Uranium oxides in technogenic aerosol of the area of Novosibirsk city

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In the article the first results of mineralogical and geochemical studying of the technogenic aerosols in area of Novosibirsk chemical concentrates plant (NCCP) are resulted. Content of uranium in technogenic aerosol are studied using ICP-MS, ICP-AES. Particles of uranium oxides are revealed in aerosol using electron microcsopy.

Key words: technogenic aerosol, uranium isotopes, uranium oxides, Novosibirsk, aerosol pollution, ecological risk

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In large cities of Siberia, there are many industrial enterprises being emission sources. Revealing local sources of pollution is of crucial importance for the improvement of urban and suburban ecology. In Siberia, snow is an ideal model object to study industrial emissions, because from early November to late March-early April, a steady snow cover contains solid aerosol particles as well as gaseous products adsorbed on solid phases. In winter, south and southwest winds prevail in the surface atmosphere layer of the Novosibirsk region, and in summer, the wind rose is more isometric [*Climat of Novosibirsk, 1979*]. At a height of 0.5 km in the boundary atmosphere layer, southwest and west winds are predominant. Therefore, aerosol emissions of the above industrial enterprises are spread mainly in the northeastern and northern directions.

NCCP – one of the greatest enterprises of Russian nuclear fuel cycles engaged in production of nuclear fuel for power and research reactors, lithium and its compounds which was founded in September, 25 1948.

Experimental part

Aerosol particles are accumulated in snow during winter. We test the snow samples. Volume of snow samples is about 70 l. To eliminate the pollution impact of highways, we took all samples at distances of more than 150 m from them. Intensity of aerosol pollution is estimated by ratio of aerosol to smelted smow volume (mg/l). Spread list of element in aerosol were detected in a wide range of concentrations by ICP MS on a Finnigan Mat mass spectrometer (Germany) with a U-5000AT+ aqueous-solution ultrasound atomizer. The detection limits of elements are listed in Table 1. ICP-AES on spectrometer IRIS Inc. is used additionally. Solid aerosol mass are dissolved by two alloying techniques with alkali KOH and $LiBO_2$. The relative standard deviation was up to 10%. Lower detecting limits were up 0.01 ppm. Ratio of isotopes $^{238}U/^{235}U$ is detected by ICP-MS, relative standard deviation was ≤ 2 %.

The integral elemental composition of solid aerosol particles was quantitatively determined by X-ray fluorescent analysis on synchrotron radiation (SR-XRFA) at the VEPP-3 Elemental-Analysis Station of the Institute of Nuclear Physics, Novosibirsk [*Artamonova, et al, 2007*]. This method permitted determination of 35 elements (Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Br, Mo, Ag, Cd, Sn, Sb, Te, Hg, Tl, Bi, Th, Pb, etc.) with detection limits of up to 0.1 ppm depending on the excitation energy of emission lines. The relative standard deviation was 10–15%. Soil standard SOIL-7 МАГАТЭ is used. X-ray diffraction analysis of aerosol particles was carried out on a DRON-3M powder diffractometer (CuK_α, U = 40 kV, I = 24 mA). This method permits a semiquantitative estimation of mass fractions of mineral phases. The morphology and chemical composition of aerosol particles were studied on an LEO 1430 VP scanning electron microscope equipped with an (EDS) OXFORD energy dispersion spectrometer. Scanning beam was ~0.5 μm in diameter, which permitted determination of the compositions of aerosol particles larger than 0.5–1 μm. Some spectra revealed

intimate intergrowths of fine grains. The particles were examined in secondary and back-scattered electron images.

The method of reduction of brightness of a field of vision of an electronic microscope is applied to search iron oxides and other heavy particles (especially uranium oxides). The lower brightness is chosen, when iron oxides are seen as dark-grey particles, another more weight particles ≥ 56 atomic mass (for example, uranium oxides) are detected as brightly shone particles. More 5000 fields of vision of 212 μm X 159 μm in size are studied at an increase of 1500 times. There were about 300–500 aerosol particles with size > 0.5 μm are on one field of vision.

Results and discussion

In melted snow concentration of U is enough lower (mkg/l): mean 0.04, variation 0.02–0.06, Th concentration variation – 0.01–0.02. Соответственно Th/U=0.42.In solid aerosol particles content of Th is more in 2 times than content of U, and mean ratio Th/U = 2.12. On distance in 0.5 to 25 rm from NCCP radionuclide' content in aerosol and in melted snow is decreased in ~ 2 times. In aerosol mass mean U content is equal (ppm) 5.64, minimal U content – 4.50, maximal U content – 9.93. In aerosol mass mean Th content is equal (ppm) 11.74, minimal Th content – 8.80, maximal Th content – 15.49.

Natural U is the mixture of its isotopes: ^{238}U: ^{235}U: ^{234}U = 99.28 : 0.714 : 0.006, so natural ratio $^{238}U/^{235}U$= 139.05. For the first time it is revealed, that aerosol of NCCP area are enriched by ^{235}U, and in aerosol ratio $^{238}U/^{235}U$ is varied in range from 77.43 to 129.26. Mean $^{238}U/^{235}U$ in aerosol is equal 107.78.

Displacement of an isotope ratio $^{238}U/^{235}U$, high total contents U, Th in aerosols become geochemical indicators of NCCP emissions. No doubt, NCCP is source of significant technogenic aerosol pollution of surrounding.

Using scanning electronic microscope 10 aerosol particles of U oxides are found in aerosol mass. Range of U oxides particles size is from 2 to 18 $\mu м^2$. The particles are distinguished by their very high brightness under back-scattered electron images. The particles are represented as fragments of the wrong form which have stuck to alumino-silicate spheroids (fig.1). Stucking of weight U oxides fragment to hollow alumino-silicate microspheres get possibility for aerosol migration on a long distance.

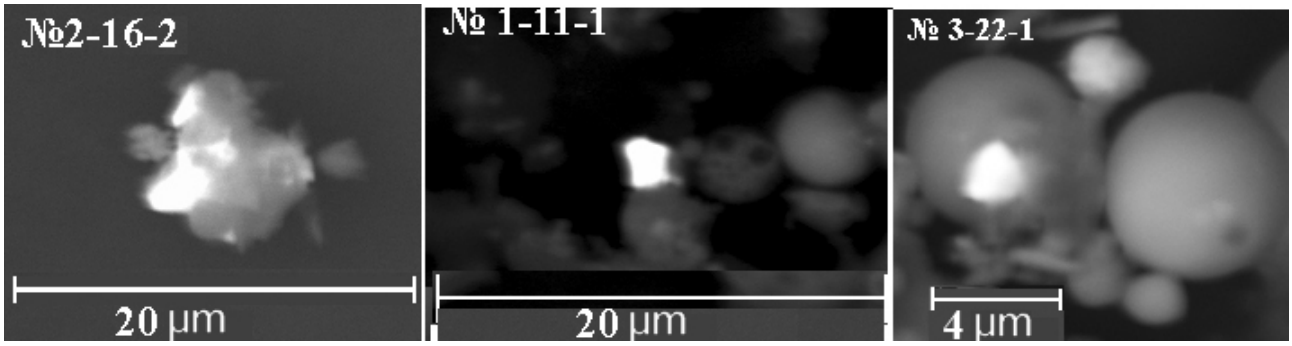

Fig. 1. Oxides of U, stucked to alumino-silicate particles and to hollow alumino-silicate microspheres

Range of U content in U oxides particles is varied from 33.83 to 78.80 %. There are Fe – 3.19 %, Cu – 1.23 % in the particles (table.1). The one large particle of U oxides is found. Its size is 64 $\mu м^2$ in form of slag with a rough wavy surface (fig.2, at the left). The alunino–silicate slag particles riched Zr – 9.87 %, Y – 6.05 %, U – 2.47 % is found (fig 2, at the right, table 2).

Table 1. Element composition of U oxides particles in technogenic aerosol of NCCP area

№ of the particle	Distance from NCCP, km	Size of the particle, $\mu м^2$	O , %	Fe, %	Cu, %	U, %
1—11-1	4.8	9	27.88	0	0	72.12
1—38-1	4.8	6	49.49	0.85	0	49.66
1—48-1	4.8	3	37.72	1.68	1.23	59.38
2—16-2	9.15	64	28.16	0.00	0.82	71.02
2-16-2a	9.15		52.81	3.19	0	44.00
2—18-1	9.15	6	34.39	0.98	0	64.63
2—32-1	9.15	8	23.90	0.99	0	75.11
3—22-1	9.15	3.9	65.18	0.98	0	33.83

4—14-1	17.5	12	26.00	1.54	1.09	71.37
4—22-2	17.5	2.25	37.18	2.11	0	60.71
5—9-1	22.8	3	25.89	1.34	0	72.77
5—18-1	22.8	18	21.20	0.00	0	78.80

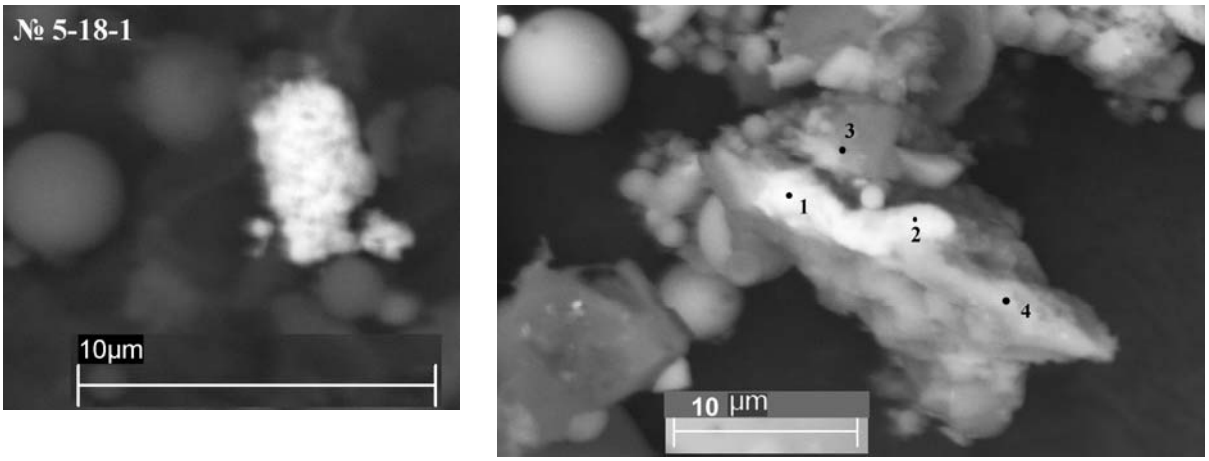

Fig. 2. Large slag aerosol particles with U (the element composition of right particle is shown in the table 2).

Table 2. Element composition of the slag particle (fig. 2, on the right), %

№	O	Na	Mg	Al	Si	P	K	Ca	Ti	Fe	Y	Zr	U
1	48.31	0.77	0.55	3.71	13.02	1.74	0.37	0.85		17.83	3.77	6.8	2.28
2	48.92	1.49		4.28	14.9	1.95	2.04	1.06		6.96	6.05	9.87	2.47
3	56.76	1.37	1.98	8.98	22.07	1.09	1.76	0.58	0.37	5.04			
4	45.68	2.22		10.69	33.24		3.07			5.11			

Conclusions

The new date about NCCP emission is revealed. Technogenic aerosol of NCCP area are enriched by Th, U, especially by ^{235}U isotope, and mean ratio $^{238}U/^{235}U$ is 107.78. This technogenic U isotope ratio is smaller than natural ratio (natural $^{238}U/^{235}U$ is equal 139.05). For the first time aerosol particles of U oxides are found in aerosol mass of NCCP area.

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References

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