Analysis of the Variation in Coil Character by Carbonized Coal with Q-Meter

By Sadaharu TOYODA

(Received April 27, 1961)

It is well known that the variation of character of a circuit, containing a coil or a condenser-type electrode, can be utilized to find a neutralization point on high frequency titration, though many other applications of the coil have been reported in several papers[1-11]. Many significant results[12,13] have been obtained by considering the variation of coil character, which is caused by inserting an aqueous solution into the coil. Recently, the calculation[14] of the relation between the variable resistance of platinum wire and the resistance of an aqueous solution has been extended on the basis of Ref. 12. However, some of the calculated values have not agreed with the experimental values in the case of a coil-type instrument. As a result of calculation, it has also been shown that the consideration of the dielectric constant of a sample solution would help to solve this problem.

The Q-change of the coil with aqueous solution has been explained in another paper[15]. The variation of coil character when a substance is inserted into the coil is visualized in Fig. 1. According to the experimental result, the value of Q/Q_1 for an aqueous solution ($\varepsilon'=80$) changes with the resistance of the solution, as is shown by the full-line in Fig. 2. This variation seems to be explained by the equivalent circuit (Fig. 4 in Ref. 15) and the following relation (Eq. 15 in Ref. 15), which are based on Refs. 13, 16 and 14:

$$\frac{Q}{Q_1} \doteqdot \frac{1}{1+\alpha\left(\dfrac{px}{1+x^2}+\dfrac{1}{pMx}\right)\dfrac{\omega L}{R_1}} \qquad (1)$$

where

$$x \equiv \omega(\varepsilon' C_1 + C_0)R, \quad R \equiv kr, \quad p \equiv \frac{C_0}{\varepsilon' C_1 + C_0}$$

$$\alpha \equiv \omega^2 L C_0$$

After some calculation using the above relation, the dotted line in Fig. 2 is obtained in the case of a low dielectric constant (for example, $\varepsilon'=1$). Comparing these two curves, the minimum value of Q/Q_1 in the dotted line is smaller than the value in the full-line, while the maximum value of Q/Q_1 does not depend

---

1) F. Bloch, *Phys. Rev.*, **70**, 460 (1946); F. Bloch, W. W. Hausen and M. Packard, ibid., **70**, 474 (1946).

2) N. Bloembergen, E. M. Purcell and R. V. Pound, ibid., **73**, 679 (1948).

3) R. V. Pound and W. D. Knight, *Rev. Sci. Instr.*, **21**, 219 (1950).

4) P. W. West, T. Robichaux and T. S. Burkhalter, *Anal. Chem.*, **23**, 1625 (1951).

5) P. W. West, P. Senise and T. S. Burkhalter, ibid., **24**, 1250 (1952).

6) M. Honda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 529 (1952); **74**, 371 (1953).

7) H. Honda, S. Toyoda and Y. Hirose, *J. Fuel Soc., Japan* (*Nenryō Kyokaishi*), **35**, 526 (1956).

8) H. Honda, 2nd Int. Coal Preparation Congress, Essen (1957), C 9,

9) F. J. Schmidt, *Anal. Chem.*, **29**, 1060 (1957).

10) Isidore Bady, *J. App. Phys.*, **29**, 393 (1958).

11) R. D. Ray, *B. C. U. R. A. Mon. Bull.*, **24**, 117 (1960).

12) K. Nakano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 776 (1954).

13) M. Honda, K. Nakano and A. Satsuka, ibid., **75**, 1299 (1954).

14) S. Toyoda, This Bulletin, **33**, 504 (1960).

15) S. Toyoda, ibid., **34**, 944 (1961).

16) W. J. Blaedel et al., *Anal. Chem.*, **24**, 198 (1952).

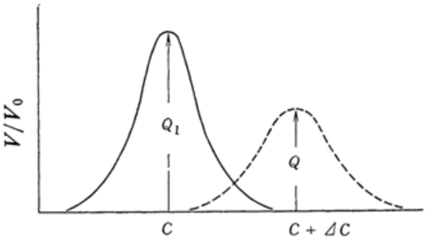


Fig. 1. Two curves showing variation of coil character.

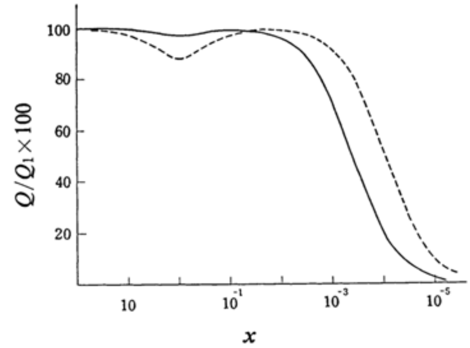


Fig. 2. Curves of Q/Q_1-change ($x \equiv \omega(\varepsilon' C_1 + C_0)R$, $R \equiv kr$), full-line ($\varepsilon'=80$), dotted line ($\varepsilon'=1$) at 3×10^6-cycle.

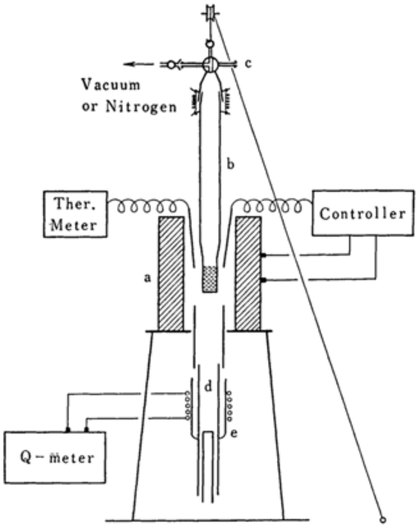


Fig. 3. Apparatus for experiment.

a Furnace b Quartz pipe
c Three-way cock
d Quartz pipe serving as a guide
e Quartz pipe for coil

on the dielectric constant. The present paper is concerned with the variation in coil character caused by carbonized coal. The experimental results seem to be understandable by taking account of the above-described difference between the full-line and the dotted line.

Experimental Equipment and Method

Fig. 3 shows an experimental apparatus. The explanation of the parts except a furnace (a) and its accessories are omitted, since they have been reported in Ref. 15. Although a long quartz pipe (b) shown in Fig. 3 has not been illustrated in Ref. 15, it had been attached to a quartz vessel of a sample solution. The length of the quartz pipe is about 45 cm., and the outside diameter, 2.5 cm. A three-way cock (c), suspended by a string and a pulley as shown in Fig. 3, is connected to another end of the quartz pipe with a spring, and so the coal sample in the quartz vessel is located in the center of the furnace, which is regulated at the heating rate of 2°C per minute. When the temperature of the coal sample is raised to an appointed temperature, the connection to a vacuum or a nitrogen system is set off, and the heated quartz vessel containing the coal is inserted into a coil by using the string and the pulley. After measuring the Q-value of the coil as fast as possible, the quartz vessel is pulled up to the original position, the three-way cock is connected again to the vacuum or the nitrogen system, and the quartz vessel with the coal is heated to the next desired temperature.

When the heated quartz vessel is inserted into the coil, the Q of the coil is apt to decrease due to the heat conduction and the radiation from the vessel, in addition to the Q-change caused by the character of carbonized coal. The following method

TABLE I. ANALYSIS OF VARIOUS COALS

Coal	Proximate analysis, %				Ultimate analysis (d. a. f.), %		
	Moisture	Ash	VM	Fixed carbon	C	H	O+N+S
Tempoku	—	2.07*	—	—	68.12	5.63	26.25
Nakagō	13.32	3.96	38.03	44.69	74.33	5.26	20.41
Takamatsu	4.45	2.63	41.42	51.50	79.52	5.53	14.95
Yūbari	1.13	2.67	44.85	51.35	84.85	6.16	8.99
Shikamachi	1.16	2.52	21.16	75.16	88.76	4.70	6.54
Yatake	1.67	11.82	19.06	67.45	88.95	4.93	6.12
Uonuki	1.68	1.80	10.80	85.72	91.16	3.97	4.87
Hongei (Indo-China)	1.92	1.08	6.25	90.75	92.65	3.48	3.87

* Dry basis

was employed in order to suppress this tendency caused by the heat conduction and the radiation. Taking account of the heat conduction, the quartz tube (d) serving as a guide for the vessel containing the sample as shown in Fig. 3, is attached inside the quartz tube (e) on which the coil is wound; moreover, because of the radiation, the outside surface of the transparent quartz tube (d) is frosted. In spite of these attentions, the Q-change of the coil still remains somewhat, so that the coil must be cooled by a fan after the heated quartz vessel with coal is drawn up.

The coal specimens were pulverized to pass through a 30- and stand on a 60-Tyler mesh sieve. The vitrain of coals of specific gravity less than 1.30, except for Yatake coal, was isolated by the float-or-sink method using mixtures of benzene and carbon tetrachloride. Shikamachi and Yatake coals were pulverized to pass through a 200-Tyler mesh sieve. All samples were dried in air for several days. The characteristics[17] of the various coals are listed in Table I. Taking account of the loss in weight of coal by carbonization as shown in Fig. 4, the initial coal sample length in the quartz vessel was made longer than 6.5 cm. (refer to Table III and Ref. 15).

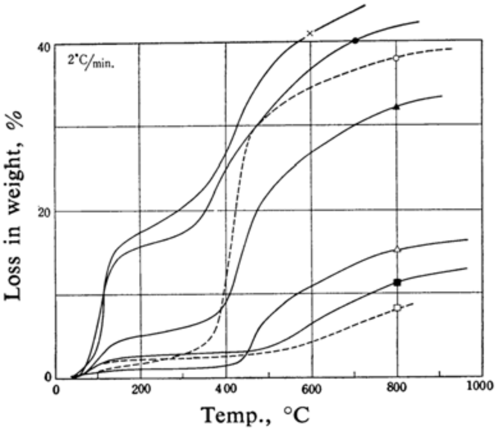


Fig. 4.

● Tempoku
× Nakagō
▲ Takamatsu
○ Yūbari
△ Shikamachi
■ Uonuki
☐ Hongei

In the previous experiment (Ref. 15), the Q-value did not change when the quartz vessel without a sample solution was inserted into the coil. This seems to be attributable to the high resistance or low loss of the quartz vessel at 3×10^6 cycle. On the contrary, it can be imagined that the properties of the quartz vessel will change in the present case because the vessel is heated to about 1000°C. Therefore, it is necessary to investigate the variation in coil character due to the property change of the heated quartz vessel without a sample. The Q of the coil is measured when the heated quartz vessel without a sample is put into the coil; the results obtained are shown in Table II.

TABLE II

Temp °C	Quartz vessel Q/Q_1 ×100	Shikamachi Q/Q_1 ×100	Shikamachi $\Delta C'$ (pF)	Yatake Q/Q_1 ×100	Yatake $\Delta C'$ (pF)
20	100	99.5	−0.10	99.2	−0.17
100	〃	—	—	—	—
200	〃	99.9	−0.11	99.5	−0.24
300	〃	—	—	—	—
400	〃	99.9	−0.10	99.2	−0.20
500	〃	〃	−0.12	99.5	−0.22
550	〃	99.7	−0.11	98.9	−0.20
600	〃	〃	−0.18	95.1	−0.38
625	〃	96.7	−0.22	93.5	−0.42
640	—	—	—	94.8	−0.53
650	100	98.2	−0.19	99.0	−0.54
675	〃	91.7	−0.44	89.4	−0.56
690	—	96.8	−0.53	—	—
700	100	98.7	−0.47	82.6	−0.63
725	—	98.4	−0.54	—	—
750	100	98.7	−0.54	45.7	−0.62
775	—	55.6	−0.64	—	—
800	99.7	40.5	(−0.44)	≈5	—
825	—	15.6	—	—	—
850	99.5	≈5	—	—	—
900	99.2	≈8	—	≈2.5	—

The notation Q_1 means the Q-value of the coil without a quartz vessel, just before measuring the Q-value of the heated quartz vessel with or without coal. In order to measure the Q-value correctly, the capacity of the condenser in the Q-meter most be adjusted at the tuning point, but it is not changed when measuring the heated quartz vessel without coal, after adjusting it without the vessel. It may be considered that the Q/Q_1-value of the heated quartz vessel, at least, would not be smaller than the one in Table II, because the V/V_0-value of coil has a tendency to decrease when the capacity of condenser is not tuned. According to the experimental result, the decrease of the Q-value is so small that it can not be detected up to 750°C, while the value of Q/Q_1 decreases slightly with the increase of temperature in the range from 800 to 900°C. Therefore, it may be concluded that the variation in Q-value caused by carbonized coal is hardly affected by the heated quartz vessel, because the variation due to the carbonized coal is much larger than that due to the heated quartz vessel at a high temperature.

When the Q-value is measured, as mentioned above, the capacity of the condenser must be adjusted again after the heated quartz vessel with coal sample is inserted into the coil. It is not unreasonable to assume that the tuning capacity of the condenser has a tendency to decrease when carbonized coal is inserted into the coil, because an aqueous solution has the same tendency. Thus, the capacity of the condenser decreases at a suitable rate from the tuning capacity without the heated vessel, and the maximum value of V/V_0, that is to say, the Q of the coil, is measured after the heated vessel with coal is put into the coil.

---

[17] H. Honda and Y. Hirose, *Fuel*, **37**, 323 (1958).

The time required for each measurement of Q-value is usually less than five seconds. The temperature at which the Q-value is measured is selected according to the quantity of variation of Q. As the temperature of the heated coal decreases when the coal is inserted into the coil, the next measurement of Q-value must be carried out after enough time to recover the decline in temperature and keep the heating rate of 2°C per minute on an average. Therefore, the narrowest interval of temperature for measurement has been decided as 20°C. The reading of the thermometer goes down about 5°C to 20°C over the range from 500°C to 900°C after the quartz vessel containing the coal is withdrawn into the furnace, but this decrease is recovered and the reading of the thermometer becomes the desired value after 2 to 5 min. In the measurement at higher temperatures, there is still a small decrease of Q_1, in spite of cooling the coil with the fan after the Q-value is measured and withdrawing the heated quartz vessel as fast as possible. It must be remembered, however, that this decay of Q_1 does not interfere with the following experiment, since the ratio, Q/Q_1, is discussed instead of the Q-value, and the variation in the Q-value due to the coal sample is rather large in the higher temperature range.

Experimental Results

The measurements were made of the samples under vacuum, and the results are shown by the dotted lines in Figs. 5a—5d. There is a slight danger under a vacuum condition that some of the coal samples may suddenly expand and lose packing uniformity by the gas given off on thermal decomposition. In order to avoid these errors, the variation of the Q-value was also measured for the sample in a nitrogen atmosphere (1 atm.) substituted for the air around the coal before the start of heating. In this case, the initial coal sample in the quartz vessel has a length of 10 cm., as is shown in Table III. The experimental results in the nitrogen atmosphere are shown by the full-lines in Figs. 5a—5d. Minimum and maximum values of the full-line and the dotted line in Figs. 5a—5d are listed in Table III, together with the temperature at which they were measured. These values are classified into first and second values by depth of minimum value. The shape of the curves which have one minimum is similar to that of aqueous solution, as shown in Ref. 13 and Fig. 2. As the length of coal in the quartz vessel changes with heating, the variation of Q/Q_1 and tuning capacity ($\Delta C'$) must be measured for an aqueous solution with the corresponding length in order to compare the results of coal with those of aqueous solution. They are listed in Table IV. It can be concluded from Table IV that the concentration of an aqueous solution which shows a minimum or a maximum has nothing to do with the change of length. However, the minimum value of Q/Q_1 slightly changes with the length, while the maximum value is

TABLE III

Coal	Initial sample length, cm.		Minimum and maximum values of Q/Q_1, % Temperature at each value, °C							
	Nitrogen	Vacuum	Nitrogen				Vacuum			
			1st		2nd		1st		2nd	
			min.	max.	min.	max.	min.	max.	min.	max.
Tempoku	10	10	97.4 475	98.7 540	90.5 640	93.2 680	96.8 500	97.9 550	89.8 620	96.8 680
Nakagō	〃	〃	97.6 510	98.7 560	—	—	97.3 500	98.1 550	91.4 620	98.1 690
Takamatsu	〃	8	—	—	92.4 600	96.7 670	96.3 520	97.7 580	92.6 640	95.0 680
Yūbari	〃	〃	—	—	92.3 570	96.5 660	95.7 570	96.5 600	92.9 640	93.5 660
Shikamachi	〃	7.5	—	—	88.5 600	96.2 660	—	—	90.1 615	94.2 675
Shikamachi (1000 kg./cm^2)	6.5	—	96.7 625	98.2 650	91.7 675	98.7 700	—	—	—	—
S-550°C	—	6.5	—	—	—	—	—	—	91.0 590	97.8 660
Yatake (10% Graphite, 1000 kg./cm^2)	6.5	—	—	—	93.5 625	99.0 650	—	—	—	—
Y-550°C	—	6.5	—	—	—	—	—	—	91.0 570	98.7 650
Uonuki	10	10	—	—	90.8 640	95.4 710	96.3 580	98.4 620	88.0 680	93.1 740
Hongei	〃	7.5	—	—	89.7 580	96.5 740	96.1 375	97.2 500	90.6 640	96.7 760

TABLE IV

Aq. Soln. KCl (N)	Aq. Soln. HCl (N)	$l_0=5.5$ cm. Q/Q_1 ×100	$l_0=5.5$ cm. $\Delta C'$ (pF)	$l_0=6.5$ cm. Q/Q_1 ×100	$l_0=6.5$ cm. $\Delta C'$ (pF)	$l_0=7.5$ cm. Q/Q_1 ×100	$l_0=7.5$ cm. $\Delta C'$ (pF)	$l_0=8.5$ cm. Q/Q_1 ×100	$l_0=8.5$ cm. $\Delta C'$ (pF)	$l_0=10$ cm. Q/Q_1 ×100	$l_0=10$ cm. $\Delta C'$ (pF)
(Dist. water)		99.7	−0.42	99.7	−0.44	99.5	−0.43	99.5	−0.44	99.2	−0.46
10^{-5}		〃	〃	〃	−0.43	99.3	−0.44	99.6	−0.45	99.0	−0.47
	10^{-5}	99.2	−0.43	99.0	〃	98.7	〃	98.8	〃	98.3	〃
10^{-4}		98.7	−0.42	98.5	−0.44	98.5	−0.45	98.3	−0.47	97.9	−0.50
	10^{-4}	98.3	−0.44	98.3	〃	97.9	−0.46	97.8	−0.46	97.4	−0.55
3×10^{-4}		97.9	〃	97.8	−0.46	97.1	(−0.44)	96.9	−0.48	96.7	−0.56
10^{-3}		96.9	−0.47	96.5	−0.49	96.0	−0.50	94·8	−0.50	93.8	〃
	10^{-3}	97.4	−0.52	97.0	−0.52	96.4	−0.52	95.8	−0.54	94.8	(−0.66)
3×10^{-3}		98.1	−0.50	97.3	−0.54	96.3	−0.50	95.7	−0.52	94.7	−0.59
0.01		97.9	(−0.47)	97.7	〃	97.2	−0.56	97.4	−0.56	96.2	−0.66
0.03		99.0	−0.53	98.1	−0.56	97.9	−0.60	98.7	−0.62	98.9	−0.64
	0.01	97.3	−0.54	97.5	−0.55	97.3	〃	97.0	−0.70	95.6	−0.69
0.1		95.2	−0.50	95.2	〃	95.1	−0.66	94.7	〃	93.2	−0.74
0.3		91.9	−0.54	91.2	−0.61	90.0	−0.74	89.5	−0.74	87.4	−0.80
	0.1	90.8	−0.52	89.7	〃	89.6	−0.73	87.9	−0.79	85.9	−0.90
1		83.3	−0.66	82.6	−0.76	82.1	−0.80	81.7	−0.84	82.2	−0.86
3		69.7	−0.69	69.5	−0.94	69.2	−0.86	69.2	−0.88	69.4	−1.05
	1	67.0	−0.80	66.9	−0.97	67.4	−1.00	68.5	−0.99	68.3	−1.07

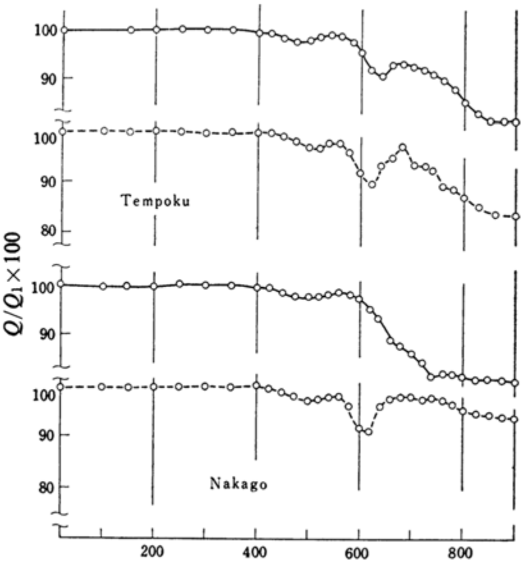


Fig. 5a. Tempoku and Nakagō coals.

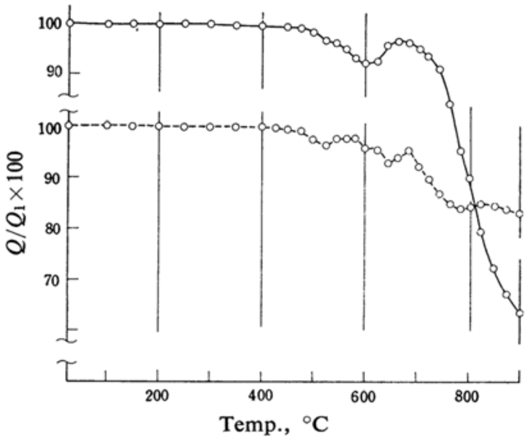


Fig. 5b. Takamatsu coal.

approximately constant. The value of the tuning capacity decreases with the increase of the concentration of the aqueous solution, although it becomes slightly smaller with the increase in the length of solution.

It seems impossible to neglect the change of length in a discussion of the experimental results of coal obtained under heating. Therefore, the following experiments were made. The powder of Shikamachi or Yatake coals was moulded like brick[18] under a pressure of 1000 kg./cm², and it was cut into the proper size for blocks. They were buried in other coal powder, and their temperatures were raised at a suitable rate so as to prevent oxidation and expansion by the gas evolved. In order to keep the heating uniform, they are kept in the last-desired temperature for one hour. After cooling, a cylindrical bar of carbonized coal was made by lathe. The length and the diameter are 6.5 cm. and 1.70 cm. respectively. The results made by measuring these samples at room temperature, are shown by the full-lines in Fig. 6 (refer to Table II, except 640

---

[18] H. Honda, N. Mochida and Y. Sanada, *Rep. Resources Res. Inst.*, No. 44 (1958).

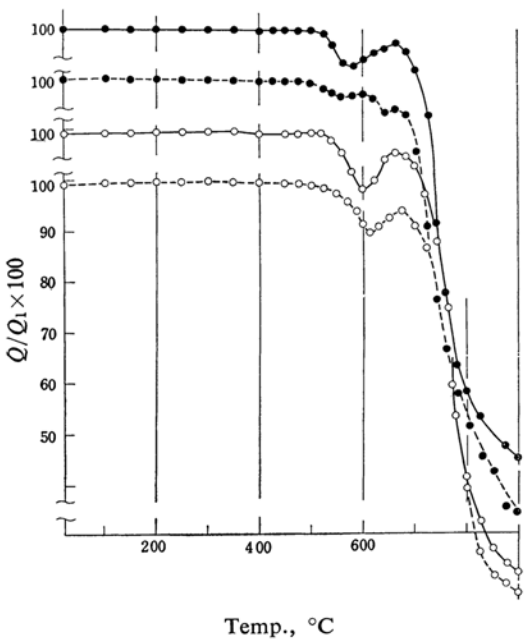


Fig. 5c. Yūbari and Shikamachi coals.
● Yūbari ○ Shikamachi

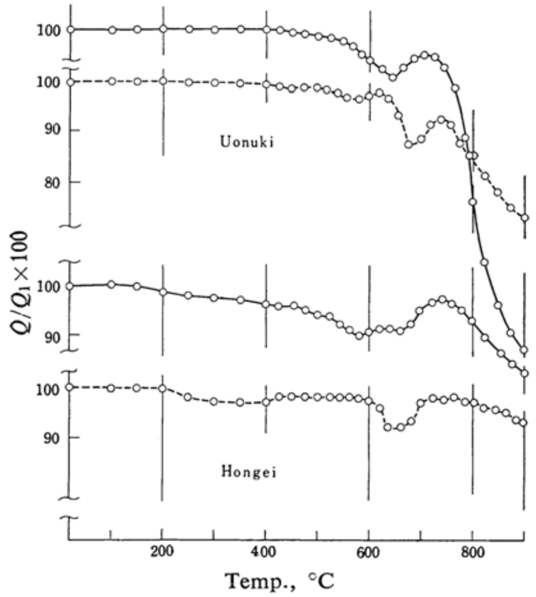


Fig. 5d. Uonuki and Hongei coals.

and 690°C). There exists at least one minimum value near 675°C (Shikamachi) or 625°C (Yatake). To make sure of the depth of the minimum, the bar of Shikamachi or Yatake coal, which had already been heated up to 550°C, was put into the quartz vessel and heated again from room temperature at the rate of 1°C per minute in vacuo. The results obtained are also shown by the dotted lines in Fig. 6.

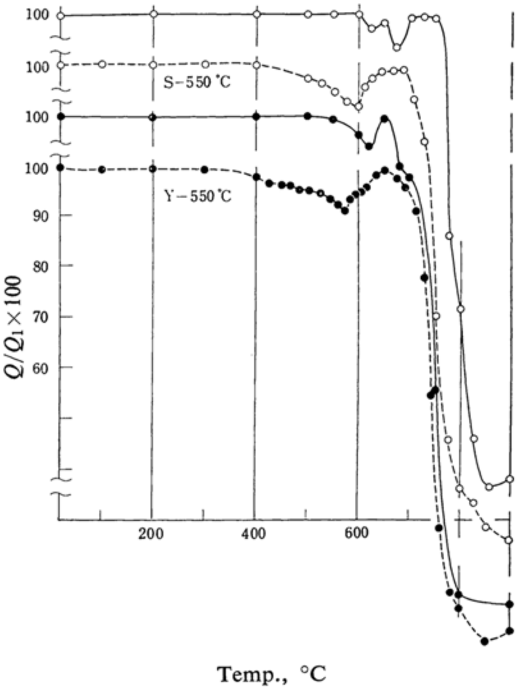


Fig. 6. Shikamachi and Yatake coal bars
○ Shikamachi ● Yatake

Discussion

There exist several papers[19-25] on the subject of the dielectric sonstant of coal. According to Ref. 19, the dielectric constant and loss factor of various coals were measured at room temperature. Each of the test pieces was cut from the vitreous portion of a large block of coal and then carefully made into the form of a circular plate about 4 cm. in diameter. The test pieces thus prepared were kept in the desiccator over phosphoric anhydride for three or four months. The present writer measured the dielectric constant and the dielectric loss factor of various coals by using the abovementioned method, as shown in Fig. 7. There have been few papers[26-28] concerning the

---

19) I. Miyasita, *Bull. Res. Inst. Appl. Elec., Hokkaido Univ.*, 5, 123 (1953); 6, 117 (1954); 7, 17 (1955).

20) M. P. Groenewege, J. Schuyer and D. W. Van Krevelen, *Fuel*, **34**, 339 (1955).

21) I. Miyasita, R. Miura and K. Higasi, This Bulletin, **28**, 148 (1955).

22) I. Miyasita and K. Higasi, ibid., **30**, 513 (1957).

23) K. Higasi, I. Miyasita and Y. Ozawa, ibid., **30**, 546 (1957); I. Miyasita, K. Higasi and M. Kugo, ibid., **30**, 550 (1957).

24) K. Higasi, Y. Higasi and I. Miyasita, ibid., **30**, 556 (1957).

25) K. Chitoku and K. Higasi., ibid., **34**, 320 (1961).

26) Y. Zyomoto and K. Higasi, *Kagaku*, **26**, 638 (1956).

27) Y. Zyomoto, *J. Fuel Soc., Japan*, (*Nenryō Kyokaishi*), **37**, 248 (1958).

28) D. K. Sen, S. K. Sengupta, K. A. Kini and A. Lahiri, *J. Sci. Ind. Research*, **19 B**, 184 (1960).

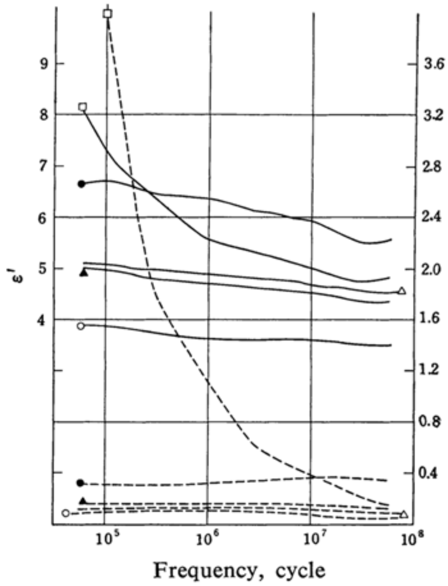


Fig. 7. Frequency dependence of dielectric constant (full-line) and loss factor (dotted line) of various coals.

● Tempoku	△ Shikamachi
▲ Takamatsu	□ Hongei
○ Yūbari	

dielectric constant of carbonized coal. According to Ref. 26, a method using the powder of carbonized coal and paraffin was adopted for measuring the dielectric constant of carbonized bituminous coal. It has been described how the dielectric constant of the mixture increases beyond 600°C, while the dielectric loss factor increases with the temperature to a maximum at about 650°C, above which it decreases with the temperature, reaching a minimum at about 700°C; there is then a sudden increase above about 700°C. According to Ref. 28, a sudden increase in the dielectric constant of the original coals was observed at 600°C. Therefore, the present writer prepared many test pieces of circular plates (5.1 cm. in diameter, about 0.6 cm. in thickness) by pressing the powder of Shikamachi coal under 1400 kg./cm². These samples were carbonized up to the desired temperature at the heating rate of 1°C per minute. The dielectric constant and the loss factor of the sample were measured at room temperature by the method in Ref. 19, but the measurement was rather difficult for the sample beyond 550°C. The results are illustrated in Fig. 8.

It has been implied in Ref. 19 that Japanese coals are constituted mainly of non-polar substances. Furthermore, in Ref. 23, brown coals are found to have a moment near to that of one O–H group and that the polarity of bituminous coal is in general too small to be distinguishable from zero. According to Ref. 20, the ε' values of coals were found to rise very rapidly above 88% carbon content, and the rise was ascribed to a progressive increase in electrical conductance. The dielectric constant of coals used in the present experiment is less than ten, as is shown in Fig. 7. In Ref. 28, the sudden increase in the dielectric constant at 600°C has been attributed to an increase in the electrical conductivity of coals in the region of this temperature. Taking the above-mentioned results into account, it is unlikely that the ε' value of carbonized coal or coal being heated increases to a large value due to the mechanism shown by such polar molecules as water or methyl alcohol.

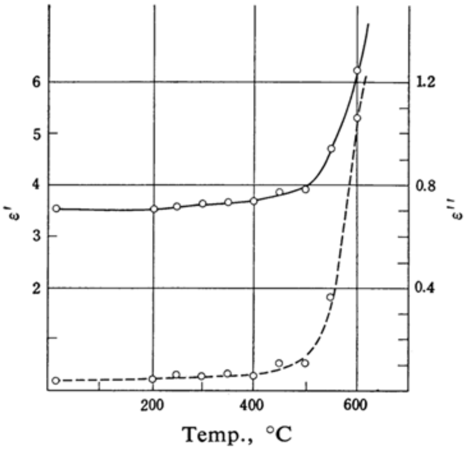


Fig. 8. Relation between dielectric constant (full-line), loss factor (dotted line) and carbonization temperature of Shikamachi coal (circular plate) at 3×10^6 cycle.

The specific resistance, r, at 3×10^6 cycle of carbonized Shikamachi and Yatake coal bars was obtained by the following method. The coal bar, of which a tin-foil with a short wire is attached to each side, was connected parallel to the variable condenser of Q-meter to measure the Q-value, so that the next relation (Eq. 18 in Ref. 15) can be used:

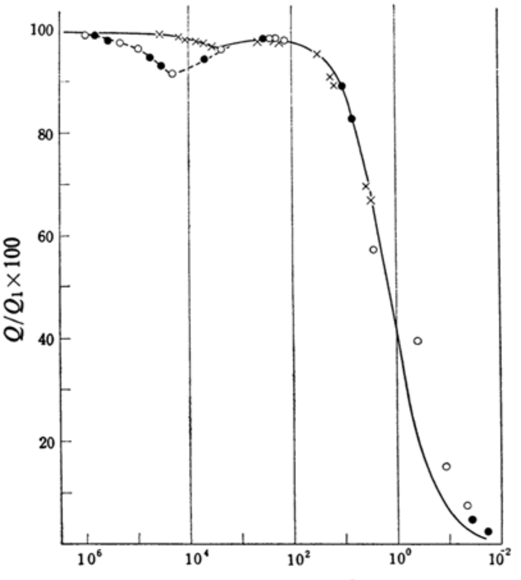
$$r=\frac{1}{\omega C}\cdot\frac{QQ_1}{Q_1-Q}\cdot\frac{\sigma}{h} \tag{2}$$

in which σ is the section area of the coal bar and h its length. There is no sample having the value of $10^2\sim10^4$ $\Omega\cdot$cm., so that the coal bars, S-675°C and Y-625 shown in Table II, are heated again up to 690 and 640°C respectively in vacuo. These results are listed in Table V, and the relation between the value of Q/Q_1 and the specific resistance is shown in Fig. 9 together with that of aqueous solution. The value of specific resistance at direct current

TABLE V

	Shikamachi				Yatake (10% Graphite)			
Temp. °C	r, Ω·cm.		$\varepsilon' C_1 + C_0$ pF	ε' 3×10^6-cycle	r, Ω·cm.		$\varepsilon' C_1 + C_0$ pF	ε' 3×10^6 cycle
	D. C.	3×10^6 cycle			D. C.	3×10^6 cycle		
500					1.4×10^6	$6._6\times10^5$	0.643	4.8
550						$3._6\times10^5$	0.625	4.1
600	5×10^6	$9._7\times10^5$	0.687	6.5	1.7×10^5	$5._6\times10^4$	0.672	5.9
625	7×10^5	$9._5\times10^4$	0.644	4.8	5.9×10^4	3.0×10^4	0.752	9.0
640	—	—	—	—	7.3×10^3	4.7×10^3	1.30	31
650	1.75×10^6	$1.9_6\times10^6$	0.607	3.3	275	300		
675	3.2×10^4	$2.0_3\times10^4$	0.738	8.5	11.9	*13.3		
690	6.5×10^3	$3.5_8\times10^3$	2.33	71	—	—	—	—
700	270				6.6	*7.5		
725	130				—	—		
750	240				0.43	*1.3		
775	3.1	*2.07			—	—		
800	0.366	*1.07			0.034			
825	0.10				—	—		
850					—	—		
900	0.040				0.016			

* Calculated value obtained by Eq. 1.



Specific resistance, Ω·cm.

Fig. 9. Relation between $Q/Q_1\times100$ and specific resistance of carbonized coal or aqueous solution at 3×10^6 cycle.

○ Shikamachi ● Yatake
× Aqueous solution

for some coals carbonized at a higher temperature is used instead of that at 3×10^6 cycle since the latter can not be obtained by using the Q-meter. This manipulation results in several points in Fig. 9 not being located on the curve obtained by Eq. 1 over the range of lower specific resistance. The minimum value of carbonized coals in Fig. 9 is smaller than that of the aqueous solution. The description as shown in Ref. 15, "the minimum value of Q/Q_1 depends on the dielectric constant", is very helpful in understanding this difference in minimum value, because the original coal sample used in the present experiment has a dielectric constant value of less than ten. Therefore, this fact may support the view that there must be the dotted line as shown in Fig. 2 obtained by calculation. The dielectric constant of some of the carbonized coals is calculated by using the value of r at 3×10^6 cycle in Table V and Eq. 1. Above about 2×10^4 Ω·cm., in Table V, the values of ε' of the carbonized Shikamachi and Yatake coals are less than ten, but at the specific resistance lower than this value, they increase rapidly.

The calculation of the dielectric loss factor was done for the carbonized Shikamachi coal bar using the following relation from Ref. 15 and the value of $r(=\rho)$ as shown in Table V:

$$\frac{1}{\rho}=\frac{f(\varepsilon'/\varepsilon_0)\tan\delta}{1.8\times10^{12}}$$

or

$$(\varepsilon'/\varepsilon_0)\tan\delta=\frac{1.8\times10^{12}}{\rho f} \tag{3}$$

From these values, ε' in Table V and Fig. 8, the variation in the dielectric property of the circular plate and the cylindrical bar of Shikamachi coal for carbonization temperature are visualized in Fig. 10, although the value of ε'' of the circular plate and the cylindrical bar at 600°C is slightly different since the value of

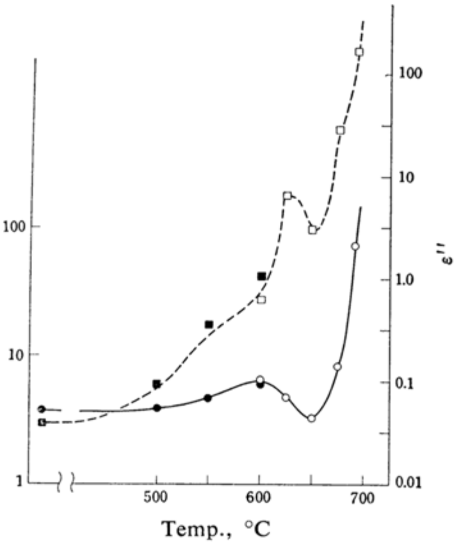


Fig. 10. Relation between dielectric constant (full-line), loss factor (dotted line) and carbonization temperature of Shikamachi coal at 3×10^6-cycle.

● ■ Circular plate
○ □ Cylindrical bar

ε'' of Shikamachi coal increases greatly in the vicinity of this temperature. The dielectric constant not only slightly increases from room temperature to 400°C, but also increases substantially beyond 400°C (refer to Fig. 8), shows a maximum and minimum at 600 and 650°C respectively, and then increases again rapidly. There is a similar tendency in the variation of the dielectric loss factor. However, the dielectric constant decreases in the neighboring range of 625°C, at which the dielectric loss factor shows a maximum value. It seems that this relation has something to do with the anomalous dispersion of carbonized coal shown at about 700°C in Refs. 26 and 27.

Returning to Fig. 6, the Q/Q_1 value of the full-line of the Shikamachi coal bar hardly changes over the range from room temperature to 500°C, since it may be considered that the values of ε' and r do not change greatly over this temperature range. Moreover, the Q/Q_1 value of the full-line has only a little change at the interval of 500~600°C, although the values of ε' and r changes substantially in this range. The variation of Q/Q_1 due to the effect of r appears beyond 600°C. In this case, the value of r, at which the dotted line in Fig. 9 begins to show the decrease of Q/Q_1, is larger than that of the aqueous solution, owing to the difference of dielectric constant between the carbonized coal and the aqueous solution. The Q/Q_1 value of the full-line of the Shikamachi coal bar in Fig. 6 increases in the range of 625~650°C, because the value of r increases greatly in spite of the decrease of ε', and then decreases to the minimum value. Under the conditions of the increase of ε' and the decrease of r, the value of Q/Q_1 increases from this minimum value to the maximum value determined by the effect of the eddy current in the coal sample. Furthermore, the eddy current causes a sudden decrease in the value of Q/Q_1 at a higher temperature, as deduced from the descriptions in Refs. 12—15, because the powders in the coal sample connect with each other owing to the strong caking property of coal. The first minimum of the full-line of the Yatake coal bar is not found in Fig. 6, although it might exist near 600°C. The dotted lines in Fig. 6 have not the first minimum. This result may be considered as due to the fact that the specific resistance in the sample is not uniform because of the low heat conductivity of this sample. It is reasonable that the temperature at the minimum value of Q/Q_1 shifts to the lower temperature side, comparing the dotted line with the full-line since the measurement was done at a high temperature with lower heating rate. The second minimum of the dotted lines in Fig. 6 seems to correspond to the minimum of the dotted line in Fig. 9. According to Table IV in Ref. 15, it is likely that the ε' values of S-550°C at 590°C and Y–550°C at 570°C are the order of 9~10.

The results of the coals in Figs. 5a—5d under the carbonization process show many different curves depending on the grade of coal. They may be caused by the different chemical structures of coal, as deduced from the result of analysis in Table I and the above-mentioned dielectric character. All the curves in Fig. 5a have the first and the second minima except Nakagō's full-line which has no second minimum, the reason for which is difficult to ascertain. These first minimums may be understood by considering the increase of r-value near 500°C, although the length of the samples changes during the carbonization process. Takamatsu coal does not show the first minimum on the full-line in Fig. 5b. It may be considered that the value of ε' would be less than about twenty over the range from room temperature to the second minimum temperature. The sudden decrease of Q/Q_1 in the full-line appears in the range of higher temperatures, whereas the one in the dotted line can not be located. The Yūbari coal lines in Fig. 5c are similar to those of Takamatsu coal as far as the first minimum is concerned. The value of Q/Q_1 of both the lines at higher temperatures sharply decreases to near zero, as do those of Shikamachi and Yatake coals in Figs. 5c and 6. It may be considered that these decreases have shown the effect of eddy current due to the strong caking property of the coals. The ε' value of the carbonized Yūbari coal may be less than twenty till near 560°C. In Fig. 5c, the ε' value of the carbonized Shikamachi coal may be as small as the one of the original coal till the second minimum temperature. The value of Q/Q_1 of Uonuki coal in Fig. 5d decreases quite a bit at higher temperatures, although Uonuki coal is not a strong caking coal. The second minimum value is small, as is that on the full-line of Shikamachi coal in Fig. 5c. It seems that the value of ε' is less than ten at the second minimum temperature. The temperature, at which the first minimum value is shown, is below 600°C except that of Shikamachi coal. Above all, the first minimum value of Hongei (anthracite) under vacuum is located at rather a lower temperature. Both lines for Hongei coal in Fig. 5d begin to change the value of Q/Q_1 from a lower temperature than do those of other coals. These phenomena seem to be attributable to the special chemical structure Hongei coal, as imagined from the frequency dependence of the dielectric constant and the loss factor shown in Fig. 7. Although the coal samples change their length by thermal decomposition, the second minimum values are less than 93.8 per cent, which corresponds to the minimum value of aqueous solution having the length of 10 cm. This fact seems to support the deduction about the dotted line in Fig. 9, by taking it into account that the dielectric constant of the coals under carbonization would be quite a bit less than eighty over the range from room temperature to the respective temperature of the minimum.

Finally, the value of the variation in tuning capacity of carbonized Shikamachi and Yatake coals in Table II decreases with the increase of carbonization temperature over 600°C. It can be considered that these value seems to decrease monotonously with the increase of the dielectric loss factor, because the aqueous solution shows the same relation in Table IV. Comparing the carbonized coal and the distilled water, the variation in the tuning capacity of carbonized Shikamachi and Yatake coals, having a specific resistance of the same order or larger than that of distilled water, is less than that of distilled water, owing to the difference in the dielectric constant between the coal and the distilled water, as expected by Eq. 14 in Ref. 15.

Summary

The relation between the value of Q/Q_1 and the carbonization temperature of coal has been studied for various coals. The shape of the curve depends on the grade of coal. It is significant that the Q/Q_1 value of both the full-line and the dotted line in strongly caking coal suddenly decreases at higher temperatures. Most of the curves have a second minimum value which is smaller than that of the curve for the aqueous solution. This can be understood by taking account of the difference in dielectric constant between the coal and the aqueous solution. This result seems to support the existence of the dotted line in Fig. 2, as well as the opinion in Ref. 14 that the factor, p, would be very important.

The author desires to thank Dr. Hidemasa Honda and Mr. Naoyuki Mochida for their kind discussion and support.

Shigengijutsu Shikenjo
Resources Research Institute
Kawaguchi-shi, Saitama