Study of industrial metabolism of sulfur in coal-based power production

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Possible integration of the studies that are being conducted at the institutes of Siberian Branch of the Russian Academy of Sciences within the framework of the program of the interdisciplinary study of sulfur transformations in the course of industrial use of coal is discussed. The program is based on the concept of industrial metabolism. In that, it involves a wide scope of fundamental and applied problems. Implementation of the program would provide progress both in the policy of fuel resources use and in the environmental protection activity. In particular, it would enable evaluation of the environmental protection strategies through analysis of material flows.

The aim of the research, discussed in this paper, is to reveal thoroughly the ways of transport and the mechanisms of transformation of sulfur [industrial metabolism of sulfur (IMS)] at all stages of the industrial use of fossil fuels and in the environment. During the last two decades, a marked progress has been achieved in understanding the geophysical cycle of sulfur.[1] At the same time, the problems on man-caused contribution to the sulfur cycle and the degree of the anthropogenic effect in the natural geophysical cycle of sulfur are still to be studied. This is caused by the absence of sulfur balance at all (with rare exceptions) stages of the use of sulfur-containing materials. The deficit of the data on sulfur flows in technical systems is redoubled by the growing requirements to details of the data on the qualitative and quantitative composition of these flows. Drawing a detailed balance calls for analysis of all forms of sulfur in industrial processes, including recycling of wastes.

Sulfur in nature and industry

Sulfur cycle

Industrial processes with participation of sulfur can be divided into two categories. In the first one, sulfur-containing compounds act as reagents and products of goal transformations; in the second category, they are associated admixtures in raw materials. The most important of the processes of sulfur transformation are the production of sulfuric acid, non-ferrous metallurgy, production of rubber, antioxidants, and fertilizers. The processes of power production make up the largest fraction, in the second group, i.e., burning and processing of fossil fuel. The contribution of power production to the global anthropogenic cycle of sulfur reaches 80%. It is well known that burning of coal is responsible for 67% of the total power of anthropogenic sources of sulfur, burning of oil products accounts for 12%, and copper smelting accounts for 13%.

Intense industrial use of sulfur-containing substances has reached the level, at which the anthropogenic cycle of sulfur is comparable with its natural flows, and utilization of sulfur-containing wastes threatens with the distortion of the natural geophysical cycle of sulfur on the global scale. Distortion of the natural cycle of sulfur manifests itself in the increase of precipitation acidity, acidification of soil and surface in-land waters, and this leads to negative economic consequences.

The natural sulfur cycle covers all geospheres and involves active participation of organisms. The activity of denitrifying bacteria and sulfobacteria provides for continuous transformation of sulfur in soil by the general scheme: $S^{2-} \rightarrow SO_4^{2-} \rightarrow H_2S \rightarrow S^{2-}$. The same reactions proceed in the ocean. In the form of H_2S, the sulfur comes into the atmosphere. Another important natural source of H_2S in the atmosphere is volcanic activity accompanied by decomposition of sulfides. The mean lifetime of H_2S in the midlatitude atmosphere is about a day and it is determined by natural photochemical interactions resulting in transformation of sulfur into sulfates. Absolutely all sulfates under atmospheric conditions are condensed substances, many of which are easily soluble in water. These properties provide for relatively fast removal of sulfates from the atmosphere by means of dry sedimentation and washing-out with precipitation.

Description of sulfur flows

The models used to numerically describe global flows of chemical elements take into account, as a rule, the following reservoirs: soils, underlying rocks (with different degree of detail), surface in-land waters, Global Ocean (surface layer is sometimes considered as a separate reservoir), bottom deposits, biota, and the atmosphere. Since the exchange of substances between the atmosphere and contiguous media occurs only in the lower, boundary, layer, the atmosphere is often described as a single reservoir. For the case of sulfur, this assumption is not doubtless, since at the altitude of 18–20 km there exists a layer of sulfate aerosol (Junge layer), 90% of whose mass consists of submicron droplets of sulfuric acid with the concentration about 75%. The mechanism of formation of the Junge layer is still not clearly understood.

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The anthropogenic component in the global sulfur balance is taken into account by introducing an additional reservoir into the model. The inflow into this reservoir corresponds to extraction of fossil fuel and raw materials, and sink corresponds to emissions, discharges, and dumps of sulfur-containing wastes. Gaseous industrial emissions serve as largest sources of sulfur dioxide SO_2 in the atmosphere, and their contribution in the majority of regions exceeds the contribution of natural sources. The efficiency of different sinks of SO_2 in the atmosphere is estimated as follows: dry sedimentation – 45%, liquid-phase oxidation – 35%, washing-out with precipitation – 11%, gas-phase oxidation – 9%. The dominant forms of sulfur in discharges are sulfate ion and organic sulfur compounds. Large amounts of sulfates come into soil and water because of washing out of ash dumps of power production and metallurgical industries by atmospheric precipitation.

Quantitative characteristics of mass exchange at the boundary of the anthropogenic subsystem are the subject of continuous discussion. This is connected with the objective difficulties in aggregation of incomplete and uncoordinated instrumental data, as well as with the absence of reliable information on flows of sulfur-containing materials within the anthropogenic sphere. In the processes of fuel burning and processing, the sulfur balance cannot be drawn, as a rule, even at the level of an individual installation; therefore, there are not enough data for drawing the balance on the regional level. The deficit of information on the quantitative and qualitative composition of sulfur flows is most pronounced when studying and modeling transborder air pollution. A number of regional models of pollutant diffusion are currently being developed. These models are used in decision making support systems such as RAINS and RAINS-ASIA (IIASA, Austria), EURAD (EURAD Project, Germany), RADM (NCAR, the U.S.A.), STEM–II (University of Iowa, the U.S.A.), and others.[2] The experience in application of such models indicates that the initial information on the amounts of consumed fuel and emissions is yet the most important and most vulnerable unit in analysis of the anthropogenic impact on the nature.

Concept of industrial metabolism

Key theses

In the late 1980's, several scientists independently put forward the ideas on the significant change in the policy of the use of natural resources and formation of a new system for its control. These ideas included the concepts of input management and industrial metabolism. The former proposes selection of the industrial resources in order to diminish production of wastes instead of their utilization.[3] The latter is the systematic approach to minimizing production of toxicants that assumes analysis of all their sources, ways of transformation, and sinks into the environment.[4] This analysis is not restricted to inventory of industrial objects, at which a given substance is produced, but requires consideration of all the stages of the life cycle of technologies and products.

Apparently, these concepts conform to each other. In the early 1990's they were called the policy toward ecological sustainability.[5] Now many ideas of both approaches are considered within the framework of industrial ecology,[6] although this term is ambiguous and seems unhappy. Actually, the study of industrial metabolism is an instrument of decision support in control of any resources, including both raw materials and power and finance resources. For efficient implementation of the concept of industrial metabolism (CIM), not only the measurement data should be integrated, but also the economic data on production, transport, and material and energy consumption should be analyzed.

The three main CIM components are the following[5]:

1. Matching of economic data on substance flows in industry and in the consumption sector with the data on the pollutant input into the environment and its accumulation there.

2. Joint analysis of data on the distribution of a pollutant in time and space in order to estimate quantitatively the places of pollutant income and its load in time.

3. Evaluation of changes in the resource usage policy, the need in which follows from the results of analysis of material flows.

The boundaries of the region under study coincide, as a rule, with the boundaries of the corresponding catchment basin. The study includes, as a rule, the following stages:

1. Comprehensive inventory of the organized sources, including their arrangement, inputs and sinks, specific characteristics of the emissions.

2. Evaluation of unorganized sources of the substance under study, such as dumps, fertilized farmlands, transportation systems, etc.

3. Modeling of the atmospheric transport and transformation of the pollutant, including its gaseous and aerosol forms.

4. Drawing of the pollutant balance in the hydrographic grid of the region using, for example, hydrological model of sink.

Application of the concept

By now successful studies of the industrial metabolism dealt with nonvolatile pollutants, mostly compounds of the transition metals. This is explained only by difficulties in describing the processes of diffusion of gaseous emissions in the atmosphere and does not point to inapplicability of this approach to substances that have volatile forms. The selection of transition metals allowed the CIM authors to minimize the use of numerical models of diffusion and to demonstrate, in full measure, the capabilities of the approach, because all surface flows of metal compounds can be measured instrumentally.

The application of the CIM to studies of sulfur flows has some peculiarities. As sulfur has volatile forms, the processes of atmospheric transport should also be considered. Besides, sulfur compounds are emitted by soil and come from other regions due to remote transboundary transport. This undoubtedly makes the study of the IMS more complex as compared to the study of the transition elements. At the same time, some peculiarities facilitate the problem.

Thus, the main branches of industry that emit sulfur-containing compounds are power production and non-ferrous metallurgy. The content of sulfur in coal varies from 0.5 to 7%, in the natural gas it reaches 35% (Astrahan' gas field), and in ore it can be 53% as high. Because of the high value, the content of sulfur in raw materials is necessarily fixed. Therefore, the available data on the sulfur income into the industrial metabolism is far more voluminous than the data on the transition metals. Moreover, industrial sulfur flows far exceed flows in the consumption sector. Since the flows at the stage of consumption are much less organized than the industrial flows and often are difficult to be fixed, this fact may give a marked gain in the accuracy of final estimates.

Current capabilities of analysis and numerical models allow the program of IMS study to be completed successfully. Moreover, both the CIM and sulfur as an object for the study look a happy choice for the development of the general technique of constructing the detailed scheme of flows and balances of an arbitrary pollutant.

Program of the interdisciplinary study

In our opinion, it is interesting and important to study the IMS in Baikal region. This region is a reservation and it is included in the UNESCO's World Heritage List. It is natural that complex ecological studies are especially urgent just there. In addition, the Baikal region possesses some advantages as a territory for application of the CIM to the study of sulfur flows. This region is characterized by the absence of the branches of non-ferrous metallurgy using sulfur-containing raw materials. For this reason, industrial and municipal power production plants emit almost all sulfur-containing substances, and the problem of inventory of pollution sources is much easier. Another important peculiarity is the presence of a sole river run-off (Angara River). Hydrochemical analysis at different points along Angara allows us to monitor the water transport of pollutants, as well as the contributions of individual industrial centers. In particular, estimation of the role of Irkutsk–Cheremkhovo industrial region (ICIR) in the regional ecosystem has important applied outcomes. Another important factor is the availability of corresponding specialists and equipment in the Siberian Branch of the Russian Academy of Sciences (this will be demonstrated below).

According to CIM, we have constructed the general scheme of research into the IMS at the power-production use of coal (see Table). The scheme has united the largest parts of the research. At the same time, it does not deny the necessity to perform thematic studies, such as studies of fuel transport, dynamics of river run-off, promising treatment technologies, etc. The main parts of the research are the following:

1. "Coal" – the study of qualitative and quantitative characteristics of sulfur content in raw materials including the review of available fields and deposits, as well as estimation of losses at the stages of extraction and transportation;
2. "Burning and Gasification" – the study of the goal processes of fuel usage, including chemistry of transformation of sulfur compounds in various plants at different modes of their operation;
3. "Purification" – the study of the chemistry of processes at the stage of utilization of power-production wastes;
4. "Atmospheric Diffusion and Transformation" – two closely related but independent parts dealing with, respectively, physics and chemistry of sulfur-containing pollutants, including gaseous and suspended ones, in the atmosphere;
5. "System Effects" – the study of sulfur sinks into the environment needed to close the sulfur balance drawn in the previous parts.

The studies in each part involve both solution of particular applied problems and development of certain branches of basic research. To elucidate the range of related problems, as well as the content and adequate methods of the corresponding studies in each part, let us discuss them briefly.

Coal production and transportation

This section includes two components: (1) the study of coal mining fields and bassets in a region and (2) the analysis of information on coal production and transportation to the places, where it is consumed.

The study of coal mining fields assumes analyzing qualitatively and quantitatively the composition of sulfur-containing components and fragments of coal, as well as obtaining the mean characteristics for active and planned open casts. The functional composition for some coals of the Eastern Siberia has been determined at the Irkutsk State University (ISU).[7] It has been shown that the organic mass of coal contains 0.5–1.0% sulfur, and the rest part of sulfur is in the mineral part. The basic mass of organic sulfur is in heterocycles, and in young coal, it is on the surface in the form of thiolic groups (–SH). Unfortunately, the research group that has made this study has stopped the research.

An important characteristic is the fraction of sulfur that can transit into the gas phase while burnt. The results of the study conducted in the Melent'ev Institute of Power Systems showed that this fraction makes up about 50%. Determining the composition of sulfur-containing components of coal is the problem of instrumental research. Thus, the fraction of combustible sulfur can be determined by combining different methods of element analysis, for example, combustion method with X-ray fluorescent method.

Table. Interdisciplinary study of sulfur transformations at power-production use of coal

Research part (stage of coal use)	Coal	Burning, gasification	Purification	Atmospheric diffusion and transformation		Verification/ system effects
Object of the study	Form of sulfur in coal	Transformation of sulfur in the process of burning of organic matter	Forms of sulfur in power production wastes	Scientific aspects of diffusion are of independent interest; there are no specific problems connected with diffusion of sulfur compounds	Mechanisms of chemical and photochemical transformations	Distribution of sulfur between components of the environment
Research problem	Functional composition of sulfur-containing fragments	Mechanisms of transformation	Phase distribution of sulfur, including the case of particulate matter		1) Formation of sulfates; 2) Formation of aerosols, including homogeneous nucleation	Generalization and analysis of collected information
Adequate methods	Instrumental methods of analysis	Numerical kinetic and thermodynamic models; analytical methods	Numerical thermodynamic models, analytical methods	Within the framework of the project – engineering problem requiring only standard methods	Numerical kinetic simulation, experimental studies	Analysis of sulfur content in air and fallout
Associated applied problems	Power-production technological usage of coal, including treating technologies	Drawing the detailed sulfur balance, selection of equipment for long-range outlook		Control of air quality	Transborder pollution of air	Rational nature management, ecological expertise
Associated basic problems	Mechanisms of formation of shows of ore of some elements	Predicting development of power-production technologies, justifying the corresponding studies		Simulation of atmospheric dynamics	Climatic effects of the atmospheric cycle of sulfur	Study of the structure of power-production technologies
Institutes*	I, II	III, IV	III, IV	III, V	IV, V, III	III, II, VI

* Institutes of SB RAS that have experience in solution of listed or analogous problems: Irkutsk State University (I), Institute of Geochemistry (II), Melent'ev Institute of Power Systems (III), Institute of Chemical Kinetics and Combustion (IV), Institute of Computational Mathematics and Mathematical Geophysics (V), Limnological Institute (VI).

The content of sulfur in coal determines the possibility of its use in power production technologies. In coals burned in the Irkutsk Region and Buryatiya, it ranges from 0.3 to 3.5%. In addition, there exist proven coal deposits, the high sulfur content in which does not allow them to be used for power production without expensive preliminary desulfurization. In the Baikal region there are no industrial desulfurization technologies now. As the reserves of low-sulfur coal diminish and the total amount of consumed coal increases, development of high-sulfur coal resources becomes more urgent. Therefore, in this part of IMS studies, the choice of the coal processing technology is one of the related applied problems. The Melent'ev Institute of Power Systems has an experience in such studies.

As to inventory of coal deposits – from active and proven deposits to bassets – a significant experience has been gained at the Institute of Geochemistry SB RAS. Thus, the group headed by Yu.P. Troshin has conducted extensive field studies of sulfur content in both high- and low-quality coal and shale oil.

Another problem in this part of the research is analysis of statistical data on the amounts of coal production and transport flows of coal in the Baikal region. Such data are collected and compiled at the Melent'ev Institute of Power Systems. The information on the structure of fuel consumption in Irkutsk Region is available; thermal and electrical loads of many consumers are known.

Burning and processing

The object of study in this part is transformation of sulfur compounds in the process of fossil fuel burning, namely, the component composition and mechanisms of chemical transformations of sulfur-containing substances in a wide range of burning conditions. It is important to determine the distribution of sulfur among the combustion products, including different fractions of solid particles in emission, and to close the sulfur balances for individual power production technologies. The technologies to be considered include flame combustion, continuous and periodic laminar combustion, combustion in a boiling layer, gasification, and some others.

In addition to the instrumental methods, it is planned to use numerical models of chemical thermodynamics and chemical kinetics. An experience in this field has been gained at the Melent'ev Institute of Power Systems, in which the models of the extreme intermediate states have been developed. These models allow studying chemical processes far from their equilibrium states.[8] Some progress has already been achieved in the development of computational instruments for thermodynamic and kinetic modeling of the processes of fuel burning and processing[9,10]; model studies of some such processes can now be performed. In cooperation with the Research Institute of Biology at Irkutsk State University and Limnological Institute SB RAS, extensive field studies of the processes of formation and transformation of pollutants at active power production plants have been conducted.[11,12]

The experience in the development and study of the models of chemical kinetics for burning process has also been accumulated at the Institute of Chemical Kinetics and Combustion SB RAS. In this institute, numerical simulation of the kinetics of sulfur transformation at burning of hydrocarbon fuel has been done.

Drawing the detailed balance of sulfur is the solution of an important applied problem. Besides, the results obtained within the framework of this part of the research can be used for optimizing the operating modes of power production equipment and for selection of equipment to be used in the future.

Another one important part of this section is a comprehensive inventory of power sources on the territory considered. It is rather a laborious problem that requires cooperation among various institutions including local administrations and local bodies of the State Ecology Committee and the State Power Inspection. Some progress in inventory of power sources in Irkutsk Region has been achieved in the Melent'ev Institute of Power Systems.

Recycling of wastes

The study of forms of sulfur in wastes of the power production industry assumes the study of the phase distribution of sulfur, including the case of particulate matter with the allowance made for the actual size distribution of particles. As in the previous section, we can outline the treatment technologies to be considered. They include scrubbers, emulsifiers, and electric filters. It is important to study the efficiency of entrapping not only gaseous sulfur compounds, but also particles, because the sulfur content in the particulate matter is often high.

The most efficient methods for solution of this problem are instrumental studies of outgoing gases, volatile particles, and slag. The experience of such studies has been gained at the Melent'ev Institute of Power Systems and the Institute of Chemical Kinetics and Combustion, SB RAS. Along with the instrumental studies, numerical models of heterophase systems, in particular, thermodynamic models of solutions developed at the Melent'ev Institute of Power Systems, may prove to be efficient.[8,10]

As in the study of fuel burning, the related applied and basic problems in this part are prediction of development of power production technologies and optimization of the operating modes of the equipment used.

Atmospheric diffusion and transformation of emissions

When studying the ways, in which the man-caused sulfur comes into the environment, the study of physics and chemistry of sulfur-containing pollutants in the atmosphere is needed to close the ecoindustrial balance of sulfur in a region. At present, the most efficient approach in this field is numerical simulation.

Scientific aspects of the development of diffusion models are of independent interest and beyond the scope of IMS studies. Sulfur compounds have no specific peculiarities that could require modernization of the existing diffusion models. Therefore, within the framework of the research discussed, it seems to be worth using the approved models that are now used for solution of similar applied problems.[2,13]

The allowance for chemical and photochemical transformations important for atmospheric chemistry of sulfur compounds calls for invoking numerical models of chemical kinetics. The need in considering the gas-phase transformations when studying the industrial metabolism is a new subject and needs for the development of new methods for aggregating individual characteristics. Two most important problems in simulation of the transformation of sulfur-containing compounds are the evaluation of atmospheric formation of sulfates and revealing the role of heterogeneous processes, including homogeneous nucleation (aerosol generation from gases). The works on the development and study of photochemical models of the atmosphere were conducted at the Melent'ev Institute of Power Systems and the Institute of Chemical Kinetics and Combustion. Only the group headed by G.I. Skubnevskaya (Institute of Chemical Kinetics and Combustion) is experienced in the study of homogeneous nucleation of SO_2.

Participation of sulfur in chemistry of atmospheric aerosols includes numerous aspects having their own applied significance. Thus, the joint transport of gaseous sulfur compounds with dust affects the ways and the rate of removal of both of these pollutants.[14] The absence of acid rains with $pH < 4$ over Siberian territory does not agree with voluminous emissions of sulfur-containing pollutants. To explain this phenomenon, the hypothesis that an additional heterogeneous sink of these substances exists in Siberia was put forward at the Institute of Chemical Kinetics and Combustion. Model computations performed at the Melent'ev Institute of Power Systems are indicative of a more frequent occurrence of fogs and precipitation in the atmosphere gas-laden with sulfur oxides,[15] and this fact is confirmed by field observations. Approaches to estimation of the scales of secondary pollution were developed at the Melent'ev Institute.[16] The cooperation of the Melent'ev Institute with the Institute of Chemical Kinetics and Combustion and the Institute of Computational Mathematical and Mathematical Geophysics has been organized within the framework of the project under the Integration Grant from SB RAS.[17] The Institute of Computational

Mathematical and Mathematical Geophysics has reach experience in the development of regional diffusion models describing both the transportation and transformation of pollutants.

System effects

The stage of verification of the results and analysis of system effects allows checking the ecoindustrial balance of sulfur drawn at the previous stages and assumes studying the distribution of sulfur between environmental components. Two main problems are (1) the generalization of the quantitative data on man-caused sulfur incoming into the environment and (2) the development and analysis of the sought IMS scheme.

The former includes collecting and analyzing the data on the forms and content of sulfur in atmospheric precipitation and river waters. When studying natural media, it is often difficult to clearly separate the man-caused and natural sulfur. For such a separation, ingenious methods are usually needed, such as isotope analysis or tracer studies. The information on the technical capability of performing these works in Siberia is now unavailable. At the same time, some positive experience in this field has been gained in the Institute of Geochemistry. In addition, for a decade the Institute of Geochemistry monitored the total content of sulfur in different components of natural ecosystems of the Irkutsk Region: soil, water, parts of plants, leaves of different levels. The Institute of Geochemistry and the Limnological Institute have the experience in surveying the snow cover; Irkutsk State University performs extensive hydrochemical research. The study of waterways of sulfur migration can be based on the data of monitoring of the quality of waters in the biggest rivers of Baikal region (this monitoring is performed by local bodies of the State Ecology Committee).

To determine the sought scheme of anthropogenic flows of sulfur, it is necessary to solve the problem of correctly combining the characteristics. This problem has a methodical character and does not require experimental studies. At the same time, for this research to be accomplished as a whole, it is necessary to estimate the contribution of sulfur-containing oil products, in particular, black oil, to the regional anthropogenic cycle of sulfur. The more precise recording of these materials and their lower consumption (as compared to coal), as well as the higher degree of organization of black-oil-based power production plants could make this task accomplishable.

The most important result of this part of the project is identification of the emission sources that makes it possible revealing unaccounted sources and refining the characteristics of already known sources. The result of analysis of the complete scheme of industrial metabolism will be conclusions on the efficiency of the current practice in using sulfur-containing raw material resources.

Conclusion

The completion of this research program would provide for obtaining the results pertinent to both improvement of the policy of using fuel resources in the Baikal region and expansion of the scientific basis for the environmental protection activity. In particular, this would make it possible the evaluation of environmental protection strategies by means of analysis of material flows. The program as a whole is technically realizable and meets the Concept of Ecological Policy of Russia until 2010 that is now under development.[18]

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