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Kinetics of Volatile Matter Release from Pennsylvania Anthracites

E. T. NELSON, JEAN WORRALL, and P. L. WALKER, JR.

Fuel Technology Department, The Pennsylvania State University, University Park, Pa.

Experimental results obtained under both isothermal and non-isothermal conditions are presented on the rates of H_2 and volatile matter release from Pennsylvania anthracites. The effects of particle size and heating rate were investigated, and for two of the anthracites the volatile matter evolved was subjected to chromatographic analysis. For linear heating rates ranging from 2° to 16°C. per min. and for temperatures between 760° and 1000°C. the rate of volatile matter release with respect to temperature has been found to be essentially constant for particle sizes within the range of 200x325 mesh (Tyler) to pieces of approximately 1.2 cm. equivalent radius. Under isothermal conditions rates of H_2 evolution obey a logarithmic time law and exhibit a complex dependency upon particle size.

Despite the fact that the Pennsylvania anthracite fields are located near major steel-producing areas, the role of anthracite as a metallurgical fuel has fallen to that of a minor blending component in producing metallurgical coke. Attempts to use raw anthracite for modern blast furnace and cupola operations have repeatedly shown that it is less satisfactory than coke. Although suitable in all other respects for use in present day metallurgical processes, anthracite is restricted by the following two unfavorable characteristics:

(1) The physical strength of the raw anthracite, as indicated by the ASTM tumbler and drop-shatter tests for coke (*1*, *2*), is inferior to that of metallurgical coke.

(2) Raw anthracite decrepitates when subjected to appreciable temperature gradients.

'iese two characteristics give rise to excessive pressure drop during cupola
..nd blast furnace operations, with the ultimate pressure drop increasing be-
yond blower capacity. This leads to irregular descent of the furnace charge,
pressure fluctuations, and partly frozen stock columns. These difficulties are
partly caused by improvements in furnace design during the present century
which have led to increased heating rates and hence to increased thermal shock.

Of the two objectionable features of anthracite mentioned above, thermal
decrepitation appears to be the more serious. Neither of the two physical
strength tests appear to be related to the behavior of the fuel in either blast
furnace or cupola operations except with respect to handling and load carrying
ability. The problem of handling can be overcome by using appropriate trans-
port equipment. Although it appears possible that the load carrying problem
can be overcome by using shorter stock columns, this characteristic is probably
more closely related to thermal decrepitation than to physical strength alone.
Thus, if methods could be developed to reduce thermal decrepitation, anthra-
cite would be much more widely used as a metallurgical fuel.

With this point in mind, the Fuel Technology Department in 1953 began
to investigate the possibility of improving the strength of anthracite by a heat
treatment process which would increase its thermal stability. This work has
led to the view that the release of volatile matter during the primary thermal
decomposition of anthracite is the most important controlling factor with
regard to decrepitation and that a relationship should exist between the average
particle size and the critical heating rate. As a result of these conclusions,
several attempts have been made to heat-treat anthracite in such a way that
the rate of release of volatile matter does not lead to an internal pressure
exceeding that required to overcome the physical strength of the material.
Some success has been achieved in this direction.

The thermal decrepitation of anthracite is undoubtedly caused by a com-
bination of factors such as moisture evolution, crystallite growth, the differen-
tial thermal expansion of its petrographic constituents and mineral matter, as
well as volatile matter evolution. For anthracite containing a large percentage
of moisture, the internal pressure produced by the presence of superheated
steam within the micropore structure will obviously influence its thermal sta-
bility. However, anthracites of high moisture content would probably be
avoided for metallurgical applications; with regard to anthracites of normal
moisture content, the moisture would probably be reduced below that per-
centage which would cause excessive internal pressures by countercurrent
contact with hot effluent gases. Crystallite growth was originally suggested as
a possible decrepitation mechanism; however, x-ray diffraction studies have
yielded no distinct correlation between crystallite dimensions and decrepita-
tion (5). Consequently, this explanation has received little attention by recent
investigators. With regard to differential thermal expansion, it has been shown
by previous investigators (6) and also by qualitative tests carried out by the
authors that there appears to be no preferential rupture along planes of in-
homogeneity within the material. Thus, it is reasonable to assume that the
release of volatile matter is a major factor in thermal decrepitation, and a more

complete understanding of the mechanism involved would assist considera!
in developing a process for producing thermally stable anthracite.

In this paper the kinetics of volatile matter release from anthracites have
been studied in some detail. Rates of volatile matter release from different
particle sizes of anthracite as a function of heating rate and temperature have
been measured. The change in composition of the volatile matter with vola-
tilization temperature has been studied.

Experimental Procedure

Measurement of Volatile Matter Release Rates. Volatile matter release
rates from anthracite were determined by using the apparatus shown diagram-
matically in Figure 1. The power input to the 1-kw., 20-volt Hoskins tube
furnace and transformer was controlled by means of a Leeds Northrup duration-
adjusting type program controller which permitted linear heating rates up to
20°C. per min. to be selected with varying soak times and temperatures. A
maximum temperature of 1000°C. was used since this was the maximum tem-
perature at which the furnace could be operated continuously. The tempera-
ture of the furnace was measured by a chromel-alumel thermocouple inside a
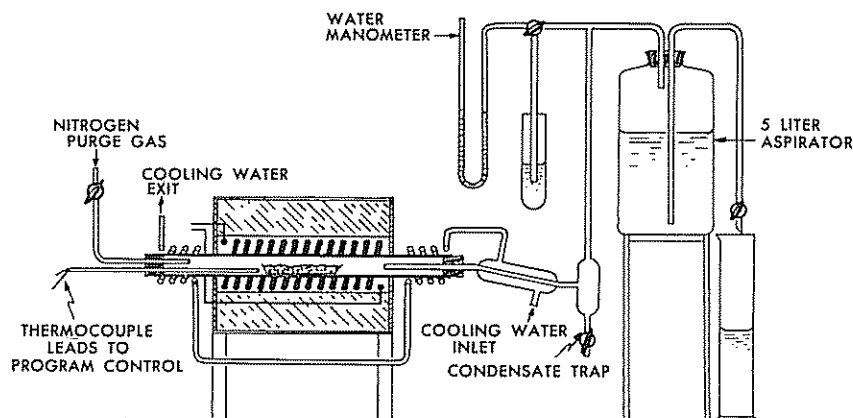

Figure 1. Apparatus for measuring volatile matter release rates

protecting tube and was recorded by the program controller. The controller
was capable of maintaining a preset temperature within ±1°C.

Essentially two types of heating runs were made. In one case, the rate of
heating up to maximum temperature was held constant (not greater than
20°C. per min.). In the second case, the rate of heating to maximum tem-
perature was more rapid than 20°C. per min. and was not held constant as
temperature was increased. In the first case, we were interested in the rate of
volatile matter release as a function of heating rate and soak time at maximum
temperature. In the second case, we were interested only in the rate of volatile
matter release at maximum temperature for more extended soak times. In both
cases the following procedure was used for a run. An as-received sample of
anthracite of known weight was placed inside the 1-inch internal diameter
Coors Sillimanite furnace tube. Nitrogen (of greater than 99.9% purity) was
then passed through the apparatus for about 10 minutes to provide an inert
atmosphere. With the N_2 turned off and the system open only to the water
manometer, the power to the furnace was turned on. The volatiles evolved

ere then passed through a water-cooled condenser and were allowed to dis-
place water from a 5-liter aspirator at constant pressure. The pressure, as
indicated by the water manometer, was held at atmospheric pressure by allow-
ing water to flow from the aspirator to the measuring cylinder.

Analysis of Volatile Matter Evolved. An attempt was made to establish
the particular volatile component or components responsible for decrepitation
by using a Beckman gas chromatography apparatus as described below. It
was considered that comparing the analyses obtained at different temperatures
with the corresponding rate of volatile matter evolution from the experimental
work described previously would perhaps indicate the presence of a thermal
decomposition reaction of controlling importance.

The furnace, as shown in section in Figure 1, was coupled to a gas
chromatograph apparatus as shown in Figure 2. A supply of carrier gas was
provided for the chromatograph apparatus and for purging the system prior to
the commencement of each run in order to provide an inert furnace atmos-
phere. The electrical output from the thermal conductivity detector cell was
fed to a Minneapolis-Honeywell 1-mv. range recorder which traced a curve
showing the separation of the sample into its components. The instrument was
calibrated for each component by plotting peak height against percentage
composition. Several gas mixtures of known composition were used for this
purpose together with commercial gas cylinder samples of the pure components.

The most satisfactory column for estimating H_2 was found to be a 6-foot
length of Linde $13\times$ molecular sieves used in conjunction with argon as a
carrier gas. The remaining components found to be present in significant
quantities were CO_2, CO, and CH_4. These were estimated by using a 4-foot
silica gel column in conjunction with helium as a carrier gas. This column was
also found to be satisfactory for ethane; however, this component was not
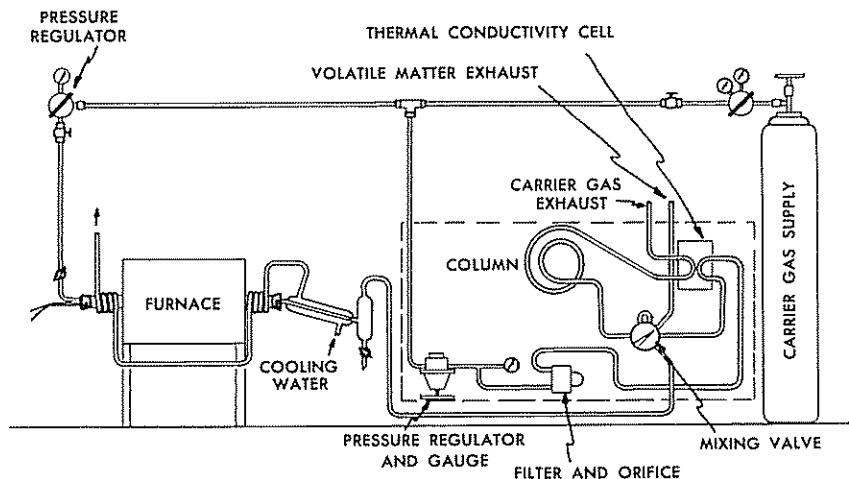present in sufficient quantity to be detected.

Figure 2. Flow diagram of volatile matter analysis apparatus

Analyses of Anthracites Used. For most of the experimental work an
anthracite from the St. Nicholas breaker was used. Its proximate analysis (dry
basis) was as follows: C, 84.3%; V.M., 4.5%; ash, 11.2%. Anthracites from
other breakers used in this program had the following volatile matter contents

(dry basis): Jeddo, 2.9%; Dorrance, 4.9%; Loree, 5.4%; Glen Burn, 6.1%
Woodward, 7.5%.

Results

Volatile Matter Release Rates from Anthracites as a Function of Heating
Rate and Particle Size. A typical experimental run, expressing the total volume
of gas released as a function of temperature for St. Nicholas anthracite, is
plotted in Figure 3. At a temperature of about 760°C. there is a sharp in-
crease in the amount of gas released with increasing temperature. Above
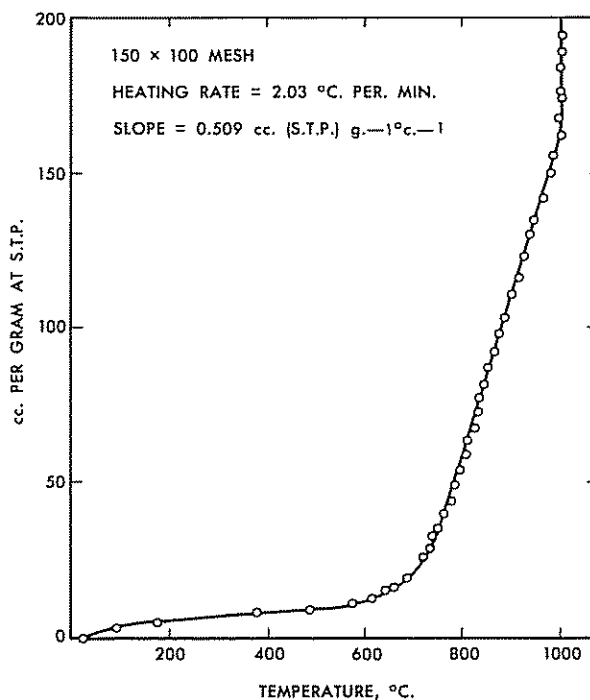760°C. there is an extended region of temperature (760°C. to the maximum

*Figure 3.   Relationship between the volume of vola-
tile matter evolved and temperature for St. Nicholas
anthracite*

temperature of 1000°C.) where the amount of gas released per degree rise in
temperature is constant. The temperature at which this region commences will
be referred to as the critical temperature. Once the maximum temperature of
1000°C. is reached, the volatile matter continues to be evolved if the tem-
perature is held at 1000°C. for some soaking period.

Table I summarizes the volatile matter release rates from St. Nicholas
anthracite above the critical temperature. The data show that these rates are
essentially independent of heating rate or particle size of the anthracite over
the ranges studied. The critical temperature is found to increase, on the aver-

Table I. Volatile Matter Release Rates in cc. (S.T.P.)/gm./°C. for Varying
Particle Size and Heating Rates of St. Nicholas Anthracite
Above the Critical Temperature

Particle Size (*Tyler Mesh*)	*Nominal Heating Rates in °C. per minute*				
	2	*4*	*8*	*12*	*16*
200 × 325	0.541	0.524	0.475	0.500	0.590
100 × 150	0.509	0.489	0.490	0.533	0.600
42 × 65	0.476	0.484	0.535	0.543	0.600
28 × 35	0.506	0.491	0.489	0.520	0.615
12 × 16	0.520	0.514	0.500	0.526	0.593
consolidated pieces (approx. 2.4 cm. in equiv. dia.)	0.611	0.625	0.550	0.585	0.659

age, by *ca.* 70°C. with an increase in heating rate from 2°C. per min. to 16°C. per min. However, at a constant heating rate, the critical temperature is not affected by particle size. From the loss in weight of the anthracite and the total volume of volatile matter released after heating, the average molecular weight of the volatile matter can be calculated. For all the runs on St. Nicholas anthracite the mean average molecular weight was 6.9 ± 0.7. This value did not show a trend with variation in heating rate or particle size.

The rate of volatile matter release for a heating rate of 8°C. per min. was also determined on 150 × 200 mesh fractions of Loree and Woodward anthracites. Three separate runs were made on each sample. For the Loree, the rate of volatile matter release above the critical temperature (740°C.) was 0.611 ± 0.013 cc./gram/°C. For the Woodward the rate of volatile matter release above the critical temperature (770°C.) was 0.666 ± 0.014 cc./gram/°C. The mean average molecular weights of the volatile matter released from the Loree and Woodward were 9.2 ± 0.1 and 7.8 ± 0.3, respectively. As might be expected, the volatile matter release rate increased as the volatile
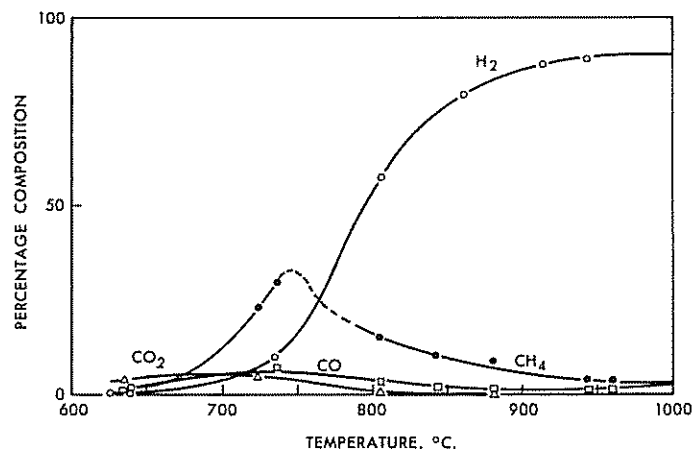

Figure 4.   Relationship between volatile matter composition and temperature for a 150 × 200 mesh fraction of St. Nicholas anthracite

matter content of the anthracite increased. Of course, the rate of volatile matter release would also be expected to be a function of the molecular weight of the volatile matter and the distribution of the pore sizes in the anthracite.

Composition of Volatile Matter Evolved from St. Nicholas and Woodward Anthracites as a Function of Temperature and Soak Time. Figure 4 shows the composition of the volatile matter released from a 150 $\times$ 200 mesh fraction of St. Nicholas anthracite *vs.* temperature. The difference between 100% and the sum of the percentages of H_2, CH_4, CO, and CO_2 is the percentage of N_2 in the product gas. It is recalled that before commencing a heating run the apparatus was flushed with N_2. Up to 650°C., the rate of release of volatile matter was too low for analysis. The rapid rate of gas evolved above the critical temperature can be attributed primarily to a large increase in the rate of H_2 evolution. Below the critical temperature, more CH_4 is in the product gas than H_2, but the percentage of CH_4 decreases rapidly until at 1000°C. only about 1% is in the product gas. No ethane was detected. Only small percentages of CO and CO_2 were evolved during the heating-up period, but during the constant temperature period at 1000°C. the percentage of CO in the product gas progressively increased to a value of 19% after a soak time of 164 minutes. The last item is shown in Figure 5 where the composition of the gas is plotted against the cumulative time the sample was above 600°C.
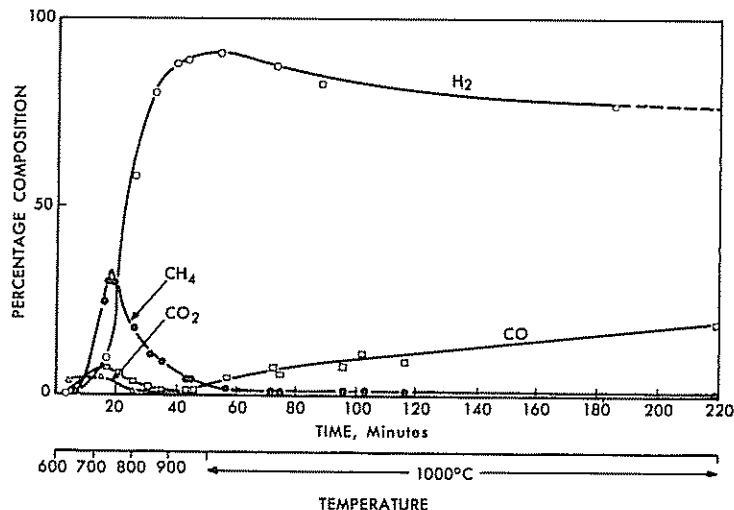

Figure 5. Relationship between volatile matter composition, temperature, and time for a 150 $\times$ 200 mesh fraction of St. Nicholas anthracite

Figure 6 shows the composition of the volatile matter released from a 150 $\times$ 200 mesh fraction of Woodward anthracite *vs.* temperature. The percentage of N_2 analyzed is also shown. Some significant differences between Figures 6 and 4 are noted. For the Woodward anthracite, much larger percentages of CO and CO_2 are found in the product gas released below 700°C.
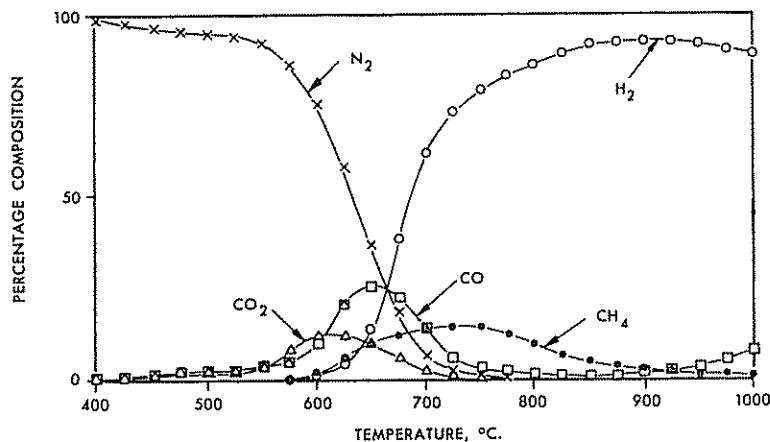
Figure 6. Relationship between volatile matter composition and temperature for a 150 × 200 mesh fraction of Woodward anthracite

than are found for the St. Nicholas anthracite. This increase in the percentage of carbon oxides in the product gas for the Woodward anthracite is accompanied by a decrease in the maximum percentage of CH_4 found in the product gas. For the St. Nicholas anthracite the maximum percentage of CH_4 found in the product gas was 30% (at 737°C.); for the Woodward anthracite the maximum percentage of CH_4 found was 15% (at 735°C.). The relative positions of the H_2 and CH_4 curves for the two anthracites should also be noted. For the St. Nicholas anthracite, the maximum amount of CH_4 in the product as was found at a position where only *ca.* 15% H_2 was in the product gas. For the Woodward anthracite, the maximum amount of CH_4 in the product gas was found where 75% H_2 was in the product gas. These data indicate some fundamental difference in the desorption kinetics of H_2 and CH_4 from the two anthracites. The formation of CH_4 is presumably caused by the rupture of C-C single bonds, whereas the progressively increasing concentration of H_2 with increasing temperature is probably related to the increasing rupture of the higher energy C-H bonds at the surface and also in the gas phase, for example from methane.

Rate of Release of Hydrogen from St. Nicholas Anthracite at Selected Temperatures as a Function of Soak Time. Initial rates of H_2 release from a 150 × 200 mesh fraction of St. Nicholas anthracite were determined at temperatures between 700° and 755°C. and are shown in Figure 7. Zero time starts when the sample reached the designated maximum temperature. It is seen that after the carrier gas was displaced from the apparatus, the rate of H_2 release at each temperature studied was constant over the interval of times plotted in Figure 7—i.e., the rate of H_2 release did not depend on the amount of H_2 remaining on or in the anthracite. From these initial rates of H_2 release an activation energy of 96 kcal./mole is calculated. When the soak time at a particular temperature below 755°C. was extended sufficiently, the rate of
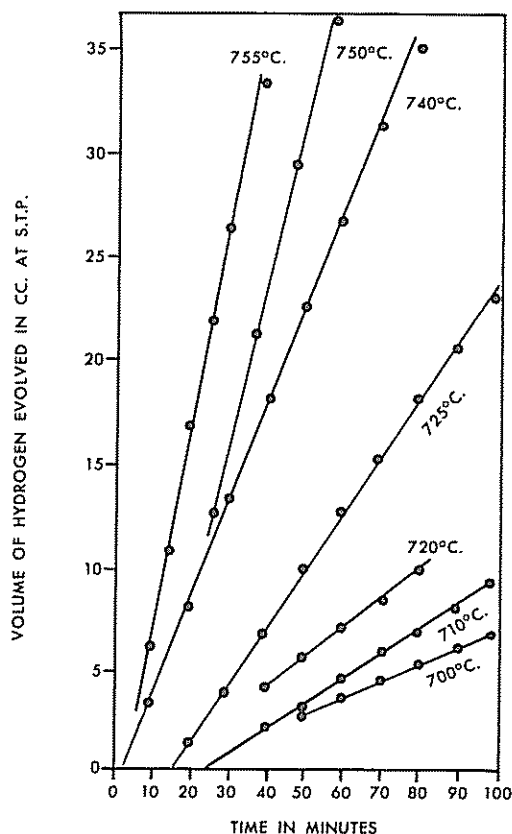
*Figure 7. Variation of initial hydrogen release
rates with temperature for 5.5 grams of 150 ×
200 mesh St. Nicholas anthracite*

evolution of H_2 progressively decreased with time. Indeed, at temperatures
above 760°C. the initial rate of H_2 release was so rapid that only the region of
decreasing evolution rate was apparent. For this region of decreasing evolution
rate, a linear plot is obtained if the volume of H_2 evolved is plotted against the
log of time. Such plots are shown in Figure 8 for desorption studies in the
temperature range 800°–860°C. As discussed by Redmond and Walker (7),
among others, this type of plot (frequently called an Elovich plot) can be
explained theoretically on the basis of a linear increase in activation energy of
desorption of H_2 with decrease in surface coverage. If desorption rates at dif-
ferent temperatures are taken at the same value of surface coverage (same
volume of H_2 evolved), activation energies at fixed values of coverage can be
determined from Arrhenius plots. This was done for the data in Figure 8. The
activation energy for H_2 evolution was found to increase linearly with decreas-
ing fractional coverage (Θ) from 96 kcal./mole at $\Theta \to 1$ to 137 kcal./mole
at $\Theta = 0.5$ (or ½ of the total H_2 removed from the anthracite).

Effect of Particle Size on the Rate of Desorption of Hydrogen from St. Nicholas Anthracite at Constant Temperature. If the rate of evolution of H_2 is controlled by the rate of desorption of H_2 from the surface of anthracite and not by the rate of transport of the H_2 from the pore system, the rate of evolution should be independent of particle size. However, this was not found to be the case. For St. Nicholas anthracite, the initial rate of H_2 release was determined on a 12 × 16 mesh fraction over the temperature range 700°–750°C. and compared with the previous results for initial rate of release on a 150 × 200 mesh fraction. Results are summarized in Table II. The results show clearly that the rate of H_2 evolution at all temperatures studied was more rapid from the larger particle sized sample. The activation energy for H_2 evolution at $\theta \to 1$ from the 12 × 16 mesh fraction is calculated as 89 kcal./mole, compared with 96 kcal./mole for the 150 × 200 mesh fraction over the same temperature interval.

The initial H_2 release rate at 750°C. was investigated for different particle sizes ranging from a consolidated piece of approximately 2 cm. equivalent
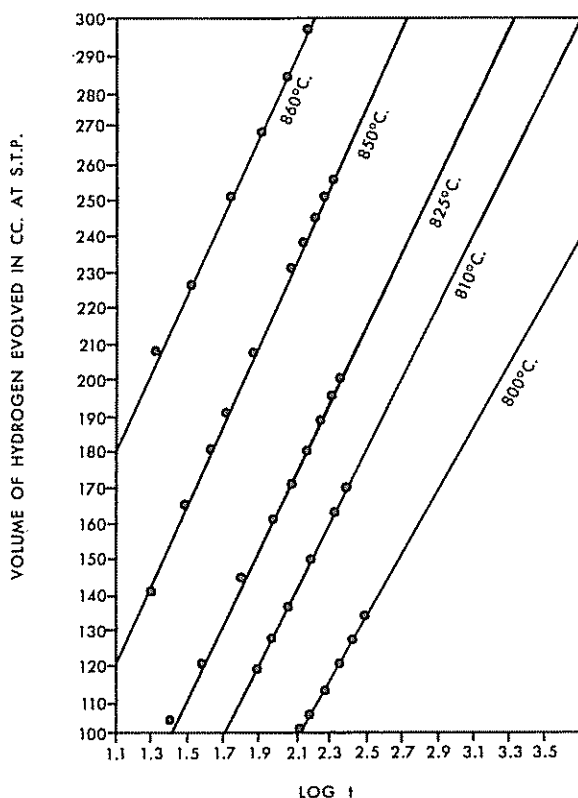

Figure 8. Variation of dq/d log t with increasing temperature for 5.5 grams of 150 × 200 mesh St. Nicholas anthracite

**Table II. Effect of Particle Size on the Rate of Hydrogen Release from
5.5 Grams of St. Nicholas Anthracite**

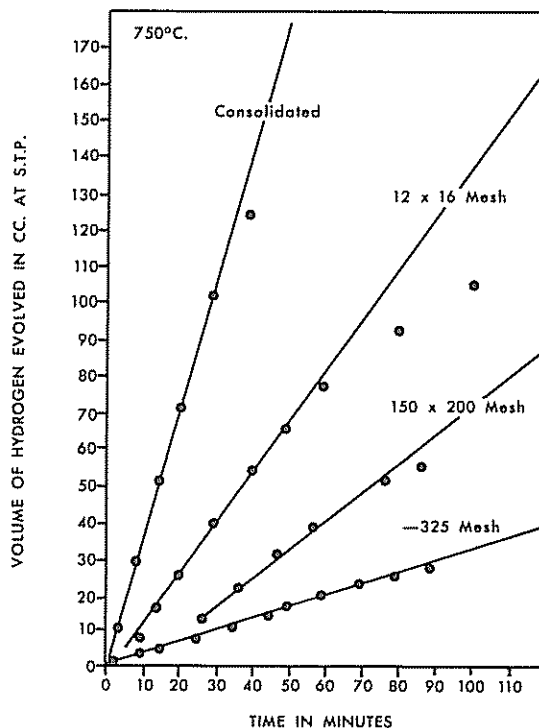| Particle Size (Tyler Mesh)	Temperature °C.	Rate cc./min.
12 × 16	700	0.17
150 × 200	700	0.08
12 × 16	710	0.27
150 × 200	710	0.13
12 × 16	725	0.41
150 × 200	725	0.30
12 × 16	740	1.00
150 × 200	740	0.50
12 × 16	750	1.50
150 × 200	750	0.85

*Figure 9. Variation of the initial rate of hydrogen
release with particle size for 5.5 grams of St. Nicho-
las anthracite*

diameter to a —325 mesh fraction. The results are shown in Figure 9. The
marked decrease in H_2 evolution rate with decrease in particle size is clearly
seen.

**Effect of Particle Size on the Rate of Volatile Matter Release at Constant
Temperature from Different Anthracites.** On the basis of the results for St.

icholas anthracite, we investigated the effect of particle size on the rate of volatile matter release at constant temperature from other anthracites. In all cases H_2 represented a large fraction of the total volatile matter released. Evolution rates were measured at 800°C. on 5.5-gram samples. As previously discussed, at 800°C. plots of the volume of volatile matter released *vs.* the log of time gave straight lines, with the slope of these lines ($dq/d \log t$) being a measure of the relative rate of volatile matter release. Results are summarized in Table III and Figure 10. The effect of particle size on volatile matter release rate is complex and depends upon the anthracite studied. However, in every case particle size has a pronounced effect on volatile matter release rate at constant temperature.

Table III.   Rates of Volatile Matter Release from 5.5-gram Samples of Selected Anthracites at 800°C.

Anthracite	Particle Size (Tyler Mesh)	$dq/d \log t$, cc.
St. Nicholas	—325	142.0
	150 × 200	160.0
	12 × 16	183.0
Loree	—325	217.0
	150 × 200	191.0
	16 × 20	176.5
Dorrance	—325	153.0
	150 × 200	83.0
	12 × 16	191.5
Glen Burn	—325	158.6
	150 × 200	123.0
	16 × 20	190.0
Jeddo	—325	166.6
	150 × 200	170.0
	16 × 20	131.8

Discussion

Our primary objective has been to present the experimental results in a convenient, combined form rather than to discuss their significance in great detail. In view of the extreme physical and chemical complexity of anthracite and the limited amount of experimental investigation to which the material has been subjected at present, an elaborate theoretical discussion would be pointless. Indeed, it is improbable that the kinetics of volatile matter release for such a complex material will ever submit to a satisfactory correlation by simple functional relationships. In spite of these difficulties, it is of interest to discuss some of the general trends exhibited by the experimental data and their interpretation by suggesting approximate theoretical and mathematical models for the release mechanism.

A Chemisorption Mechanism for the Release of Hydrogen from Anthracite. In recent years considerable experimental justification has been obtained for the view that in many cases surface interactions during chemisorption can give

rise to a linear dependency of activation energy upon surface coverage. :
assuming a velocity equation of the type

$$- \frac{d\Theta}{dt} = Ae^{-(E_0 - \beta\Theta)/RT} \qquad (1)$$

where Θ is the fraction of surface coverage, E_0 is the activation energy at $\Theta = 0$,
and β is the change in activation energy as Θ goes from 1 to 0, it can be shown
that by making appropriate simplifying assumptions a logarithmic time law
can result. The assumptions and theoretical considerations involved have been
fully discussed by Redmond and Walker (7), and for our purpose it is sufficient
to state that a relationship between surface coverage and time under isothermal
conditions can be expressed in the form:

$$\Theta = k_1 + k_2 \log t \qquad (2)$$

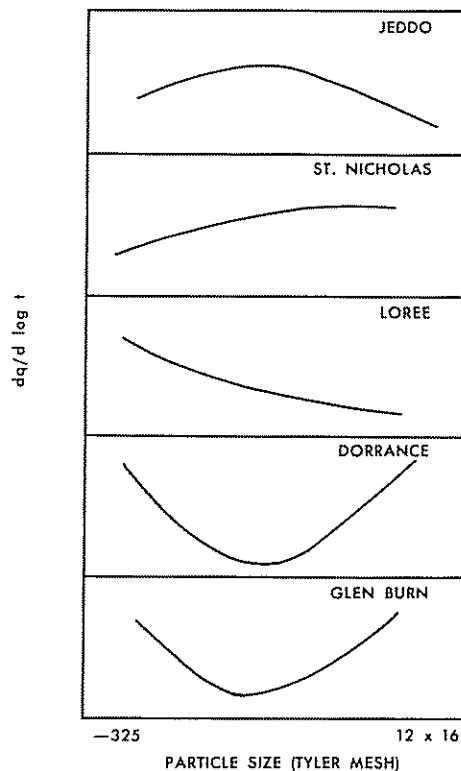where the constants k_1 and k_2 are related to the constants appearing in Equation 1.

Figure 10. Qualitative variation of dq/d
log t with particle size for various anthra-
cites at 800°C.

In view of the linearity of the curves presented in Figure 8 and the high activation energies obtained by using Equation 1 at constant values of Θ, there seems to be considerable justification for the chemisorption model of volatile matter release. The fact that the initial rates of H_2 release show a zero-order dependency may be attributed to the fact that for raw anthracite the fraction of surface coverage is practically unity. Under these conditions, where almost all of the sites available for H_2 adsorption are filled, Equation 1 leads to the result that the rate of change of coverage with respect to time is initially constant.

On the basis of a chemisorption hypothesis, no dependency upon particle size would be expected; consequently the results presented in Table II and Figure 9, showing that the release rate increases with increasing particle size, are difficult to explain. Although it is conceivable that, owing to the existence of size-dependent temperature gradients within the material there could be a tendency for the rate of release to increase with increasing particle size, it would be preferable to await further experimental evidence before attempting to fit particle size dependency to the proposed model. As Table III and Figure 10 show, anomalous results were also obtained with respect to particle size for other anthracites. However, as with results for St. Nicholas anthracite, it would be preferable to await further experimental evidence before attempting to attach any significance to this complex behavior. In the isothermal work a significant time was required for the furnace to reach its controlled temperature, and this may have resulted in an apparent size dependency. No such dependency was observed for the volatile matter release data at the linear heating rates shown in Table I where the samples were not subjected to discontinuities in thermal treatment.

Although the use of linear heating rates introduces considerable comexity into the mathematics, it is of interest to note that the slope of the curve (above the critical temperature) shown in Figure 3 can be related to desorption theory. By differentiating Equation 1 with respect to time, it follows that

$$- \frac{d^2\Theta}{dt^2} = A e^{-(E_0 - \beta\Theta)/RT} \left[\frac{\beta}{RT} \frac{d\Theta}{dt} + \frac{E_0 - \beta\Theta}{RT^2} \frac{dT}{dt} \right] \qquad (3)$$

When $d^2\Theta/dt^2 = 0$, it follows that

$$- \frac{d\Theta}{dt} = \frac{E_0 - \beta\Theta}{\beta T} \frac{dT}{dt} \qquad (4)$$

or, since $1 - \Theta = V_t/V_\infty$, it follows that in terms of volatile matter release

$$\left(\frac{dV_t}{dT} \right)_{H_2} = \frac{V_\infty E_0 - \beta (V_\infty - V_t)}{\beta T} \qquad (5)$$

where V_t equals the volume of H_2 released at time (t) and V_∞ equals the total amount of H_2 released. Substituting $E_0 = 178$ kcal./mole, $\beta = 82$ kcal./mole, $T = 1073°K.$, $V_t = 30$ cc./gram, and $V_\infty = 135$ cc./gram leads to the result that $(dV_t/dT)_{H_2} = 0.16$. Since the volatile matter is approximately 50% H_2

at 800°C., it follows that dV_t/dT for the total volatile matter should be abou 0.32, which at least agrees in order of magnitude with the tabulated values given in Table I. In this calculation, the value of $V\infty = 135$ cc./gram was derived from the original data used to prepare Figures 4 and 5. The value of $V_t = 30$ cc./gram was obtained from Figure 3 assuming that the cumulative volatile matter was 50% H_2 at 800°C. Although the point of inflection in Figure 3 is not well defined, it is clear that such a point must exist, and the apparent linearity of Figure 3 could be caused by the existence of an extensive region in which the second derivative, $d^2\Theta/dt^2$, is almost zero.

A **Diffusional Mechanism for the Release of Volatile Matter from Anthracite.** The fact that the quantity of H_2 released appeared to be related linearly to the logarithm of time could lead to interpreting the isothermal results in terms of surface chemistry as shown. However, Figure 11 shows that within the limits of experimental error, the solution to the unsteady state diffusion
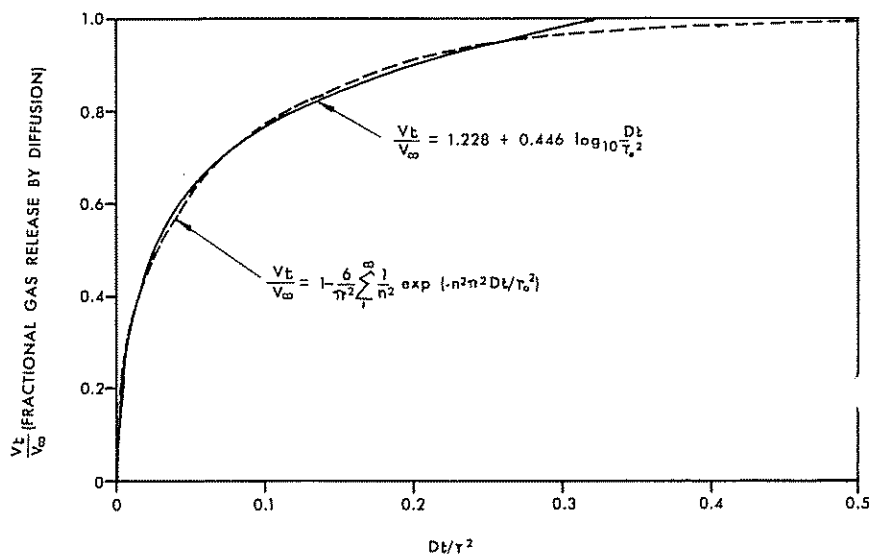

Figure 11. Diffusion theory compared with an approximating logarithmic time law

problem can be represented by a logarithmic time law up to 97% completion of the diffusion process as well as by the conventional equation for diffusion from a spherical particle (4). This suggests that the isothermal kinetics of volatile matter release could be interpreted equally well as a pure diffusion process in which the chemical release rate is almost instantaneous compared to the subsequent slow diffusion process through the anthracite. Although, for a homogeneous medium, a diffusion controlled process would not lead to release rates independent of particle size, it is conceivable that the release of volatile matter could be diffusion controlled within relatively nonporous structural units of much smaller dimensions than the external dimensions of the particles them-

:lves. It is analogous to the reasoning used in an attempt to explain the rate of fission product release from uranium oxide (3).

In an attempt to provide further information relative to the validity of the diffusion mechanism, a typical set of results was selected from the isothermal release work, and the volume of volatile matter released was plotted against the square root of time. For a pure diffusion process such a plot should be almost linear initially (4) whereas for a true logarithmic time law, $dV_t/dt^{1/2}$ should tend to infinity for very small values of $t^{1/2}$. Figure 12 shows that by this criterion the rate controlling mechanism appears to be diffusion and not chemisorption. The fact that the curve does not pass through the origin is undoubtedly caused by the fact that it was not possible to heat the sample to
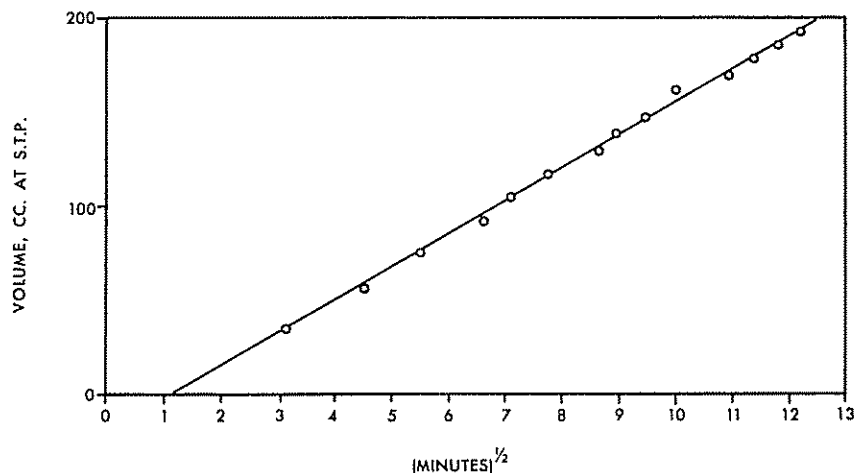

Figure 12. Volatile matter released from 5.57 grams of 150 ×200 mesh St. Nicholas anthracite at 700°C.

the control temperature at $t = 0$. Owing to the sensitivity of the diffusion process to such errors in the initial conditions, no further diffusion interpretations of the isothermal data were attempted.

The high activation energies resulting from the chemisorption hypothesis appear to favor its validity. However, it is possible that such a high activation energy could be caused by an equilibrium between the undecomposed coal molecules and the diffusion species resulting from thermal decomposition. That is, for diffusion in the Z dimension only, a simplified mass balance would lead to a differential equation of the form

$$D \frac{\partial C^*}{\partial Z^2} = \frac{\partial C}{\partial t} \tag{6}$$

where C° represents the concentration of diffusing species, and C represents the total concentration of "available" volatile matter. If C° and C were related by an equilibrium constant K such that $C^\circ/C = K = \exp(-\Delta F/RT)$, then

the diffusion coefficient would appear to possess an exponential temperatu
dependency of the type suggested by the following change of variable,

$$De^{-\Delta F/RT} \frac{\partial^2 C}{\partial Z^2} = \frac{\partial C}{\partial t} \qquad (7)$$

Although a pure diffusion process can give rise to an apparent logarithmic
time law and the initial release of volatile matter is linearly related to $t^{1/2}$,
insufficient evidence has been presented to indicate positively that the release
is diffusion controlled.

Since the chemisorption and diffusion mechanisms appear to be almost
equally acceptable, it is suggested that both of them be regarded as somewhat
questionable until they can be investigated by further experimental work.

Acknowledgments

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Discussion

Marie-Therese Mackowsky: Have you ever determined the mechanical
resistance or the strength of the different anthracites? It may be that the inde-
pendence of the grain size is caused by the fact that a cracking has taken place
and in reality you have nearly the same grain size in all the tests.

Philip L. Walker: Hardgrove grindability data for many Pennsylvania
anthracites have been determined and reported on in the Proceedings of the
1956 Anthracite Conference held at Pennsylvania State University.

We would agree that grinding should produce some macrocracks in the
particles and that these macrocracks can open up previously closed-pore
volume. This, in turn, will affect the kinetics of volatile matter release.

Bhupendra Mazumdar: Dr. Walker obtained small amounts of gas by
carbonizing anthracite up to 600°C. (about 10 cc./gram) whereas our results

tained from a South Wales anthracite (C = 93.2%) indicate that about
60 cc./gram of gas is formed at and up to 600°C., owing to pyrolysis. I would
like to know about the rank of the anthracite sample to which Dr. Walker's
results refer. Further, I would also appreciate his general comments on the
degassing of anthracite at 450°C.—is it really safe to do so?

Dr. Walker: We discuss the release of volatile matter from different an-
thracites in another paper (*Carbon* 2, 199 (1964)). For a low volatile matter
anthracite such at St. Nicholas, weight loss for a heat treatment temperature
of 500°C. is 1.7%; for a high volatile matter anthracite such as Treverton
(V.M. = 9.0%), weight loss for heat treatment to 500°C. is 4.8%. The
difference in weight loss for these two anthracites heated to 500°C. can be
accounted for almost entirely by differences in the amount of CO and CO_2
released. Thus, the higher the volatile matter content of the anthracite, the
lower the temperature to which the anthracite can be heated and still not
significantly change the magnitude of its available micropore volume. That is,
release of CO and CO_2 unblocks some previously unavailable micropores.

L. L. Newman: Dr. Mackowsky has already asked you if you related your
studies on the kinetics of volatile matter release from Pennsylvania anthracites
to the petrographic constituents of the coal. Can you not say in effect that the
coals from the various collieries differ from each other quite significantly with
respect to their petrographic composition and that identification of a coal by
source may identify it petrographically to some extent? How do the results of
these studies relate decrepitation actually experienced in industrial operations?

Dr. Walker: We have not related our studies of kinetics of volatile matter
release from anthracites to their petrographic consituents. This type of work
is planned for the future.

Generally, the decrepitation resistance of anthracites increases with de-
creasing volatile matter content, but in some cases differences in physical
properties of the coals appear to nullify this relation.

George R. Hill: Have you planned to study the kinetics of methane de-
composition over anthracite in a long packed column at constant temperature?
This should help resolve the unanswered mechanism questions.

Dr. Walker: We have not planned to study the decomposition of methane
over anthracite as you suggest. I think it would be more interesting to study
the decomposition of methane as it diffuses out of the micropore structure of
anthracite. At least two effects are possible: (1) since two moles of hydrogen
are produced for each mole of methane decomposing, an increase in the number
of moles of gas diffusing from the pores per unit time could result; (2) the
carbon produced by methane decomposition could block pores and/or decrease
their size, which could result in a decrease in the number of moles of gas
diffusing from the pores per unit time.

Norbert Berkowitz: I once again question the admissibility of the kinetic
approach. Hydrogen yields at the various temperatures are *not normalized*,
and that implies the quite untenable assumption that hydrogen yields at all
experimental temperatures would all be the same provided sufficiently long
degasification periods were allowed. I doubt whether the authors actually do
imply that, but if they don't, they ought to bear in mind that classical kinetics

cannot be used to describe a reaction whose final product-yields at t_∞ va with temperature. Most certainly, the initial slopes observed with such a reaction do not allow calculation of an activation energy.

Dr. Walker: Using the Elovich concept (—i.e., a varying activation energy for desorption with surface coverage) is not using classical kinetics. I would agree that this situation is complex because of the possible production of hydrogen from at least two sources: (1) direct desorption of hydrogen from the anthracite surface, and (2) production of hydrogen from the decomposition of methane, which is produced first. Because the situation is complex, stating an activation energy for initial rates of hydrogen release is useful only to give an expression for rate variation with temperature. Certainly this activation energy cannot be used to decide upon a final mechanism for hydrogen release.