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Abstract

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KINETICS OF THE OXIDATION OF COALS BY NITRIC ACID

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The oxidation of mineral coals in an aqueous medium is of considerable interest, since it often occurs in deposits and during storage of mined coal. Its study may also be useful for characterizing the relative chemical activity of different coals, in particular their tendency toward spontaneous combustion. The latter is especially important because existing methods are not entirely satisfactory. For these reasons, under the direction of A. A. Skochinskii, the work described below was carried out at the Institute of Mining of the Academy of Sciences of the USSR. In this work nitric acid was used as the oxidizing agent. Its reduction by coal is expressed by the stoichiometric equation

$$2HNO_3 = 3(O) + 2NO + H_2O.$$

The reduction of nitric acid proceeds through several successive stages. The intermediate reduction products have a considerably greater oxidizing power than nitric acid itself. This is unfavorable for using it as a reagent to characterize the chemical activity of different coals, since a strong oxidizing agent reacts almost equally readily with different substances, and therefore the detection of differences in the oxidizability of the latter is difficult.

Several works on the oxidation of coals by nitric acid have been described in the literature. H. H. Lowry (^{1}), oxidizing various coals with 6.3% nitric acid, found that sometimes oxidation does not begin immediately after the coal is mixed with the acid, but after a certain time has elapsed. This phenomenon was studied in greater detail by G. L. Stadnikov (^{2}).

The apparatus in which we carried out the experiments consisted of a vessel with a capacity of about 200 ml. The vessel was closed with a rubber stopper bearing a gas-outlet tube, the end of which was led under a graduated glass cylinder for measuring the volume of gas evolved. The experiments were carried out with Donets coals of homogeneous petrographic structure.

In the general case, the process begins with a latent period, during which slight gas evolution occurs. Then the rate of gas evolution increases sharply and

Fig. 1. Dependence of the oxidation rate of different coals on time

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quickly reaches a maximum, after which it decreases. Figure 1 shows typical curves of the oxidation rate of different coals by 5% nitric acid.

The experiments of this series showed the following:

1. No direct relationship is observed between the duration of the latent period, as well as the magnitude of the maximum oxidation rate, and the degree of metamorphism of the coal.
2. On average, the longer the latent period, the lower the rate of gas evolution after its end. This undoubtedly corresponds to lower chemical activity of the coal.
3. The greater the maximum oxidation rate, the more rapidly it subsequently slows down.

During the latent period, even with the aid of such a sensitive indicator as the ignition temperature of coal (^{4}), it is impossible to detect an increase in the degree of oxidation of the coal, while in the acid solution the content of substances titratable with permanganate (mainly lower nitrogen oxides) is a very small value—on the order of 0.05 meq/l. Immediately after the onset of rapid gas evolution, the degree of oxidation of the coal increases sharply, and the content of titratable substances in the solution increases tenfold. Subsequently, the degree of oxidation of the coal and the concentration of titratable substances increase slowly. Humic acids, extracted with an aqueous alkali solution, appear only after prolonged oxidation.

Fig. 1. Dependence of the oxidation rate of different coals on time

From these experiments it follows that during the latent period the chemical interaction in the system proceeds very slowly. Only after hidden preparation during the latent period does rapid oxidation of the coal begin.

The Donetsk coal of grade PZh with which the experiments were carried out had an oxidizability index $\Delta T_0 = 45^{\circ}$, i.e., it should be considered readily oxidizable. However, when it is oxidized with 5% nitric acid, a latent period of more than 50 hours is observed, and the oxidizability index does not change. This means that during the latent period activation of the coal does not occur. Therefore, the existence of a latent period in the development of the process and the subsequent sharp increase in the rate of the latter must be explained by activation of the oxidizing agent. It is most natural to suppose that it is the presence of intermediate products that activates it. To test this assumption, a series of experiments was carried out in which sodium nitrite was added to 5% nitric acid, i.e., lower nitrogen oxides were introduced into the solution from the very beginning. It is seen from Fig. 2 that, as the addition of sodium nitrite is

Figure 2

Figure 2: Figure 2

increased, the latent period is shortened and, at the same time, the maximum rate of gas evolution increases. The total amount of gas evolved in 50 hours, however, does not increase noticeably. At a nitrite concentration above 0.05%, the latent period disappears completely. It follows from this that the accumulation of a very small amount of active intermediate products is sufficient for the hidden preparation to pass into a rapid reaction.

Next, instead of nitric acid, a mixture of 5% sulfuric acid with 1% sodium nitrite was taken. The gas-evolution rate curve obtained was the same as when 1% nitrite was added to nitric acid, i.e., without a latent period and with the same high maximum. It follows from this that the oxidation of coal proceeds mainly at the expense of the lower nitrogen oxides, while nitric acid serves only as the source and reservoir of these oxides. It should be noted,

that in our experiments thermal self-acceleration could not occur, and the process may be regarded as isothermal.

The process proceeds autocatalytically, and at first its acceleration is determined by the course of the function $e^{\varphi\tau}$, where φ is the rate constant for chain branching and τ is time. However, inhibition soon begins, and the rate, having reached a maximum value, decreases. This retardation cannot be explained by a decrease in the concentration of nitric acid, which was taken in large excess.

Fig. 2. Disappearance of the latent period as a result of adding sodium nitrite: *a*–0%; *b*–0.01%; *v*–0.025%; *g*–0.05%; *d*–1%.

To elucidate the retarding mechanism, it is important that the greater the maximum oxidation rate, the faster it slows down afterward. The total amount of gas evolved does not depend on the height of the maximum and varies within certain limits. Evidently, before the process has slowed to an almost constant rate, the same amount of substance must react. This can be most simply explained by the fact that a layer of oxidation products accumulates on the reacting surface of the coal, hindering the inflow of oxidant. The formation of analogous layers that retard the process was observed in the study of the kinetics of low-temperature oxidation of coals by gaseous oxygen ([3]).

Since the reaction rate is very high, all the inflowing oxidant is rapidly consumed. Therefore the rate of chemical transformation is equal to the rate of inflow of the oxidant:

$$kC = D(C_0 - C); \tag{1}$$

C_0 is the concentration of oxidant in the bulk of the solution, C is its concentration at the reacting surface of the coal, and D is the coefficient of its inflow through the oxidized layer (“effective diffusion coefficient”).

Hence

$$C = C_0 \frac{D}{D+k}. \tag{2}$$

From equation (1) it is seen that the lower the permeability of the oxidized retarding layer and the higher the reaction rate, the lower the concentration of oxidant at the reacting surface.

For the rate of gas evolution we obtain

$$\frac{d[\mathrm{NO}]}{d\tau} = kC = kC_0 \frac{D}{D+k} = C_0 \frac{1}{\dfrac{1}{k} + \dfrac{1}{D}}. \tag{3}$$

The quantity $\frac{1}{D}$ has the meaning of the resistance offered by the oxidized layer to the influx of oxidant.

Since the coefficient k should not change appreciably with time, because it pertains mainly to the reaction of fresh coal, which does not change with time, the decrease in the rate of the process depends chiefly on the decrease in the permeability D.

It is natural to assume that the rate of influx of oxidant to the reacting surface of the coal is inversely proportional to the resistance of the oxidized layer $\left(V = \frac{1}{D}\right)$, while the rate of increase of this resistance is proportional to the amount Q of substance that has flowed in and reacted:

$$\frac{dV}{d\tau} = \frac{Q}{V}. \tag{4}$$

If, over a short interval of time, Q is regarded as constant, integration gives

$$V = \sqrt{2Q\tau}, \tag{5}$$

i.e., the retarding resistance of the oxidized layer is proportional to the square root of time, while the amount of oxidant flowing in (and, consequently, the rate of chemical transformation) is inversely proportional to V, i.e., to the square root of time:

$$kC = \frac{d[\mathrm{NO}]}{d\tau} = B\tau^{-1/2}.$$

The results obtained provide material for developing a theory of coal storage and of the influence of atmospheric nitrogen oxides. These results also show that nitric acid is unsuitable for assessing the tendency of coals to spontaneous combustion.

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