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Abstract

Full Text

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The Action of γ-Radiation on Coals in an Aqueous Medium and in a Carbon Tetrachloride Medium

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From studies on the radiolysis of water ([1,2]) it is known that, under the action of ionizing radiation, ions and free radicals are formed in water in the presence of atmospheric oxygen; these are capable of causing oxidation or reduction of substances added to the irradiated aqueous system. It could be expected that γ-irradiation of coals in an aqueous medium would lead to chemical changes in the most reactive part of the organic matter of the coals and to the transfer of the germanium contained in the coal into the aqueous medium. The use of oxidative processes occurring during irradiation in an aqueous medium is of interest not only for the extraction of germanium, but also for the study and identification of the products of radiolytic oxidation of coals.

Irradiation of coals in an aqueous medium was carried out by us in glass ampoules at a dose rate of 200 r/sec and an integral dose of 10^8 r. The source of γ-radiation was Co^{60}.

For the investigation we took four grades of coals: brown coal from the Moscow-region basin and hard coals from the Donets basin—steam-fat (PZh), gas (G), and coke (K). In the last two grades of coal the germanium content is insignificant.

After irradiation, the coal was filtered off from the water, and the content of germanium in the aqueous medium was analyzed. Germanium was determined by the method developed by the Ukrainian Institute of Rare Metals. The results of the determinations are given in Table 1.

Table 1

	Taken, g coal	Taken, g water	Germanium yield γ per 1 g coal	Germanium yield % of content in coal
Brown Moscow-region coal	5	25	2.26	41.0
Coal PZh	3	21	1.6	50.2
Coal G	5	25	0.18	5.8
Coal K	5	20	0.16	13.3

The highest yield of germanium upon irradiation of coals in an aqueous medium was obtained from coal of grade PZh (50.2%) and from brown coal (41.0%).

For further investigation of the possibility of increasing the yield of germanium from coals, we used the chlorination method, which is the most important, not only theoretically but also practically, among a number of methods for extracting rare and dispersed elements from minerals, polymetallic ores ([3]), and coal ([4,5]).

In chlorination, elemental chlorine is used chiefly. The use of such strongly chlorinating chlorine compounds as sulfur monochloride, carbon tetrachloride, etc., can significantly broaden the possibilities of this method.

In many works on radiation chemistry ([6–8]) it is indicated that, when carbon tetrachloride is acted upon by γ-radiation, the principal prod-

of the radiolysis is free chlorine. This phenomenon was used in our work on extracting germanium from coals in carbon tetrachloride. Coal samples in carbon tetrachloride were placed in molybdenum-glass ampoules and sealed in an air atmosphere. Irradiation was carried out at three different integral doses: 10^6, 10^7, and 10^8 r. The dose rate in all cases was 200 r/sec.

After irradiation the ampoules were opened, the coal was separated from the liquid phase, and the content of germanium was analyzed both in the liquid phase and in the coal, in order to obtain a complete germanium balance.

The transfer of germanium into the liquid phase in coals of grades G and K at integral irradiation doses of 10^6 and 10^7 r was insignificant. At an integral dose of 10^8, the yield of germanium from coking coal was 13%, and from gas coal only 5.6% of the total content of the element in the coal.

Higher indices of germanium extraction, reaching 53%, were obtained upon irradiation of coal of grade PZh. Table 2 gives the results of experiments on irradiation of dried coal of grade PZh in dry carbon tetrachloride.

Table 2

Coal	Integral irradiation dose, r	Germanium yield, γ per 1 g of coal	Germanium yield, % of content in coal
Steam-fat coal of the Donets Basin	10^6	0.24	7.5
Steam-fat coal of the Donets Basin	10^7	0.97	30.0
Steam-fat coal of the Donets Basin	10^8	1.70	53.0

Coal	Integral irradiation dose, r	Germanium yield, γ per 1 g of coal	Germanium yield, % of content in coal
Brown coal near Moscow	10^6	0.2	2.9
Brown coal near Moscow	10^7	1.2	17.4
Brown coal near Moscow	10^8	6.9	100.0

Complete extraction of germanium was obtained by us upon irradiation of dried brown coal in dry carbon tetrachloride (see Table 2).

At an integral dose of 10^8 r, all the germanium contained in the coal passes into the liquid phase, from which it can be extracted by existing methods.

The degree of extraction of germanium from coal depends not only on the irradiation dose but also on the presence of moisture in the system. If irradiation of dried brown coal is carried out in undried carbon tetrachloride, the yield of germanium decreases to 40.3%. Upon irradiation of moist brown coal (14% moisture) in undried carbon tetrachloride at the same integral dose, the yield of germanium was only 9.3%. Similar results were obtained upon irradiation of coal of grade PZh. Upon irradiation of dried PZh coal in dry carbon tetrachloride, the yield of germanium was 53%, while in undried carbon tetrachloride the yield of germanium decreased to 12.4%. Upon irradiation of undried PZh coal with the same integral dose (10^8 r) in moist carbon tetrachloride, the yield of germanium was only 6% of the total content.

Along with the use of radiolysis of carbon tetrachloride for extracting germanium from coals, we observed an increase in the solubility of coals in carbon tetrachloride after γ-irradiation, which undoubtedly is of great interest from the standpoint of the chemical processing of coals.

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REFERENCES CITED

1. P. I. Dolin, *Collection of Works on Radiation Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1955, pp. 7, 24.

2. V. I. Veselovskii, Ts. I. Zalkin, N. B. Miller, N. A. Aladzhalova, ibid., p. 36.

3. A. A. Cherepnev, *Problems of Chlorination of Rare Elements*, 1940.

4. B. I. Losev, A. N. Mel' nikova, I. E. El' piner, Publishing House of the Academy of Sciences of the USSR, OTN, No. 9 (1957).

5. B. I. Losev, I. E. El' piner, A. N. Mel' nikova, DAN, **114**, No. 2, 372 (1957).

6. A. V. Zimin, Z. S. Egorova, *Collection of Works on Radiation Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 241.

7. J. W. Schulte, J. F. Suttle, R. J. Wilhelm, *J. Am. Chem. Soc.*, **75**, 2222 (1953).

8. P. Günther, H. D. Horst, G. Cronheim, *Zs. Elektrochem.*, **34**, 616 (1928).

Note: Figure translations are in progress. See original paper for figures.