

DIFFUSION OF IONS INTO COAL: METHOD OF MEASUREMENT,
ORDER OF MAGNITUDE AND DIRECTIONAL EFFECTS

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1. INTRODUCTION

Incorporation of metal ions from solution into the coal structure is becoming a useful method to achieve high contact between the coal surface and the metal ions. However, no data were found in the literature relative to the diffusivity of ions in coal. In this work, preliminary results are reported on the rate of diffusion of ions into coal and on the rate of leaching of ions from coal.

The main results found are that: 1) the diffusivity of ions varies in different directions of a vitrinite particle, relative to the direction of the bedding, and 2) the diffusion coefficient of calcium ions is of the order of 10^{-12} cm²/sec in the direction of the bedding and 10^{-13} cm²/sec in the direction perpendicular to the bedding.

2. EXPERIMENTAL

The coal particles to be examined were hot pressed (70°C, 15000 psi) in polymethyl metacrylate stubs, 3/4" in diameter and 3/8 - 1/2" thick. The stubs were cut through the coal particles and the exposed surfaces were polished under petroleum ether, using cloths 220, 400 and 600 successively. Finishing was done using 0.3 micron alumina powder in petroleum ether. The polished surface was sputtered with carbon and grounded with silver paint.

The surfaces were scanned using a 20000 Volt electron beam and the K_{α} x-rays from the calcium were collected within ± 2 eV. The resolution between the Ca (K_{α}) lines and the K (K_{β}) lines appears to be adequate to allow separation of the calcium.

Scanning of the coal surface was done at the rate of 3 microns/minute and plotted at either 3 microns/inch or 16 microns/inch. The total counts of x-rays were integrated and printed every 20 seconds.

3. MODES OF CALCIUM PENETRATION

The results that are obtained are a signal proportional to the number of atoms of calcium in a segment of volume of the coal specimen, with a shape of a droplet of tear, with an average length of about 6-10 microns and a diameter of 3-5 microns near the surface. This volume will be heretofore titled the "probe volume." Obviously, the signal obtained will not resolve differences in concentrations of calcium associated with features smaller than the probe volume and consequently the signal is only an average measure of the calcium present in the probe volume in all forms. A special mathematical method is being developed to "deconvolute" the signal in order to resolve finer features.

The main modes by which calcium could have penetrated into the coal are:

1. Penetration of Ca^{+2} through pores.
2. Diffusion of Ca^{+2} ions into the solid matrix and forming a Ca-containing intercolate.

Figure 1 shows the form of the signal expected when penetration of Ca occurs into the solid, through a pore oriented parallel to the direction of travel of the beam and through a pore presented perpendicular to the direction of travel of the beam. Since the diffusion coefficient in liquid is substantially larger than in solid, a relatively low incorporation occurs via the micropores ($r < 0.01$ M) and most of the calcium incorporation occurs via the mesopores and the macropores.

Several models can be used to interpret the experimental results. First, the models and their solutions will be described and then data will be presented and interpreted.

3.1 Effective Diffusion through a Thin Layer of Solid

In the case of a thin layer the unidirectional model is applicable.

Thus:

$$\frac{\partial c}{\partial t} = D_s \frac{\partial^2 c}{\partial x^2}, \quad (1)$$

$$c(0, x) = 0, \quad (2)$$

$$c(t, 0) = c_0, \quad (3)$$

and

$$c(t, \infty) = 0. \quad (4)$$

The solution is:

$$\frac{c}{c_0} = \operatorname{erfc} \left(\frac{x}{2\sqrt{D_s t}} \right). \quad (5)$$

x is the distance from the surface, D_s is the effective diffusivity coefficient, and t is the penetration time. The concentration at (x, t) is c and c_0 is the concentration near the surface. The error function complementary, erfc , is defined by:

$$\operatorname{erfc}(z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^z e^{-u^2} du. \quad (6)$$

Obviously:

$$\int_0^\infty e^{-u^2} du = \frac{\sqrt{\pi}}{2} \quad (7)$$

was used to normalize the distributions.

Equation (5) is useful to interpret data for diffusion through a thin layer of solid or effective diffusivity through heterogeneous features smaller than the depth of penetration.

3.2 Effective Diffusion Through a Pore Full with Liquid

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2}, \quad (8)$$

$$c(0, t) = c_0, \quad (9)$$

$$c(x, 0) = 0, \quad (10)$$

$$\frac{\partial c}{\partial x}(\ell, t) = 0. \quad (11)$$

The solution is:

$$\frac{c}{c_0} = 1 - \sum_{n=1}^{\infty} \frac{4e^{-\lambda_n^2 D_L t}}{(2n-1)\pi + (-1)^{n+1}} \sin \lambda_n x \quad (12)$$

$$\lambda_n = \frac{(2n-1)\pi}{2\ell}. \quad (13)$$

The total material diffused after time t is:

$$M = - \int_0^t D \left(\frac{\partial c}{\partial x} \right)_{x=0} A dt = + 4DAc_0 \int_0^t \sum_{n=1}^{\infty} \frac{e^{-\lambda_n^2 D_L t} \lambda_n}{(2n-1)\pi + (-1)^{n+1}} dt$$

$$= - 4DAc_0 \sum_{n=1}^{\infty} \frac{1 - e^{-\lambda_n^2 D_L t}}{[(2n-1)\pi + (-1)^{n+1}] \lambda_n D_L}. \quad (14)$$

The use of equation (14) is not immediately obvious since the total area of pore mouth/unit mass, A , is not readily available and because λ_n depends on the distribution of pore lengths.

4. TESTS PERFORMED

The experimental tests performed can be divided into two classes:

- A. Tests used to develop the method.
- B. Tests on samples exposed to calcium acetate solution at room temperature and atmospheric pressures.

4.1 Method Development

The method that has been developed was described in the previous section. The possibility of inaccurate results due to overlap of consecutive scanning intervals should be addressed. Since the beam is about 4 microns in diameter and a printout is generated every twenty seconds, each printout represents counts taken over 4 microns diameter beam which moved 1 micron. Thus, the second printout will include counts taken from some of the calcium atoms which contributed to the first counts. In addition, since the electron beam damages the surface to some extent, the results may be distorted. The data show, however, that in three Ca curves almost on the same coal surface path, forward, backward and forward again, very little distortion occurred over about 200 microns.

4.2 Incorporation Tests

Samples of vitrinite from an Illinois #6 (Monterey Mine) and of the Colberg seam (W. Va.) were:

1. Leached with HCl 2:1 per 20 min.
2. Mixed with 0.05M calcium acetate solution at room temperature for 78 hours, dried and stored under nitrogen until fixed in the polymer.

The results on the HCl treated samples had a large statistical error built into them but show that:

1. Leaching of calcium occurs through a boundary layer.
2. The thickness of the leached layer is different in different directions of the seam.

For each leaching, the governing equation is:

$$\frac{c}{c_0} = \operatorname{erf} \left(\frac{x}{2\sqrt{D_e t}} \right) \quad (15)$$

The data collected for the first fourteen microns near the surface and the background information are tabulated in Table 1. In accord with equation (15), a plot of $x/(2\sqrt{D_e t})$ vs. x should give a straight line, with slope of $1/(2\sqrt{D_e t})$. The line will not necessarily intersect with the origin, since there is uncertainty relative to the exact location of the surface of the particle. Figure 2 shows that the slope of the line is 806.4 cm^{-1} which corresponds to $D_e = 1.68 \cdot 10^{-12} \text{ cm}^2/\text{sec}$ since the leaching time was 78 hours. Similar calculations for scans in different directions yielded values of D_e in the range of $10^{-9} - 10^{-13} \text{ cm}^2/\text{sec}$. However, it appears that $10^{-12} \text{ cm}^2/\text{sec}$ can be considered a representative number for this coal.

Many samples of coal were treated for periods of 1 hour to 5 days with excess solution of 0.05M calcium acetate in water. The samples were fixed in polymethyl methacrylate base, sputtered with carbon and analyzed as before. The data seem to indicate two modes of penetration of calcium: (A) by diffusion through the surface, and (B) by filling up of pores. Schematically, the calcium signal shows three types of behavior as the electron beam travels from the outside of the particle in (A) gradual decrease in calcium concentration in accord with the diffusion through the surface, i.e., $\operatorname{erfc} [x/(2\sqrt{Dt})]$; (B) large and reasonably fixed level of signal, corresponding to scanning along a pore; and (C) a Gaussian-shaped peak, corresponding to traveling across a pore.

Table 1. HCl leached coal

Distance from Coal Surface (microns)	Counts	$\frac{c}{c_0} = \frac{110}{c_0}$	$\text{erf}^{-1}\left(\frac{c}{c_0}\right) = \frac{x}{2\sqrt{D_e t}}$
-4	2	0.018	-
-3	1	0.009	-
-2	1	0.009	-
-1	3	0.027	-
0	3	0.027	-
+1	10	0.091	0.091
2	12	0.019	0.098
3	13	0.118	0.105
4	20	0.182	0.163
5	36	0.327	0.298
6	47	0.427	0.398
7	52	0.473	0.447
8	69	0.627	0.630
9	74	0.673	0.695
10	71	0.645	0.654
11	77	0.700	0.738
12	86	0.782	0.873
13	73	0.664	0.863
14	96	0.873	1.085

The results of scans of a sample of coal from the Colberg seam, West Virginia, in two orthogonal directions are described below. The data for the first 21 microns are given in Tables 2 and 3. Figure shows that the penetration in the vertical direction is much slower but more uniform than penetration in the horizontal direction. The effective diffusivity coefficient in the vertical direction is about two orders of magnitude smaller than in the horizontal direction.

Table 2. Scanning of Colberg seam coal in the direction of the grain

Distance from Surface (microns)	Counts	$\frac{c}{c_0} (c_0=1973)$	$\text{erfc}^{-1}\left(\frac{c}{c_0}\right)$
-2	1005	0.5094	-
-1	1019	0.5165	-
Coal Particle →	1973	1.0000	-
Surface	1	1860	0.9427
	2	1755	0.8899
	3	1520	0.7704
	4	1336	0.6771
	5	1139	0.5773
	6	941	0.4769
	7	818	0.4146
	8	725	0.3675
	9	566	0.2869
	10	591	0.2995
	11	461	0.2336
	12	442	0.2240
	13	444	0.2250
	14	424	0.2149

Table 3. Scanning of Colberg seam coal perpendicular to the direction of the grain

Distance from Surface (microns)	Counts	$\frac{c}{c_0}$ ($c_0=1973$)	$\text{erfc}^{-1}\left(\frac{c}{c_0}\right)$
-21	60	0.1881	-
-20	61	0.1912	-
-19	74	0.2319	
-18	61	0.1912	
-17	71	0.2226	
-16	80	0.2508	
-15	93	0.2915	
-14	80	0.2508	
-13	106	0.3323	
-12	141	0.4420	
-11	166	0.9204	
-10	166	0.5204	
- 9	184	0.5768	
- 8	217	0.6802	
- 7	205	0.6426	
- 6	253	0.7931	
- 5	278	0.8715	
- 4	271	0.8495	
- 3	282	0.8840	
- 2	260	0.8150	
- 1	278	0.8715	
0	319	1.0000	0.0000
1	264	0.8276	0.1580
2	281	0.7555	0.2210
3	301	0.9436	0.0510
4	262	0.8213	0.1590
5	238	0.7461	0.2280
6	234	0.7335	0.2480
7	235	0.7367	0.2481
8	223	0.6990	0.2750
9	209	0.6552	0.3150
10	239	0.7492	0.2280
11	232	0.7272	0.2460
12	209	0.6552	0.3150
13	175	0.5486	0.4310
14	221	0.6928	0.2790
15	202	0.6332	0.3380
16	224	0.7072	0.2750

5. CONCLUSIONS

The main objectives of this study were achieved:

1. A method has been developed which allows examination of the penetration of calcium ions into coal.
2. The method was applied to study the penetration of calcium into coals.

The data show that calcium penetrates into coal in two main modes: via pores and via regular diffusion. The diffusivity coefficient in the horizontal direction relative to the seam is $10^2 - 10^3$ times larger than in the vertical direction. In the horizontal direction it is $10^{-8} - 10^{-11}$ cm²/sec while in the vertical direction it is of the order of $10^{-12} - 10^{-13}$ cm²/sec. $D_{\text{bedding}} = 7.6 \cdot 10^{-11}$ cm²/sec. $D_{\text{vertical}} = 9.7 \cdot 10^{-13}$ cm²/sec.

Figure 1
EFFECT OF DIFFERENT FEATURES
ON THE PROBE SIGNAL

