerosols. Metals in the form of mineral particles (dust) are deposited near the emission source. The range of the metals distribution in the dust form typically does not exceed 20-30 km, depending on the wind pattern. A part of metals in gas and aerosol phases migrate on much greater distances. They are raised in this form to the upper atmosphere, creating global pollution levels. The combustion of coal in CHPP bring to the atmosphere elements in gaseous form: Al, Co, Fe, Mn (about 10% of total quantity of these elements in the emissions), Cr, Cu, Ni, V (about 30%), As, Br, Hg, Sb, Se (about 100%). The emission of steel plant contain following elements: Cr, Se, Br, Cd (about 30%), As (up to 70%), Hg (up to 100%) [1].

The estimates of gaseous transfer of high-volatile «permanent» gases are well known worldwide. Those gases prevail in volcanic steam vents, thermal waters, volcanic eruptions and other endogenous gaseous

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emissions. The chemical balances of CO₂, CO, H₂, H₂O, SO₂, SO₃ are studied well for wide ranges of pressure and temperature [2].

Multiple research programs are in progress for analysis of inflammation of coal dumps [3], [4], of metamorphism processes in dump rocks and new mineral phases formation [4], [5]. The geophysical methods [6] and well logging [7] are used to locate the underground fire sources.

The combustion of 1 kg of carbonaceous waste materials leads to polluting of 6.7 - 8.7 millions of cubic meters of air to a dangerous extent. The emissions of acidic gases, particulates, organic compounds, and trace elements from burning coal waste piles may contribute on regional and local scales to environmental degradation and a range of respiratory and other diseases [4]. The composition of emission gases are studied in works of M. Attalla, M. Masalehdani, C. Kuenzer and others [8], [9]. The gaseous transfer of elements in the process of coal burning and coal dump burning is however not studied yet in any works.

2. Materials and Methods

2.1. Objects of research

The study deals with the following materials: condensates, sampled on burning coal waste dumps and metallurgical slag dumps, the snow cover in the areas near CHP-2 and CHP-3 in Novosibirsk. We used two main methods of sampling for the study of high-temperature processes: 1) condensation of gas and aerosol phases near the source of emissions (0–1 m), 2) sampling of snow at a distance from the source (0.3 - 2 km). The condensation of samples is the most representative method for the study of high-temperature gases. This method is used for sampling of condensed natural volcanic gases. Study of snow is also used for several decades already. It allows to obtain information about the flow of pollutants from the atmosphere to the underlying surface. The snow is a natural storage system for dry and wet precipitation in the cold season.

A set of gas condensate samples was collected on the burning slag heaps of the Chelyabinsk region (Kopeysk), coal dumps in Kemerovo region (Kuznetsk coalfield, Bachatskij open-cut mine) and slag dumps of Belovo zinc plant (Belovo). Gas is emitted slowly through the small holes (5 to 10 cm in diameter) on the top of the heaps. Gas was passed through a jet-heated Teflon funnel, then through a flexible Teflon tube connected to a bubbler trap cooled by cold water. A small hand pump was used for the introduction of the gas into the trap [10].

The coals of Kuznetsk coalfield (Bachatskij strip mine) were used for the coal combustion experiment. Coal was burned in a furnace and gases passed through the attached flexible Teflon tube into a bubbler trap cooled by liquid nitrogen [10].

Snow samples were taken in areas near power plants and in the background region (Koltsovo). CHP-2 and CHP-3 are located close to each other in the north-western part of the Novosibirsk city. Both CHPs use coal of Kuznetsk coalfield as a fuel. Sampling points were chosen in open areas, taking into account the location of buildings, the nearest local emission sources (highways, the private houses and small boilers), forests and parkland. Standard techniques of snow sampling were used [11].

2.2. Methods of chemical analysis

The chemical composition of condensed gases and snow was estimated by several methods: ICP-AES analysis for the estimation of microelement composition of snowmelt water was conducted at the Analytical Center IGM SB RAS at IRIS Advantage instrument, manufactured by Thermo Jarell Ash Corporation, USA (Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia); SR-XRF multi-element analysis of the weighted samples of snow and dry residue obtained by evaporating snowmelt water was conducted at the elemental analysis station VEPP-3 (Institute of Nuclear Physics, SB RAS, Novosibirsk, Russia); ICP-MS analysis to determine the composition of the gas condensate was conducted on the high-resolution mass spectrometer ELEMENT (Finnigan MAT) in the IGM SB RAS, Novosibirsk, Russia.

3. Results and discussion

3.1. Tentative combustion

The vapour-gas condensates, obtained by this experiment, contained macro components (Ca, Na, Mg, K with the concentration of 6-60 mg/L), trace elements Zn, Al, As, Sr, Fe (0,1-0,01 mg/L), Ba, Mn, Cu, Ni, Ti, Pb (0,01-0,001 mg/L) and Cr, Rb, V, Sb, Cd, Co, Sn, Ga (less than 0.001 mg/L). The experiment allowed to collect gas condensates of the first phase of coal combustion (volatile inorganic compounds, first 15-20 minutes of burning), and the second phase (carbon residue burning). The first phase produces mainly Ti, V, Cu, Ga, the concentration of which is an order of magnitude greater in first phase, than in second.

3.2. Burning coal dumps and metallurgical slag dumps

Steam and gas condensates, collected on burning coal dumps, had a largely different chemical composition. This is due to the age of fires. If the coal waste dumps is burning for decades, the metamorphism processes inside of it lead to formation of new mineral phases and emission of specific range of elements. The metamorphism processes in burning dumps were investigated in detail by Chesnokov B.V. and Sokol E.V. [5], [4].

We conventionally distinguish the "young fires" (burning times of 1-10 years) and "old fires" (burning times of 10 - 50 years). "Old fires" are characterized by the presence of altered rocks, secondary minerals and high-temperature gases (200–500° C). "Young fires" have a surface fire with no visible changes of rocks and the temperature of their gases is low (60–100° C). They are characterized by lower concentrations of most elements in their emissions. Higher concentrations are observed only for K, Cr, Co, As (Fig. 1). The emissions of the "old fires" have the dominating elements (S, Ti, Ag, Cd, Al, P), concentrations of which are an order of magnitude greater than in "young fires" (Fig. 1).

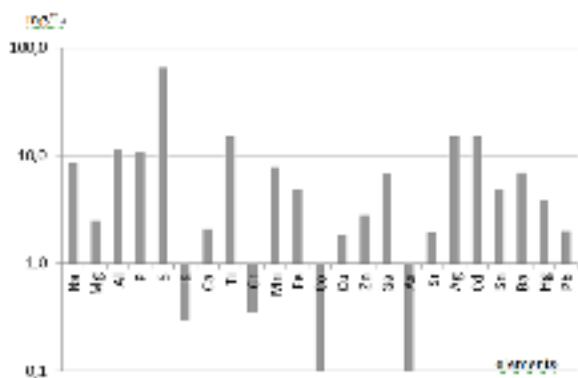


Fig. 1: The ratio of elements concentrations in condensates of the "old fires" and "young fires" at the coal dumps.

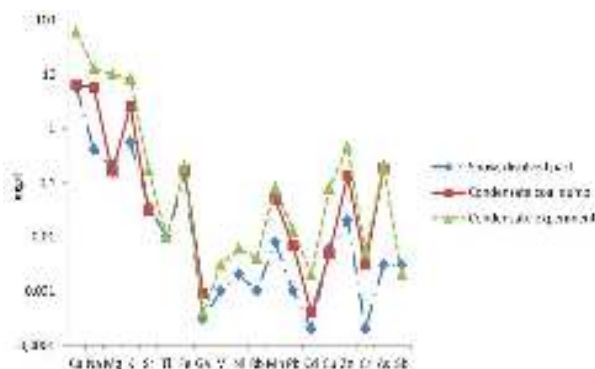


Fig. 2: Comparison of condensate composition obtained by the experimental coal combustion, condensates sampled on burning coal dumps and dissolved part of the snow cover near coal CHPs.

The condensates of the Belovo zinc plant dumps contain mostly Cu, Ag and Sn. Those elements were of high concentrations in the feedstock (Table 1), but were not extracted. Sulfur is presented in small amounts, because Belovo plant produced also sulphuric acid.

3.3. Snow cover

Snow cover study has shown that emissions of CHP-2 and CHPP-3 have similar chemical composition of emissions and the distribution of impurities. This is due to the fact that they used the same fuel type (Kuzbass coal), and they have similar characteristics of emission sources. Almost all the elements are mainly concentrated in the suspension (except for uranium). The main pollutants are Sb, Sn, Ge, U. The content of As, Nb, V, Th is also significantly higher than the background level (5 times higher on average). It is important, that these elements are mostly present in water-soluble form (remains in the filtrate during the melting of snow) and can easily migrate to water flows and be included into the food chain [6].

Comparison of the chemical composition of all three of the objects have shown that the character of elements distribution in the dissolved part of the snow cover near CHP, in condensates sampled on burning coal dumps and condensates obtained by the experiment is the same (Fig. 2). Condensate was sampled in the tentative experiment directly at the source of fire, condensate on the dumps — a few tens of meters from the source, and snow was sampled a few hundreds of meters from the source. The lowest concentrations were

observed in snow cover, and the highest — in the tentative condensates. Thus, the chemical composition of snow cover near CHPPs is primarily defined by the composition of used coals. The regional and global aerosol pollutants introduce minimal impact.

If we assume that emissions of CHP condense in the same way as in coal combustion experiment, the comparison of condensates and dissolved part of the snow will give us an estimate of mobility of elements in the system of air / snow.

A direct comparison of these compounds has shown that the major rock-forming elements (Ti, Fe, Ga, V, Ni, Sr, Rb) in the condensate and snow cover have the concentrations of same order of magnitude (Table 2) and the mobility coefficient < 1 . The other elements (Ca, Na, Mg, Mn, K, Cu, Zn, As) have the 1 or 2 orders of magnitude greater concentration in condensate than in the dissolved part of the snow cover ($K_{\text{mobility}} > 1$). That would suggest that this group of elements also was transported in the gas phase, but because of a higher migration ability it interacted and redistributed in the system dissolved/weighted part of the snow cover.

Table 1: Elements concentrations in the condensate Belovo dump and coal dumps, mg/L

	Belovo damp, Mean val. (n=5)	Coal dumps Mean val. (n=20)
Na	4,6	5,8
Mg	1,4	0,2
S	3	126
K	2	3
Ca	8	6
Al	0,07	0,69
P	0,13	0,41
Ti		0,05
Cr	0,002	0,003
Mn	0,03	0,06
Fe	0,05	0,19
Co		0,0003
Cu	0,04	0,005
Zn	0,11	0,14
Ga	0,0004	0,001
As	0,07	0,02
Sr	0,05	0,03
Ag	0,013	0,002
Cd	0,0002	0,0005
Sn	4,17	0,04
Ba	0,07	0,39
Hg		0,004
Pb	0,003	0,008
Sb	0,001	
V	0,002	

Table 2: Elements concentration in the dissolved part of the snow cover, in the condensate sampled by the experiment and the mobility coefficients

	Snow, dissolved part, mg/L	Condensate experiment, mg/L	K mobility $K = \log(C_{\text{cond}}/C_{\text{snow}})$
Ti	0,01	0,01	0
Fe	0,13	0,2	0,2
Ga	0,0003	0,0004	0,1
V	0,001	0,003	0,5
Ni	0,002	0,006	0,5
Sr	0,037	0,17	0,7
Rb	0,001	0,004	0,6
Mn	0,008	0,077	1,0
Ca	5,8	60	1,0
Pb	0,001	0,013	1,1
Cd	0,0002	0,002	1,0
Cu	0,006	0,077	1,1
K	0,56	8,4	1,2
Zn	0,02	0,46	1,4
Cr	0,0002	0,005	1,4
Na	0,4	13	1,5
Mg	0,2	10	1,7
As	0,003	0,2	1,8

4. Conclusions

The received information have shown a significant amount of gaseous transfer of trace elements. A wide spectrum of elements was released from burning coal or hot slag, not only volatile anion-forming As and Sb but also elements that are traditionally considered as refractory (Ti, Fe).

The pollution of snow in the region of Novosibirsk CHP-2 and CHP-3 (using the Kuzbass coal) and the composition of gas condensates produced by tentative burning of Kuzbass coal were similar. A group of major elements (Ti, Fe, Ga, V, Ni) have the same concentration in dissolved part of the snow cover and in the condensate. The nonvolatile and inactive elements accumulate in solution. The alkali metals and arsenic (Na, Mg, K, Ca, Cu, Zn, As) have a higher migration ability and show greater concentrations in gas condensates.

The sequence of elements ordered by the mobility coefficient for air/snow system was obtained, as follows: Ti <Fe <Ga <V <Ni <Sr <Rb <Mn <Ca <Pb <Cd <Cu <K <Zn <Cr <Na <Mg <As.

High concentrations of trace elements in the condensates collected on the burning slag heaps as well as our laboratory tentative experiments have shown that gaseous transfer occurs in high-temperature anthropogenic processes for a wide spectrum of elements. The problem of gaseous transfer of elements in anthropogenic processes deserves much more attention than currently is paid to it. The emissions of toxic trace elements can potentially occur in large scale (e.g. subterranean combustion of spoil tips or forest fires) having serious environmental impact.

5. Acknowledgements

We would like to express our gratitude to all those who gave us the possibility to compile this paper. We are deeply indebted to our supervisor Prof. Bortnikova S. B., who helped us much in all stages of study and analysis of the project and provided help, stimulating suggestions, knowledge, experience and encouragement in the pre and post research period. We are also grateful to Prof. Raputa V.F.

This work was supported by the RFBR grant № 12-05-33019 and President Russian Federation grant № MK-2574.2012.5.

6. References

- [1] A.N. Ostromogilsky, V.A. Petrukhin. *Heavy metals in the environment: sources of income and methods of assessment of their impact*. Gidrometeoizdat, 1984.
- [2] A.A. Migdisov, A.Y. Bychkov. The behaviour of metals and sulphur during the formation of hydrothermal mercury- antimony-arsenic mineralization, Uzon caldera, Kamchatka, Russia. - *Jour. Volc. Geotherm. Res.* 1998, vol. 84, pp. 153-171.
- [3] H. Wang. *Thermal decomposition of solid oxygenated complexes formed by coal oxidation at low temperatures*. *Fuel* 2002, vol 81, pp. 1913-1923.
- [4] G. B. Stracher, A. Prakash, E. V. Sokol. *Coal and Peat Fires: A Global Perspective: Volume 1: Coal - Geology and Combustion*. Elsevier 2011.
- [5] B.V. Chesnokov. Overview of results on mineralogical investigation of burnt dumps of the Chelyabinsk coal basin during 1982–1995. *10th report, Ural`sky mineralogical sbornik N 7*. 1997: pp. 5–32.
- [6] G. Schaumann, B. Siemon, Y. Changchun. *Geophysical Investigation of Wuda Coal Mining Area, Inner Mongolia: Electromagnetics and Magnetics for Coal Fire Detection*. ERSEC Ecological Book Series – 4, 2010.
- [7] X. Zhang, J.L. Genderen, S.B. Kroonenberg. Spatial analysis of thermal anomalies from airborne multispectral data. *International Journal of Remote Sensing*. 2003, vol. 24, pp 1-17.
- [8] C. Kuenzer. Uncontrolled Coal Fires and their Environmental Impacts: Investigating two Arid Mining Regions in North-Central China, *Applied Geography*. 2007, vol. 27, pp 34-67.
- [9] M. Attalla, S. J. Day, T. Lange, W. Lilley, S. Morgan *NOx Emissions from Blasting Operations in Open Cut Coal Mining in the Hunter Valley*. CSIRO Energy Technology, 2007.
- [10] H. Anon. *Spoil Heaps and Lagoons, Technical Handbook*. National Coal Board, London, England, 1973.
- [11] A.Y. Devyatova, N.V. Yurkevich, V.F. Raputa, . Predictive models of air pollution from anthropogenic sources by the snow cover study. *Proceedings of the 3rd International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE 11)*. 2011. P. 577-582.