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REMOVAL OF CHLORINE FROM ILLINOIS COAL BY HIGH-TEMPERATURE LEACHING

by

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ABSTRACT

The objectives of this research are to: (1) conduct experimental investigations of the removal of chlorine from coal by high-temperature leaching; (2) identify important factors affecting the chlorine removal process; (3) understand the mechanisms involved; and (4) develop a mathematical model to describe the process. A generalized mathematical model based on diffusion and relaxation has been developed for water leaching of chlorine from coal. The model has been fitted to four different samples of Illinois No. 6 coal: C22175, C22651, C8601, and C8602. The weight percent of chlorine ranged from 0.42 to 0.82. The experimental data on these samples covered a temperature range of 297 to 370K and a particle size range of -60 to -325 mesh. Based on the type of coal and the conditions of leaching, it was found that 40 to 80% of the original chlorine could be leached from the coal matrix. The model based on diffusion-relaxation concept predicted the leaching data within ± 5% average absolute deviation. The diffusion rate constants at different temperatures were correlated to Arrhenius type relations. Attempts made to correlate the constants in the Arrhenius equations with the chlorine content in coal and with particle size have been discussed. The water leaching data were used to extract Fickian diffusivities based on the time required for 50% desorption. The calculated diffusivity values ranged from 0.6 to 3 X 10^{-11} cm^2/sec. The effect of chemical additives on the rate of leaching has also been studied. Both HNO_3 and NH_4OH were used as additives. In the case of HNO_3 addition, the rate increased significantly in the initial phase of leaching. After two hours leaching time, the percent of chlorine removal with HNO_3 addition was more than twice as much as that obtained without addition. NH_4OH addition also improved the chlorine removal from coal, but to a lesser extent.

INTRODUCTION

The corrosive effect of chlorine on boiler tubes is well documented and, as a result, there have been renewed efforts to pretreat coal to remove sodium and chlorine prior to combustion. Crumley et al. (1955) have described the formation of bonded alkali deposits in boilers. Crossley (1948) has described the deposits on boiler tubes, and Marckell and Miller (1956) have described pilot plant studies. Ely and Barnhart (1963) have reviewed the corrosion of superheater and reheater tube banks. Jackson and Ward (1956) found, based on the experiments conducted by the Central Electricity Authority, that upon combustion, coals with chlorine content greater than 0.5 wt % formed bonded deposits. Besides the corrosion of boiler and boiler tubes, it has been reported by Newcombe (1980) that higher chlorine content causes abrasion and corrosion problems in the flue gas desulfurization equipment. Other complications that may arise by burning coal containing chlorine have been discussed by Michel and Wilcoxson (1955), Anderson and Diehl (1955), Jonakin et al. (1959), and Gluskoter and Reese (1964).

The removal of chlorine depends not only on the nature of the coal, but also on the nature of chlorine in coal. There is sufficient evidence to believe that chlorine is present in both the organic and inorganic forms. Without getting into details, it will suffice to say that interesting conclusions have been drawn by Crossley (1963), Gluskoter and Ruch (1980), Saunders (1980), and Cox (1984).

Based on a study of 29 coals, Edgecomb (1965) concluded that the removal of chlorine by water leaching depends on the particle size. He also found that most of the chlorine could be removed as hydrochloric acid by heating coal in air around 473K. Daybell and Gilham (1959) and Daybell and Pringle (1967) have also contributed to solving the problem of water leaching and have verified the conclusions of Edgecomb (1965). The work of Daybell and Gilham (1959) was continued and translated into a pilot-plant study by Gilham (1960).

The paper by Bethleheim and Hann (1980) appears to be the first paper wherein it is shown that the transport of chloride ions from coal particles by water leaching is controlled by diffusion. The authors however, used the Fickian diffusion law which is not applicable to leaching of chlorine from coal. Considerable amount of work on water leaching of chloride ions has been carried out by Readett et al. (1984,1986) at the South Australian Institute of Technology. They have modeled the leaching process based on a two-step liquid film diffusion and particle diffusion transport. The authors found better agreement with Fick's law for larger particles.

Almost at the same time, Chen et al. (1986) correlated leaching data for several Illinois No. 6 coals containing different weight percentages of chlorine. At about this time, the findings at the Battle laboratories were published by Muralidhara et al. (1986). Their results show that Fickian diffusion does not correlate their results even at very low values of $(Dt/a^2)^{0.5}$ or large values of a. This is contrary to the findings of Readett et al. (1984,1986), which may be due to the effect of pressure. These investigators have used high temperatures, up to 448.14K, and a pressure of 13 bars in their leaching experiments. The addition of CaO helped chlorine extraction, a subject also discussed by Chen and Pagano (1986) earlier.

This paper presents leaching data for Illinois No. 6 coal for different particle sizes and a generalized model which shows that the diffusion process does not follow Fickian diffusion. A previous paper by the authors presented an empirical relation to correlate leaching data for Illinois coals containing 0.42 to 0.82 wt % chlorine and for a single particle size. It is shown in this paper that the present relation also fits the data for the earlier paper, and it is shown further that the earlier empirical relation is an approximation of the present generalized model. Also, the theoretical background of the model lends itself for the calculation of approximate values of diffusivity.

Basic Considerations

The desorption kinetics in spheres of radius r at any time t is given by Crank (1957):

$$C_s/C_o = 1 - \frac{6}{\pi^2} \sum_{n-1}^{\infty} \frac{1}{n^2}\, exp\,(-Dn^2 \pi^2 t/r^2), \tag{1}$$

where C_s/C_o is the fraction of chlorine desorbed. Equation 1 describes the desorption data from spherical particles if appropriate values are chosen for diffusion coefficient, D and the effect of chlorine in the leaching solution is taken into account in the case of batch leaching processes.

However, the ability of Equation 1 to describe the leaching of chlorine from coal is limited due to the heterogeneity of particles such as the complex pore size, distribution, and tortuosity that exists in coal, the particle size and shape of coal particles, and the physiochemical changes such as swelling, etc. that occur in any coal process or treatment. Nevertheless, it is essential to understand the process as diffusion is the controlling factor in several coal modification processes. To gain an insight into the leaching process, Equation 1 is approximated to:

$$(1 - C_s/C_o) = 6/\pi^2\, exp\,(-D\,\pi^2\, t/r^2) \tag{2}$$

by retaining only the first term. We further note that as C_s/C_o is the fraction of chlorine leached, $(1 - C_2/C_o)$is the fraction of chlorine remaining in coal at any time. Therefore, in terms of the fraction of chlorine remaining in coal, Equation 2 can be rewritten as:

$$ln(1 - C_s/C_o) = ln(6\pi^2)\, \frac{D\pi^2 t}{r^2}\ . \tag{3}$$

From here on, $(1 - C_s/C_o)$ represents the fraction of coal remaining in coal at any time t. Writing $ln(6/\pi^2)$ as a constant ¢, so that it also includes any anomolies arising out of such factors as swelling, etc. and replacing $D\pi^2/r^2$ by a constant K, we can rewrite Equation (3) as

$$ln(1 - C_s/C_o) = -Kt^n + ¢, \qquad (4)$$

where n = 0.5 represents Fickian diffusion and n < 0.5 represents anamolous diffusion. Based on our previous work (Chen and Pagano 1986) and the fact that sorption-desorption in coal particles is anamolous (Crank 1957), we use a value of n = 1/3.

EXPERIMENTAL

The apparatus and the methods have been outlined in detail (Chen et al. 1986, Chen and Pagano 1986). The proximate analysis of the sample C8601 on a moisture free basis was:

ash = 7.96,
volatile matter = 35.38,
fixed carbon = 56.65, and
chlorine = 0.42.

All analyses were done on a wt % basis. The heating value, as determined by bomb calorimetric method, was 7314 cal/g. In the batch leaching experiments, 20 g of the sample was suspended in 200 g of water. The contents were rocked in a constant temperature bath (Model Lufran Type II ± 1.0°C) for different time intervals. The analysis for chlorine was carried out using an Ion 85 ion-analyzer, previously calibrated using standard sodium chloride solution. The experiments were carried out at four temperatures: 297.15, 333.15, 353.15, and 370.15K. The temperatures from now on will be rounded off to the nearest degree. Typical results are shown in Table 1 for -200 mesh size.

DATA TREATMENT

The data for different particle sizes via -20, -60, -100, -200, and -325 mesh sizes, at four temperature levels for each mesh size, were fitted to Equation 4. The values of K and ¢ are recorded in Table 2. Figure 1 shows the values of K plotted against reciprocal absolute temperature. The values of K were fitted to the equation:

$$K = A\, exp\,(B/T) \tag{5}$$

for each particle size, and the values of A and B are tabulated in Table 3. The results of Table 2 show that Equation 4 gives an excellent description of the leaching data for all particle sizes and at all temperatures. Physically, in Equation 4 the first term represents the diffusional process; therefore, the constant K has to be a function of temperature. The second term ¢ can be looked upon as representing a relaxational process such as the swelling of coal particles, changes in the internal pore structure not only due to swelling but also due to the leaching of mineral matter, etc. These processes are very weak functions of temperature; therefore, an average value of ¢ should not increase the average absolute deviations recorded in Table 2. To verify this argument, these average ¢ values (recorded along with A and B in Table 3), together with K from Equation 7, were used to predict the leaching data. The average absolute deviations shown in Table 2 were calculated using the equation:

$$AAD = Average\ Absolute\ Deviation\ Percent = \frac{(C_S/C_O)_E - (C_S/C_O)_C}{(C_S/C_O)_E}\ x\,100 \tag{6}$$

where: subscript E = experimental, and

subscript C = calculated.

These values justify the argument that ¢ is a weak function of temperature and that diffusional and relaxational parts can be separated. This type of phenomena and arguments had been extended earlier, in the case of polymeric substances (Berens and Hopfenberg 1978), and, recently, in the case of coal particles (Lucht and Peppas 1981).

A very useful approximation of Equation 1 is given by the time required for 50% desorption, which allows the evaluation of diffusivity by the relation

$$D = \frac{0.0076\, d^2}{t_{1/2}} \,. \tag{7}$$

where: d = particle diameter in cms.,

t = time in secs., and

D = diffusivity in cm^2/sec.

Table 4 gives a summary of the diffusivity calculated using Equation 7 at different temperatures and sizes. The values of diffusivities range from 0.6 to 3 x 10^{-11} cm^2/sec which are comparable to the effective diffusivity values quoted by Bethleheim et al. (1982). These diffusion coefficients should be treated as very approximate and used with caution. This is mainly because of the distribution of the particle size below a mesh size used in the leaching experiments. The distribution of the particle size for the different mesh sizes is recorded in Table 5 which shows the breadth of the size distribution. The diffusivities calculated using Equation 7 are based on the solution of the Fickian diffusion equation, $t^{0.5}$; it should hold good only for small values of t. It was, therefore, interesting to use Equation 1 and evaluate the fraction of chlorine in coal using the diffusivity evaluated using Equation 7.

Effect of Chemical Additives

Figure 2 shows a plot of percentage of chlorine removed versus leaching time for C8602 coal with -60 mesh size and at 97°C. It can be seen that a significant increase of chlorine removal resulted from the HNO_3 addition. After 2 hr, the percentage of chlorine removal with the chemical additive was twice as much as without the addition. Equilibrium values were approached after two hr of leaching with the chemical additive, whereas a slow rate of leaching continued for a long period without chemical addition.

The amount of HNO_3 added to the aqueous suspension had some effect on the percentage of chlorine removal (see Figure 3). However, the effect was only secondary after the initial addition. Table 6 summarizes the results of the HNO_3 addition study.

Some experiments were carried out with NH_4OH addition. The preliminary data are shown in Table 7.

By comparing the date between HNO_3 and NH_4OH additions, it seems that the HNO_3 addition enhanced the chlorine removal more than the NH_4OH additions.

CHLORINE DISTRIBUTION

In order to determine the chlorine distribution in coal structure for each coal studied, an apparatus is being modified to permit study of the rate of chlorine released from coal as it is heated in a tubular furnace in the presence of a flowing gas stream. It is anticipated that the chlorine evolution behavior of the different coals being studied may be related to the relative amounts of inorganic and organic chlorine present in the coals and their response to chlorine removal by high temperature leaching.

A Fisher total sulfur analyzer is being modified to perform these analyses. A replacement temperature controller has been ordered that will permit control of the heating rates at the lower temperature range (200 to 600°C) of interest for these studies. Up to eight pre-set heating rates or isothermal periods may be preprogramed; this will provide the flexibility required in development of the analytical technique.

REFERENCES

Anderson, C. H., and E. K. Diehl. 1955. ASME paper 55-A-200.

Berens, A. R., and H. B. Hopfenberg. 1978. Polymer 19:490.

Bethleheim, J., W. W. Hann, and K. G. Saunders. 1982. Journal of the Institute of Energy (London) 55:222.

Bethleheim, J., and W. W. Hann. 1980. Journal of the Institute of Energy, September.

Chen, H .L., and M. Pagano. 1986. Fuel Processing Technology 13:261.

Chen, H. L., N. M. Rao, and D. S. Viswanath. 1986. Fuel Processing Technology 13:271.

Cox, J. A. 1984. Annual Technical Report to the Department of Energy, Pittsburgh, PA.

Crank, R. J. 1957. The mathematics of diffusion. 2nd ed. London: Oxford Press.

Crossley, H. E. 1963. Journal of the Institute of Fuel 36:228.

Crossley, H. E. 1948. Transactions of the Institute of Chemical Engineering 26:131.

Crumley, P. H., A. W. Fletcher, and D. S. Wilson. 1955. Journal of the Institute of Fuel 28:119.

Daybell, G. N., and E. W. F. Gilham. 1959. Journal of the Institute of Fuel 32:589

Daybell, G. N., and W. J. S. Pringle. 1967. Journal of the Institute of Fuel, January.

Edgecomb, L. J. 1965. Fuel 35:38.

Ely, F. G., and D. H. Barnhart. 1963. In Chemistry of coal utilization. ed. H. H. Lowry, pp. 820-891. New York: Wiley.

Gilham, E. W. F. 1960. Journal of the Institute of Fuel 33:163.

Gluskoter, H. J., and O. W. Reese. 1964. Illinois State Geological Survey, Circular No. 372.

Gluskoter, H. J., and R. R. Ruch. 1980. Illinois State Geological Survey Report.

Jackson, P. J., and J. M. Ward. 1956. Journal of the Institute of Fuel 24:380.

Jonakin, J., G. A. Rice, and J. T. Reese. 1959. ASME paper 59-Fu-5.

Lucht, L. M., and V. A. Peppas. 1981. In Chemistry and physics of coal utilization, eds. B. R. Cooper and L. Petrakis, p. 18. New York: American Institute of Physics.

Marckell, W.G., and J. M. Miller. 1956. Journal of the Institute of Fuel 24:380.

Michel, J. R., and L. S. Wilcoxson. 1955. ASME paper 55-A-95.

Muralidhara, H. S., R. Venkateswar, and S. P. Chauhan. 1986. Separation Science Technology 21:625.

Newcombe, K. J. 1980. Application of Illinois coal. Carbondale: Southern Illinois University at Carbondale, Coal Research Center.

Readett, D. J., K. B. Quast, D. E. Mulcahy, and I. G. Ketteridge. 1984. In Proceedings, Symposium on Extractive Metallurgy, pp. 103-109. Australian Inst. Mining and Metallurgy, Melbourne, Australia.

Readett, D. J., S. F. Hall, K. B. Quast, and I. B. Ketteridge. 1986. Paper presented at CHEMECA, Adelaide, Australia, August, pp. 325-329.

Saunders, K. G. 1980. Journal of the Institute of Fuel 55:110.

Tables and Figures

Table 1

Typical Leaching Rate Data for Illinois No. 6 Coal Sample C8601 Particle Size: -200 mesh

Temp (K)	Time (minutes)	Fraction of Cl Left in Coal (wt %)
297	60	0.8288
	90	0.8116
	120	0.7971
	180	0.7693
	240	0.7502
	300	0.7340
	360	0.7202
	480	0.7039
333	60	0.8100
	90	0.7830
	120	0.7660
	180	0.7170
	240	0.6850
	300	0.6580
	360	0.6360
	480	0.6120
353	60	0.7420
	90	0.7120
	120	0.6870
	180	0.6740
	240	0.6420
	300	0.6120
	360	0.5910
	480	0.5720
370	60	
	90	0.6480
	120	0.6220
	180	0.6080
	240	0.5870
	300	0.5550
	360	0.5450
	480	0.5130

Table 2

Values of Constants K and ¢, Obtained by Fitting Experimental Leaching Data, Illinois No. 6 Coal C8601

Particle Size	Temperature (K)	K x 10^2	-¢ x 10^3	AAD	ADD*
-20	297	2.7719	-60.8726	1.0	1.6
	333	3.4647	-3.6312	1.8	2.3
	353	4.0247	-19.5224	0.8	0.5
	370	4.3288	3.7531	1.0	1.1
-60	297	2.7697	10.3190	0.5	0.8
	333	3.6773	6.4666	1.5	2.7
	353	4.8001	6.9324	1.5	1.7
	370	6.2697	-4.3452	2.0	1.7
-100	297	4.0270	55.0924	1.0	4.8
	333	4.0781	82.3831	2.0	2.4
	353	5.3492	35.2417	0.5	3.5
	370	7.5795	29.2490	1.5	1.7
-200	297	4.0164	33.4027	0.5	1.5
	333	7.1620	-67.49	1.0	4.4
	353	6.748	33.4146	1.0	3.5
	370	6.8062	126.0112	1.0	2.5
-325	297	6.7815	6.5010	1.5	1.6
	333	12.6771	-179.8180	2.0	4.3
	353	8.4627	178.9081	1.0	4.4
	370	13.3635	35.0236	5.0	5.1

*Average Absolute Deviation Percent using average values of ¢ and Equation 5 for K.

Table 3

Values of Constant A and B in Equation 5

Mesh Size	Average Particle Diameter (cms)*	A	B	¢
-20	0.0418	0.9576	1107.5	0.0198
-60	0.0142	1.0773	1098.2	-0.0192
-100	0.0114	1.1262	1023.5	-0.0232
-200	0.0068	1.3419	1016.3	-0.0312
-325	0.004	2.1408	1009.1	-0.0102

*The average particle diameter in cms is based on the screen diameter and percentage of particles passing throug a particular screen.

Table 4

Diffusivity x 10^{11} (cm^2/sec) from Water Leaching Data

Temperature (K)	Particle Size			
	-325 Mesh (0.004 cm)	-200 (0.0068 cm)	-100 (0.0114 cm)	-60 (0.0142 cm)
370	2.252	1.794	2.776	2.365
353	0.844	0.861		
333	0.676			

Table 5

Coal Particle Size Distribution

Mesh Size	Distribution		Mass Mean Diameter (m)
	Mesh	%	
-20	- 20	65	418
	- 60	14	
	-100	8	
	-200	4	
-60	- 60	44	142
	-100	33	
	-200	23	
-100	-100	68	114
	-200	32	
-200	-200	80	68
	-270	15	
	-400	5	
-325	-200	6	40
	-270	56	
	-400	38	

Table 6

Experimental Data of Chlorine Removal With or Without HNO_3 (0.16M) Addition at 97°C. Coal Particle Size -60 Mesh

Sample Identity	Chlorine in Coal (%)	Chlorine Removal (%)	
		Without HNO_3 Addition	With HNO_3 Addition
No. 5	0.45	23.2	45.8
No. 6	0.34	15.0	39.0
C22175	0.42	56.0	69.0
C8601	0.42	43.2	68.1
C8602	0.40	27.7	57.1
C8701	0.35	58.5	67.5

Table 7

Experimental Data with NH_4OH Addition for C8602 -60 Mesh Coal Particle Size, 97°C

NH_4OH Concentration (M)	Chlorine Removal (%)
0	26.7
0.1	30.5
1.0	36.5
2.0	37.0

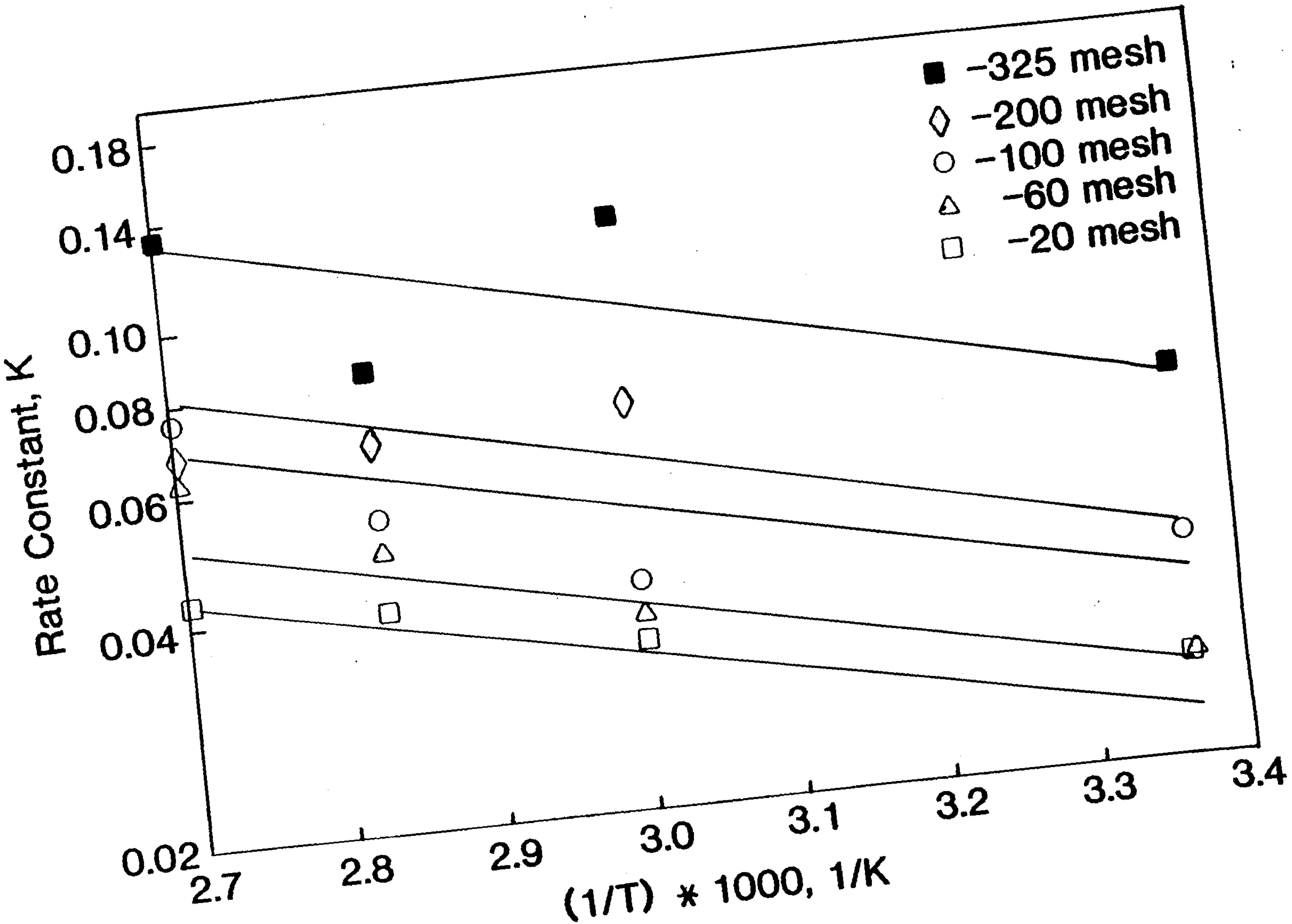

Figure 1. Value of constant K vs. reciprocal absolute temperature.

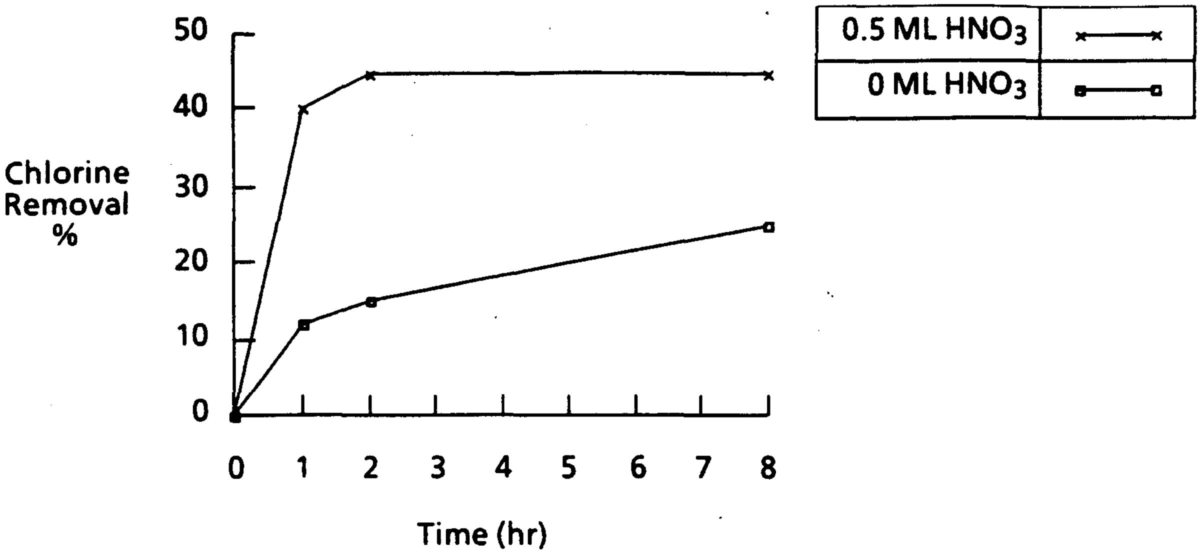

Figure 2. Effect of nitric acid addition on chlorine removal, C8602 coal, -60 mesh at 97°C.

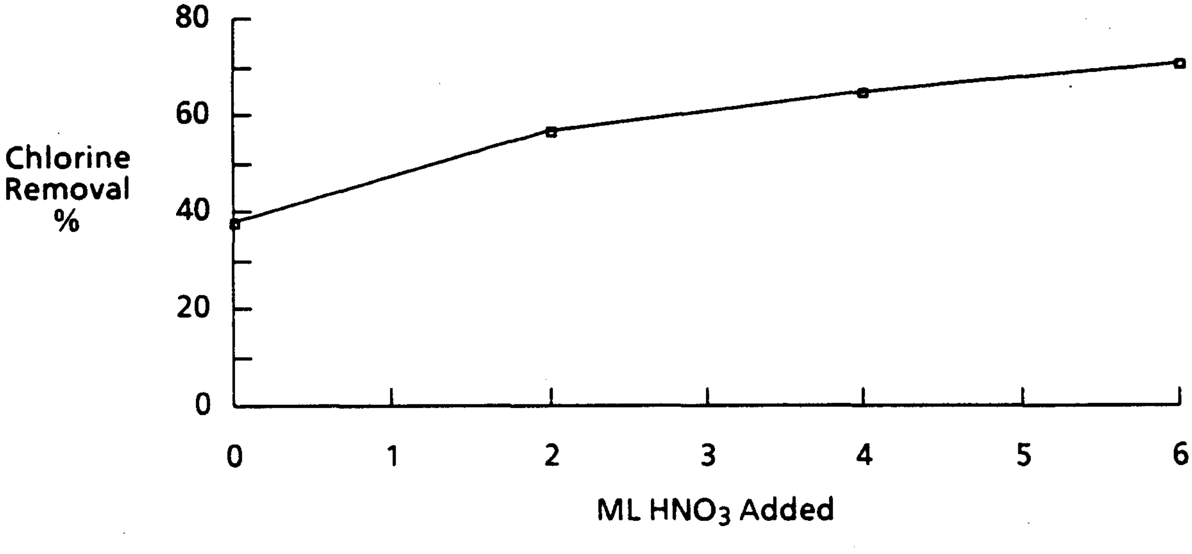

Figure 3. Effect of amount of nitric acid added on chlorine removal, C8601 coal, -200 mesh, 4 hr leaching time at 97°C.