Oil Shale, Vol. 13, No. 3
pp. 219-226
ISSN 0208-198X

https://doi.org/10.3176/oil.1996.3.06

THE ESTONIAN NATIONAL PROGRAM FOR SUSTAINABLE RESOURCE DEVELOPMENT AND ITS CONNECTION WITH TEACHING ABOUT FOSSIL FUELS IN CHEMISTRY COURSES

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The conception of sustainable resource development worked out under the initiative of the United Nations (UN) actualizes ideas for improving the health of people and the environment. The needs of people are to be addressed and, simultaneously, natural resources preserved. That is why ecological and economic expenses are to be integrated and flow sheets of industrial plants are to be reorganized in order to utilize natural resources in a rational way. The association of Estonia with the resolution of the UN Conference on Environmental Development held in Rio de Janeiro and the resolution of the Estonian Parliament concerning The National Program of Sustainable Development require changes in our lifestyle. Chemical education in schools has to support a change in the way of thinking and many concrete subjects can be connected with the problems of sustainable development [1].

This paper deals with some problems concerning fuel energetics and environmental pollution from the aspect of teaching chemistry.

Fuel Combustion and Fly Ash

The production of energy by fuel combustion is a process accompanied by the dispersion of chemical elements in the open air, the linking of elements into the biocycle and bioaccumulation in plants and animals.

Fuel combustion in a domestic furnace, boilerhouse, thermal power plant, etc. is one source of environmental pollution. Coal, oil shale, petroleum, natural gas, and wood (to a smaller extent) are used as fuels. Carbon and hydrogen present in fuels are important elements from the point of view of energy. Fuels also contain oxygen, sulfur, nitrogen and numerous macro- and microelements that are in the mineral components [2-5]. These mineral constituents are linked to atmospheric cycles through combustion processes.

Coals contain much more carbon as compared to oil shale. The latter is rich in oxygen and sulfur. Since the mineral fraction of oil shale is 1.5-2 times higher than in brown coal and coal, considerably more ash is formed when oil shale is burned. Ashes of various types of fuels contain quite different amounts of macro- and microelements. For example, oil shale fly ashes, as compared to coal fly ashes, have lower concentrations of all elements except Br, Rb and Cs. They contain 2-5 times less toxic elements (Se, Sb), radioactive elements (Th, U) and other rare elements [2].

Carbon and hydrogen are converted to CO_2, H_2O, and, in the case of oxygen deficiency, to CO. During incomplete burning smoke, soot (carbon), and a great number of organic hydrocarbons, including carcinogenic compounds (benzopyrene), are formed.

Large amounts of CO_2 in the atmosphere may lead to essential changes in the world climatic conditions due to the so-called "greenhouse effect". Workers of the Wuppertal Institute in Germany have shown that only 1.7 tons of CO_2 may be emitted into the air per person per year in Europe in order to avoid this effect. In Netherlands, this number is as high as 11 tons now, the European average being 7.3 tons. Consequently, the quantity of CO_2 emission in Europe has to be lowered by a factor of 4.

The elemental composition of the mineral component of ash reflects the composition of organisms, both terrestrial and aquatic in nature, from which in the course of millions of years fossil fuels were formed. Chemical elements which had accumulated in primitive organisms long ago have been transformed to fuel components by now. In addition, microelements could also have been accumulated in fuel beds by migration of groundwaters. About seventy chemical elements have been identified in fossil fuel mineral components and also in ash.

The accumulation of these elements within the plants or aquatic organisms had occurred before the formation of the corresponding coal or oil shale. Fly ash formed during fuel burning once again distributes these elements over a large area. Combustion residues remaining on the ground interact with soil, water and acid rain and become partially soluble. So the technogenic flow of many chemical elements is linked to atmospheric cycles.

The ash of fossil fuels contains virtually all known metals. Some of them are present even in a concentration high enough for their economically motivated commercial production. Such an option may be considered as one possibility for the implementation of a sustainable resource development program. Separation of metallic elements from ashes using a suitable process concurrently leads to the reduction of environmental pollution. For example, in some ashes the concentrations of vanadium, strontium, zinc and germanium may range from grams to almost one kilogram per ton of ash. Vanadium is even produced from petroleum ash. Peat ash is relatively rich in uranium, cobalt, copper, nickel, zinc, vanadium and lead. Besides other microelements Estonian oil shale ash contains such exotic metals as gold, silver, uranium, hafnium, zirconium, niobium, tantalum, etc. [2-4, 7].

Dictyonema argillite in Maardu deposits contains uranium, molybdenum, and vanadium in amounts ~40, ~80, and ~470 g/t, respectively [7, 8].

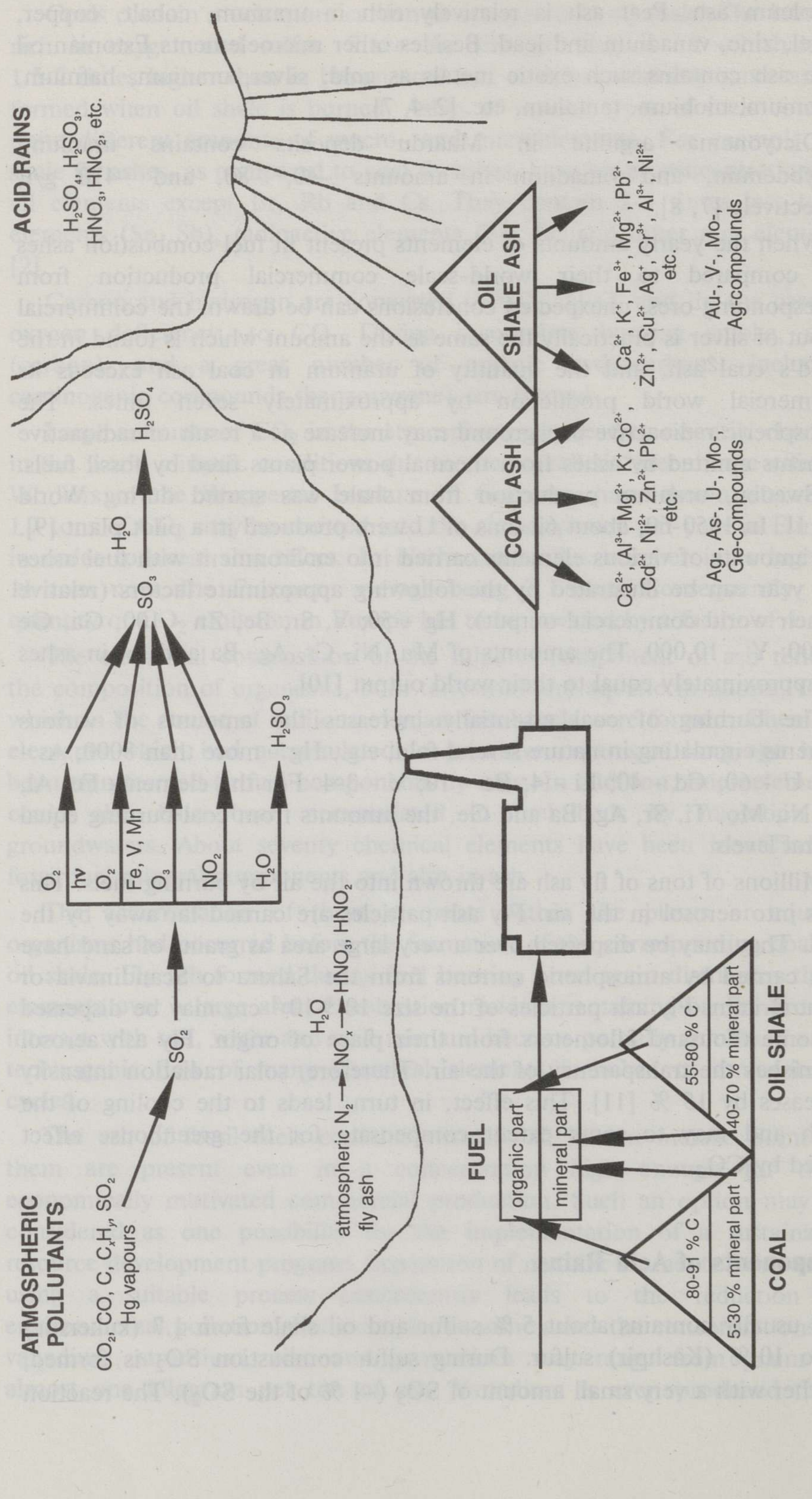
When the yearly amounts of elements present in fuel combustion ashes are compared to their world-scale commercial production from corresponding ores, unexpected conclusions can be drawn: the commercial output of silver is practically the same as the amount which is found in the world's coal ash, and the quantity of uranium in coal ash exceeds its commercial world production by approximately seven times. The atmospheric radioactive background may increase as a result of radioactive elements emitted by ashes from thermal power plants fired by fossil fuels. In Sweden, uranium production from shale was started during World War II. In 1950-60, about 62 tons of U were produced in a pilot plant [9]. The amounts of various elements carried into environment with fuel ashes in a year can be illustrated by the following approximate factors (relative to their world commercial output): Hg - 50; V, Sr, Be, Zn - 100; Ga, Ge - 1000; Y - 10,000. The amounts of Mn, Ni, Cr, Ag, Ba and Sn in ashes are approximately equal to their world output [10].

The burning of coal essentially increases the amounts of various elements circulating in nature several fold, e.g., Hg - more than 8000; As - 125; U - 60; Cd - 40; Li - 4; Be - 10; V - 3-4. For the elements Fe, Al, Co, Ni, Mo, Ti, Sr, Ag, Ba and Ge, the amounts from coal burning equal natural levels.

Millions of tons of fly ash are thrown into the air by burning fuels. This turns into aerosol in the air. Fly ash particles are carried far away by the wind. They may be dispersed over a very large area as grains of sand have been carried by atmospheric currents from the Sahara to Scandinavia or Great Britain. Fly ash particles of the size 10^{-4}-10^{-3} cm may be dispersed for some thousand kilometers from their place of origin. Fly ash aerosol diminishes the transparency of the air. Therefore, solar radiation intensity decreases by 15 % [11]. This effect, in turn, leads to the cooling of the Earth and may to some extent compensate for the greenhouse effect caused by CO_2.

Components of Acid Rains

Coal usually contains about 5 % sulfur and oil shale from 1.7 (kukersite) up to 10 % (Kashpir) sulfur. During sulfur combustion SO_2 is formed, together with a very small amount of SO_3 (~1 % of the SO_2). The reaction



Schematic representation for the migration of chemical elements in the environment of SO_2 with rainwater leads to the formation of sulfurous acid. During fuel burning NO is also formed with 30 % of it resulting from nitrogen present in the fuel and the rest from the reaction of oxygen and nitrogen in the air due to the high temperature of fuel combustion [11]. NO oxidizes to NO_2 in the air. It reacts with rainwater to form nitric acid along with some nitrous acid.

SO_2 oxidizes to SO_3 via several parallel reactions (see the equations in Figure). The molecules of SO_2 and/or O_2 may become excited under the influence of ultraviolet radiation. Direct photochemical reaction of excited molecules leads to the formation of SO_3. In fact, the process of catalytic oxidation of SO_2 is used in commercial-scale production of SO_3. Such a process may also partly occur with burning in the air by catalytic action of elements (Fe, V, Mn) present in fuel ash particles.

Ozone or NO_2 present in air also oxidizes sulfur dioxide. These four different reactions for the production of SO_3 all run parallel in nature and, depending on the conditions, one of them could be preferred. The reaction between SO_3 and rainwater yields sulfuric acid. SO_2 may be adsorbed on iron objects and under the action of air oxygen oxidizes it to ferrous sulfate. SO_2 may be adsorbed on aluminum surfaces, too. The reaction between adsorbed SO_2, air oxygen, water vapour and the film of aluminum oxide on a surface yields aluminum sulfate. Since these sulfates are soluble in water, they are washed away from the surface by rain and the corrosion of a new layer starts again. Acidic components of acid rain react in the air with microscopic particles of fly ash. Therefore the aerosol particles of precipitants having a sulfate-sulfite and/or nitrate-nitrite character are formed.

Sulfur compounds are the main components of acid rain, the amount of HNO_3 and HNO_2 are essentially smaller. Other acidic compounds like H_2S, HCl, HF, etc. are also present in the air, but their concentration is also notably smaller. Acid rains cause the corrosion of metals and acidification of fresh water and soil. They increase the solubility of the mineral part of soil, rocks and building materials and link their constituents to atmospheric circulation.

Dispersion of Microelements in the Environment

Depending on the height of the chimney and on climatic conditions, ash particles, fly ash, mercury vapours, various hydrocarbons and carbon compounds, formed during fuel burning, could be dispersed over a rather large area where they slowly fall down on the soil and water bodies, thus getting into atmospheric cycles. Ash from a combustion unit sent to ash dumps will come in contact with the surrounding soil, surface water and falling acid rains. Strong and oxidizing acids of acid rains dissolve macro-, micro- and ultramicroelements of the ash. The soluble compounds can migrate in soil and may be accumulated by plants. Dissolved compounds are carried by surface water into fresh water, from there into animals and human organisms. Man picks up these elements from plants and vegetables. The main danger is that acid rains may convert toxic elements of coal ash into soluble ones and link them to life cycles and food chains.

The content of Hg, Pb, Cd, Zn, Cu, As, Sb, and Se in the atmosphere essentially exceeds the corresponding Clark values for the earth's crust. The comparative analysis of two Greenland ice samples has demonstrated that the content of Hg and Pb in the young ice is, respectively, two and two hundred times as high as in the old ice formed before 1904. Nine kilogram Zn and five kilogram Pb precipitates on one km^2 of ground per year, as reported by Beauford and Barber [12]. Fly ashes from coal burning contain more metallic elements (except V, Mo and Hg) than petroleum fly ashes. The fraction of the elements Cd, Sc, As, Cr, Cu in the world's oceans is about $(1\text{-}8) \cdot 10^{-4}$, that of Cu $\sim 9 \cdot 10^{-3}$, Hg $\sim 2 \cdot 10^{-2}$, and Pb ~1.2 [13, 14]. The atmosphere becomes enriched with these elements mainly as a result of atmophilic elements.

The circulation of pollutants formed during solid fuel combustion is illustrated in Figure. Carbon yields CO_2, CO, various hydrocarbons and soot. The combustion of sulfur compounds leads to the formation of SO_2, the precursor for SO_3 and H_2SO_4. The reaction of SO_3 with rainwater gives microscopic drops of sulfuric acid. Nitric and nitrous acid are the products of nitrogen oxidation. About 90 % of the mercury present in a fossil fuel gets into the atmosphere in its vapour state [9].

The mineral component of fuel becomes ash. Some part of it gets into the atmosphere as fly ash, but most of it is taken to ash dumps [3-5]. In Figure, the elemental composition of coal and oil shale ashes is presented [2, 6, 15]. As stated earlier, acid rains convert the water-soluble elements of ash and they begin their circulation in nature.

Heavy metals are characterized by their ability to concentrate in living organisms. In water bodies, the content of elements may surpass their concentration in the ocean by a factor of ten, or even as much as a thousand, times. Previously, only 8-10 elements were considered biometals, now almost all of them, even including Hg, Pb, Cd, and As, are included. The concentration is the only limiting factor. The ability of metal ions to block the enzymatic system, mainly via -SH groups, is considered to cause their toxicity. This ability is in direct correlation with the solubility of metal sulfides and, to some extent, with toxicity. Toxicity of an element depends on the form of its occurrence. Hg^{2+} is toxic for various organs and to some extent for the brain. Hg^{2+} dissolves in adipose tissue, accumulates in the brain and induces specific symptoms (Minamata disease).

Conclusion

Metallic elements get into the environment mostly with fuel combustion ashes. According to various prognoses, fossil fuel resources will last for a thousand years. This means that more and more metallic compounds are thrown into the environment. Dispersion of metals in the air, water bodies and soil is continuously increasing. Finally, they reach the food chain and to the human body. As a result, toxications, illnesses, and inadvisable dislocations in organic life may occur. The trend to use ash as a raw material for metal production is considered to have some prospective economically attractive application. This would be one possible way of sustainable resource development to avoid the increase of environmental pollution and increase production of the corresponding metals.

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Presented by J. Kann
Received May 17, 1996