

RADIATION AND ENVIRONMENT

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Use of Radiation Technology in environmental protection processes has been studied at various scientific centers all over the world [1-4].

At the National Academy of Sciences of Azerbaijan Republic radiation researches were conducted in the following areas:

1. RADIATION CLEANING OF SMOKE GASES

1 a. *Electron beam treatment of smoke gases*

The radiation-chemical yields of SO₂-removal have been defined for gas mixtures of air-H₂O-SO₂-CO-C_xH_y-H₂-NO_x under fast electron irradiation. For this purpose the kinetics of pollutant molecule destruction at various starting amounts has been studied. A kinetic diagram of about 100 of the most prominent reactions was analyzed by means of computer simulations.

Kinetic investigations of radiation conversion of the noxious components of exhaust gases have been performed since the 1970s (Masua *et al.*, 1981; Bugaenko *et al.*, 1981). Studies have shown the advantage of the radiation-chemical method of gas purification to eliminate noxious components if their concentration does not exceed 0.2%. However, the problems that deal with the polycomponentity of the exhaust gases have been partially solved: only the influence of humidity and content of O₂ were considered. We have studied the SO₂-removal process in the presence of some other possible accompanying molecules via electron-beam treatment of the exhaust gases. In the present paper we submit the obtained results.

Three series of experiments were conducted with various sets of components of gas mixtures:

1. Air-SO₂-H₂-CO-CH₄-H₂O
2. Air-SO₂-H₂-CO-CH₄-H₂O-C₂H₄
3. Air-SO₂-H₂-CO-CH₄-H₂O-NO_x

In all cases the consumption kinetics of the pollutant molecules was studied. Some typical conditions for each of the experimental series are given in Table 1.

Table 1. Exemplary Initial compositions (in %) of experimental series

Series #	SO ₂	CO	CH ₄	H ₂	C ₂ H ₄	NO ₂	NO
1	0.23	0.23	0.16	0.04	-	-	-
2	0.28	1.70	0.90	1.22	0.11	-	-
3	0.33	2.15	1.11	0.84	-	0.02	0.004

The results of the 1st series indicate that the following order of consumption takes place: SO₂ > CO > CH₄ > H₂. Consumption of CO, CH₄ and H₂ molecules occurs only after the

removal of SO₂ from the irradiated gas mixture. Radiation-chemical yield of SO₂-removal, G (-SO₂) is equal to 7.5. In the studied range of absorbed doses, no change in hydrogen concentration was detected.

Radiation-chemical yields of the consumption of pollutant molecules by the e-beam treatment of smoke gases in various relations of M/SO₂ concentrations (where M= H₂ +CO +CH₄) are given in Table 2.

The results of the 2nd series show a strong effect of ethylene molecules on the consumption rate of SO₂-removal. Radiation-chemical yields for C₂H₄ and SO₂-removal processes are equal to 5.1 and 3.3, respectively (for the given example).

Table 2. Values of G for various M/SO₂

M/SO ₂	G molec/100 ev				G (-M)
	SO ₂	H ₂	CO	CH ₄	
0.04	7	0	0.02	-	0.02
0.12	7	0.003	0.06	0.05	0.113
0.13	7	0.002	0.05	0.03	0.082
1.86	7	0	0.21	0.05	0.26
17.7	4.5	0.13	0.27	0.27	0.67
18.7	1.17	0.05	0.42	0.25	0.72
27.5	0.16	0.11	0.33	0.20	0.64

Radiation-chemical yields of NO₂ and SO₂-removal processes in the 3rd series are found to be equal to 0.14 and 1.0, respectively (for the given example).

In all cases, regions of relative chemical stability are observed in CO molecule consumption curves. The CO molecules are consumed after substantial removal of SO₂, NO₂ and C₂H₄.

A computer simulation was performed to examine homogeneous gas phase reactions in electron beam radiolysis of air-H₂-SO₂-H₂-CO-CH₄-NO-NO₂ mixtures. We used a reaction set with some 100 measured rate constants taken from the literature (Person and Ham, 1988) to fit the data obtained. Kinetic calculations have been executed by means of a variable order multi step method for stiff differential equations (Gear, 1971).

As distinct from the kinetic model of Person (1988), we used additional elementary reactions of active particles with accompanying molecules of CH₄, H₂ and CO with values of G given in Table 3.

The dominant removal mechanisms have been determined by including reactions of active species (N₂⁺, N⁺, N, N(P), O₂⁺, O, e⁻, OH, H, O, HO₂, H₃O⁺, NO₂⁻, O₂⁻), stable products (O₃, NO₂, NO, HNO₃, SO₃) and main components of our gas phase system (SO₂, CO, H₂, NO_y, H₂, CH₄).

The simulation results support the following estimations:

- SO₂-removal is due to reactions with OH-radicals;
- CO-removal is due to reactions with HO₂- and OH-radicals;
- H₂- and CH₄- removal is due to ion-molecule reactions.

1 b. E-beam Treatment of Natural Gases

Non-traditional methods based on e-beam application may be useful for thin cleaning of natural gas having low concentration (<1%) of H₂S.

Hydrogen Sulphide is always present in natural gas and its concentration may reach 20-25%. There are many cleaning processes for natural gas with high concentrations of H₂S. But thin cleaning of natural gas with low concentrations of H₂S is performed at present.

The aim of present work is the experimental and theoretical study of H₂S-destruction processes in CH₄-H₂S gas mixtures via e-beam treatment.

The influence of initial H₂S concentration, temperature and applied dose rate on Hydrogen Sulphide removal yields has been studied. Radiation-chemical yields of H₂S-removal for various concentrations of H₂S and dose rates are given in Table 3.

Table 3. Values of G (-CH₄) at various H₂S concentrations and dose rates (D)

H ₂ S (%)	1	2	5	10
7.5 Gy/s	5,6±0,7	5,0±0,5	7,0±0,7	7,1±1,7
450 Gy/s	5,0±0,8	4,5±1,3	5,0±0,7	10±1,0

As seen from the data for G (-H₂S), G increases with rising initial H₂S-concentrations but slightly diminishes with increasing dose rate. This indicates that e-treatment is efficient for low concentrations of H₂S.

Rate of H₂S-removal increases with rising temperature from 6 to 50 molecules per 100 eV of absorbed energy for a temperature rise from 423 to 773 K.

Very reactive free radicals, ions and excited-state molecules can, under the force of fast electrons, react with small components and reduce the latter's content. In the case of natural gas, such a component is Hydrogen Sulphide.

The productivity of purification can be calculated by the expression:

$$Q = 2.6 \cdot 10^{-4} G \cdot M \cdot P \cdot \eta \text{ (m}^3\text{/h)}.$$

For G = 5 molec/eV, in a plant with P = 100 kW: Q = 4 m³/h, which is equivalent to the purification of 1000 m³ natural gas containing 0.4% H₂S.

2. RADIATION-THERMAL DESULPHURIZATION OF COALS [8-9]

The desulphurization of solid fuels is one of the main ways of decreasing the environmental impact of their combustion products.

The radiation-thermal desulphurization of Turkish and Russian lignites in the presence of methane under accelerated electrons at a dose rate P = 350 Gy/s in the temperature interval T = 200-500 °C, with an absorbed dose up to 60 kGy were studied. It has been established that, under the more favorable conditions (T = 400-450 °C, D > 60 kGy) about 80% of the sulphur is removed from the samples; and in the solid product sulphur is decreased from 4% down to 0.8-1.1%. Under these conditions, selectivity of desulphurization is s = 2.6-3.8 and energy consumption of sulphur removal is E = 0.5-0.6 kWh/kg. The selective activation of sulphur bounds under radiation is connected with high density of electrons around the sulphur atoms.

3. DETERMINING THE RADIOLOGICAL SITUATION IN AZERBAIJAN [10-12]

An analysis of all radiation sources in Azerbaijan is considered. It is mentioned that, in our country, the radiation situation is mainly conditioned by natural and technogenic origins. Uncontrollable emission of natural radionuclides and the radioactive gas radon-222 into the biosphere is the cause for the noticeable radiation level. It is noteworthy that the Azerbaijan Republic is on a radon-bearing tectonic zone.

Oil production is one of the key sources of technogenic radioactive pollution both onshore and offshore. But it should be taken into account that the concentration of natural uranium (U) in the Caspian Sea is much higher than in other seas. In connection with the new deep-water field development in the Contract area the study of these nuclides become an urgent issue.

On the order of the State Oil Company of Azerbaijan Republic, the Radiation Situation was studied and assessed in the oldest oil production area of the Absheron Peninsula.

Given the fact that the occurrence of radiation through natural and technogenic sources is a pressing issue for all countries participating in the Eurasia Conference, it is necessary to develop an international program of joint activity on minimizing the consequential impact of the natural and technogenic radioactive pollution upon the environment.

Economic development of Azerbaijan directly depends on resource management, particularly in the energy and raw-material sectors. Today, these sectors are assuming the responsibility for the environmental pollution of the past. The problems in environmental pollution would sharply increase if we did not pay maximum attention to the present ecological situation, its management and to the safekeeping of present natural resources. The existing normative acts do not have much effect because of the restricted possibilities and facilities. Fundamental problems continue to exist and become deeper, and the reason is due to the cut in ecological spending, lack of competent specialists and an absence of basic knowledge. A steadfast increase in the anthropogenic impact on the environment, combined with local and global changes in climate, together with the change in the water conditions of the Caspian Sea, negatively affect the environmental situation in Azerbaijan and could cause irreversible changes, such as spontaneously arising emergency situations and various types of disasters.

The real sources of radioactive wastes in our Republic are enterprises and organizations related with oil extraction. As basic knowledge in radiochemistry and radiology was not very high during the early years of oil extraction, wide-spread soil pollution is caused on the Apsheron Peninsula. Technical processes in oil extracting, petrochemical and oil refinery industries have not been studied with radioecology in mind.

Serious problems due to radioactive area pollution occurred, especially in the Apsheron region. For example, gamma logging of oil wells have shown different levels of radioactive anomalies, with detected activities of 100 to 1000 $\mu\text{R}/\text{hour}$.

The result of analysis of single core samples showed high content of natural radionuclides (uranium, radium, thorium, potassium) in the soil. Actually, these

places have become biologically dead zones. Technogenic pollution of these areas causes formation of new diseases, deflection in the physical evolution of children, and an increase in the number of associated diseases. The Apsheron Peninsula could be the best example to demonstrate the direct link between the environmental situation and people's health. More than three hundred thousand people in Baku (1/6 of its population) live in industrial zones: territories of oil-gas extraction, petrochemical and oil refinery enterprises, and neighboring areas.

After determination and recording of the dose levels at all locations, soil and water samples from the most contaminated areas were taken. The selected samples were analyzed in a laboratory on a gamma spectrometer with the intent to determine the qualitative and quantitative structure of the radionuclides in the soil and produced water.

The soil samples were tested for activity of ^{238}U , ^{232}Th and ^{40}K . It is established that, in a number of items of the Apsheron Peninsula, the levels of concentration of ^{238}U , ^{232}Th in the soil was up to 400 times greater than the control sample. The reason for these elevated results is due directly to past oil activities in the area from which the samples were taken. These readings are, unfortunately, typical for soils that have been subjected to extracted oil fluids.

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