

1-1-1999

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# Chlorination of Two Turkish Lignites in Water and Water-Carbon tetrachloride Media

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Received 10.06.1997

The chlorine uptake of two Turkish lignites during chlorinolysis with chlorine gas in water and water-carbon tetrachloride media at ambient pressure ( $\cong 610$  mmHg) was examined. The effects of speed of stirring ( $5-20 s^{-1}$ ), particle size (74-88, 150-180 and 250-425  $\mu m$ ), temperature (13-70°C) and chlorination time (0-18000 s) were studied. It is shown that the amount of chlorine uptake of both coals increased with decreasing particle size and increasing temperature.

## Introduction

The chlorination of coal is being considered on the basis of some empirically designed experiments as a possible method for coal desulfurization<sup>1,2</sup>. From a practical point of view knowledge of the characteristics of the chlorinated coals and their relationship with the operation conditions are of the utmost importance. Structurally, coals are extremely complex. It is believed that coals contain alkyl-substituted polynuclear aromatic aggregates linked to each other by methylene, ether and heteroatom (O, N, S) bridges<sup>3,4</sup>. These complex units contain diverse aliphatic, cyclic and aromatic C-C and C-H bonds with very different reactivities with chlorine. Therefore, it is probable that chlorination of these complex molecules will result in C-Cl bonds with very different properties and in varying proportions, which depend on the experimental conditions, as in the chlorination of alkyl-substituted aromatic compounds<sup>3,5</sup>.

The chlorine is strongly bounded to aromatic structures to the coal matrix by chlorination of coal in the gas phase at high temperature ( $\cong 400^\circ C$ ) and elevated pressure. Latter removal of the chlorine would be very difficult and, therefore, expensive<sup>6</sup>. For the coal chlorinated at low temperature and ambient pressure in aqueous and organic media, the chlorine can be slightly bounded to coal and removed completely as hydrogen chloride by heating at 350-550°C<sup>6,7</sup>.

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Some aspects of coal chlorination have been studied<sup>5,8-11</sup>. In most of these studies, the coal chlorination have been carried out with chlorine gas in high temperature in bituminous coals. Halogenation is one of the most powerful classic methods used in the chemical investigation of the structure of a compound and in the preparation of commercially useful materials<sup>8-11</sup>. Ball and Mitchell<sup>12</sup> investigated the halogenation of a low rank coal (76%C) using chlorine gas and characterization of the residue by means of elemental analysis, infrared analysis, solvent extraction, hydrolysis, and reactivity with ethanolamine and butylamine. They found that the amount of chlorine taken up, and the proportion evolved as the halide, is controlled by mass-transfer processes at temperatures up to 200°C and at higher temperatures there may be a change in the reaction mechanism. Furthermore, Gonzalez de Andres et al<sup>3</sup> reported that chlorination of bituminous coals seems to occur through substitution and addition mechanisms, the additions taking place mainly at long reaction times and that aliphatic or aromatic nature of C-Cl bonds can be determined by FT-IR spectroscopy, by measuring the changes in the absorbances at 2920 and  $\approx 800\text{cm}^{-1}$ .

The most commonly investigated chemical reaction of chlorinated coal has been hydrolysis. Much of the chlorine may be removed not only by heating at 350-550°C in steam or inert gas but also by one of several hydrolysing reagents. Amines, aniline-nitrobenzene dimethyl aniline- and dimethyl benzyl amine-carbon tetrachloride solution are used as hydrolysing reagents<sup>9,12</sup>.

Consequently, the nature of resulting C-Cl bonds during chlorination and their relationship with the experimental conditions were investigated. Although the uptake of chlorine of coal during chlorination has been repeatedly reported there is little of information about its kinetics, the rate of chlorine uptake as relationship with chlorination and experimental conditions. The information nature of C-Cl bonds formed during chlorination and kinetics of occurring reactions are necessary for the design of coal desulfurization methods<sup>6,7</sup>.

This paper is concerned with the halogenation of two Turkish Lignites using chlorine gas under various experimental conditions. For this, the effects of chlorination time, stirring speed, particle size and temperature on the rate of chlorine uptake of coal were studied.

## Experimentals

### Materials

Dadađı and Mengen coal samples used in this investigation were collected from Dadađı and Mengen coal mines, respectively, in Turkey. The samples were air dried, ground and then sieved to give 250-425, 150-180 and 74-88  $\mu\text{m}$  size fractions using ASTM standard sieves. The analysis performed by ASTM<sup>13</sup> methods for the two coal samples are given in Table 1.

### Methods

The chlorination experiments were carried out in a 250 mL glass flask reactor heated by a constant temperature bath at ambient pressure ( $\cong 610\text{ mmHg}$ ), furnished with a mechanical stirrer, a chlorine gas bubbler and a reflux condenser. For each run, 6 g of coal plus 150 mL of water or water-carbon tetrachloride (5mL water + 145 mL carbon tetrachloride for Dadađı coal and 10mL water+140 mL carbon tetrachloride for Mengen coal) presaturated with chlorine gas at the desired temperature were placed in the reactor and then chlorine gas was bubbled through the system for various periods of time at the desired temperature. In the experiments, speed of stirring, gas flow rate and solid-to-liquid weight ratio were  $14\text{s}^{-1}$ ,  $350\text{mL min}^{-1}$  and 1/25, respectively, unless otherwise stated.

At the end of treatment for the experiments in aqueous media, the reactor contents were filtered as rapid as possible in order to prevent going on of the chlorination, washed with distilled water. Then, the solid was dried in oven for 2 h at 105 °C, cooled and weighed. The chlorine content in coal was determined by Eschka method as described in the ASTM method<sup>14</sup>.

For the water-carbon tetrachloride runs, after the chlorination step the solvent phase was evaporated under reduced pressure and then 350 mL of distilled water was added to the chlorinated coal and it was hydrolyzed at the boiling temperature (94 °C) of water for two hours and then filtered, washed with distilled water. The coal filter cake was dried in oven for 2 h at 105 °C, cooled and weighed. The chlorine content was determined as stated before<sup>14</sup>.

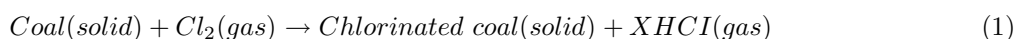
**Table 1.** Proximate, sulfur forms analysis and heating value of studied coals. Results are averages of duplicate analyses (as received)

	Coal	
	Dadağı	Mengen
Proximate analysis (wt %)		
Ash	21.05	25.93
Volatile matter	35.98	41.58
Fixed carbon	37.04	26.21
Moisture	5.93	6.28
Sulfur distribution (wt %)		
Total	7.93	12.25
Sulfate	0.25	0.06
Pyritic	4.31	1.69
Organic	3.37	10.50
Chlorine	0.14	0.10
Heating value (cal/g)	5936	5825

## Results and Discussion

### Chlorination

If the reaction between coal and chlorine gas is adequately expressed by the equation<sup>12</sup>.

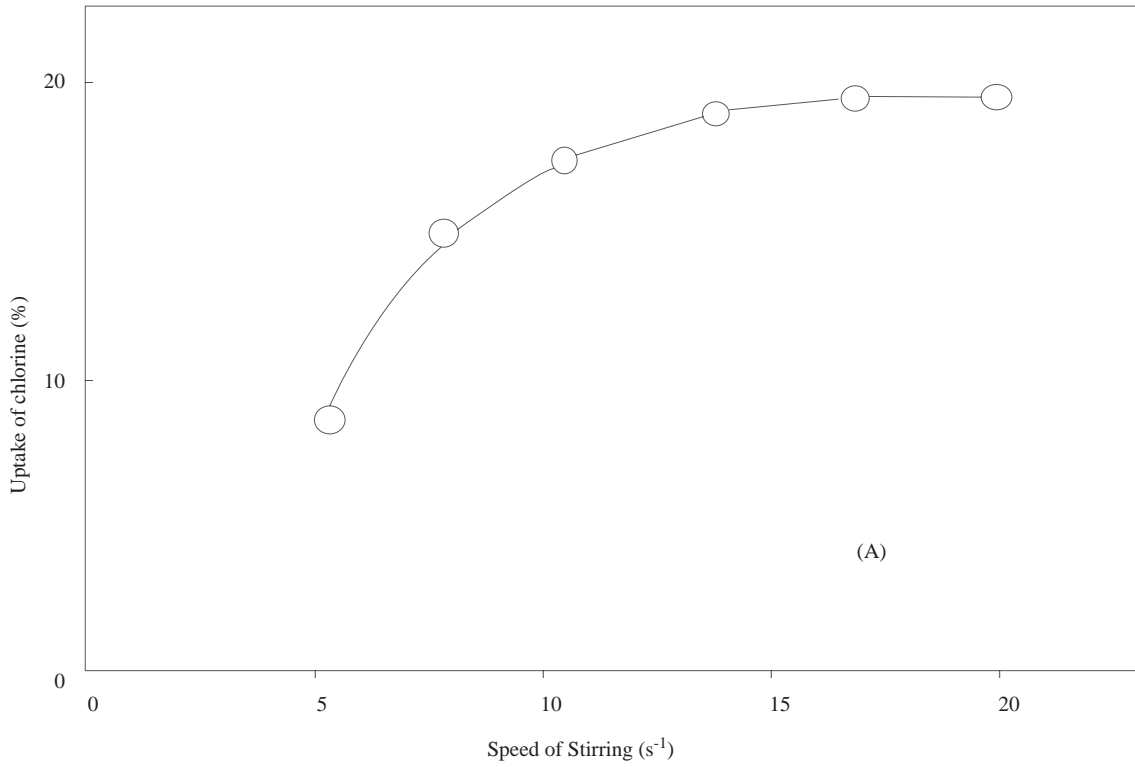


then some or all of the following processes may occur.

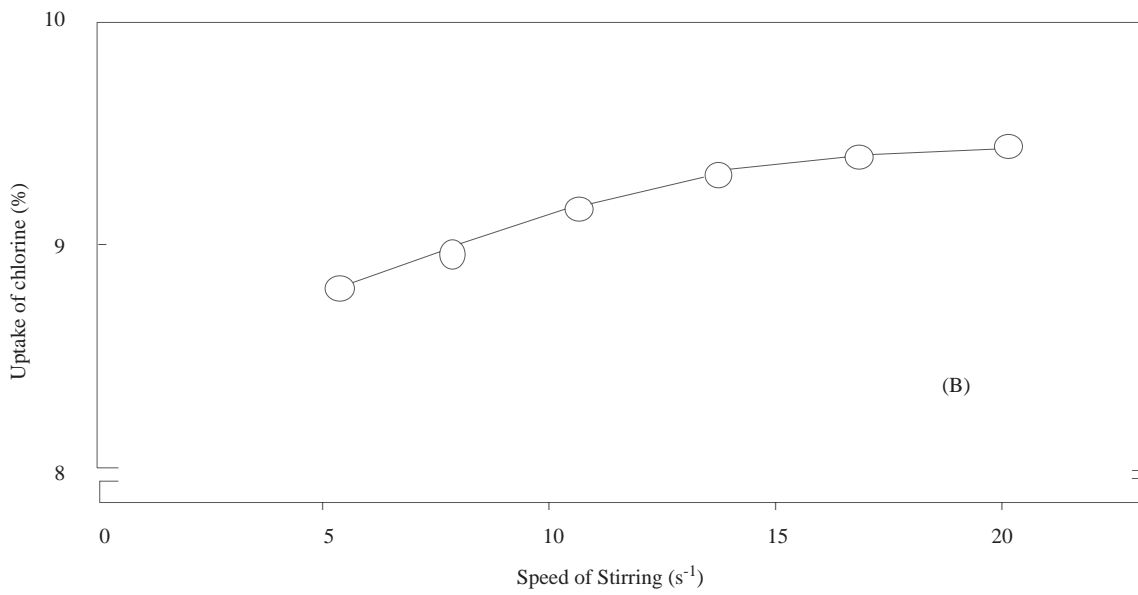
1. Diffusion of chlorine through the fluid film surrounding the solid particle
2. Chemical reaction producing chlorinated coal and hydrogen chloride
3. Diffusion of hydrogen chloride from the particle surface to the bulk of the gas

The overall rate of reaction is controlled by the slowest of these steps, because the process occur in series<sup>12,15</sup>. In principle, a solid in contact with an aqueous phase is covered by a thin layer of a stagnant solution adhering to the solid through which ions or molecules (chlorine and hydrogen chloride) have to diffuse, either to or from the solid surface it is reacted on surface of solid (coal surface). If the rate of

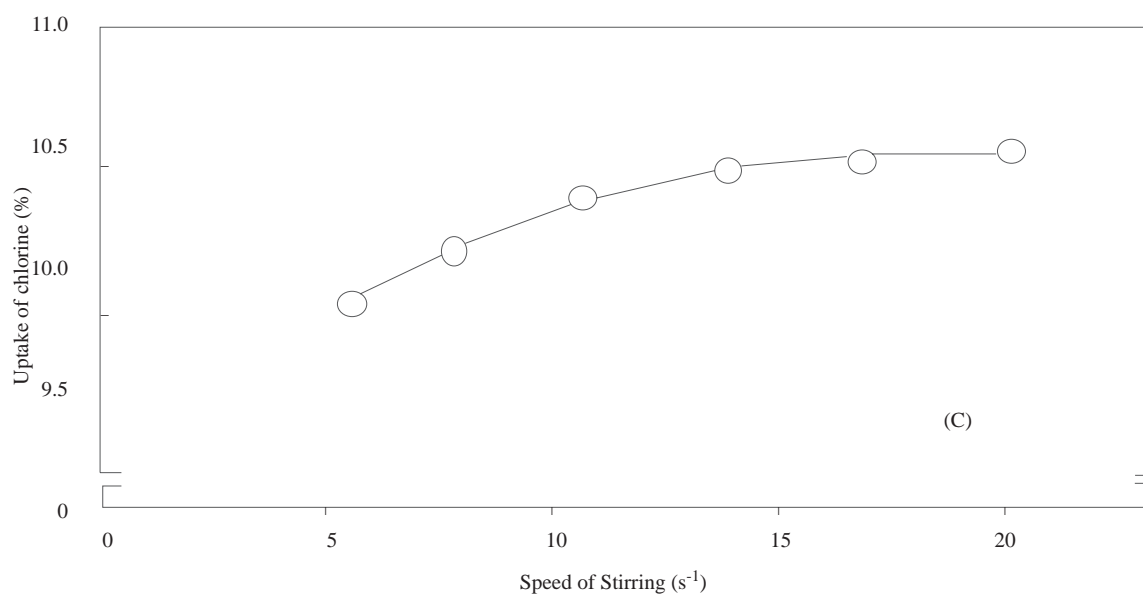
diffusion of chlorine through the fluid film is slow it will become a diffusion-controlled process. If the rate of reaction of chlorine in the coal surface is slow it will control the overall process and the process will be chemically controlled<sup>15,16</sup>. The relative importance of the reaction steps 1 and 2 is discussed in according to the results reported in Figures 1-3.



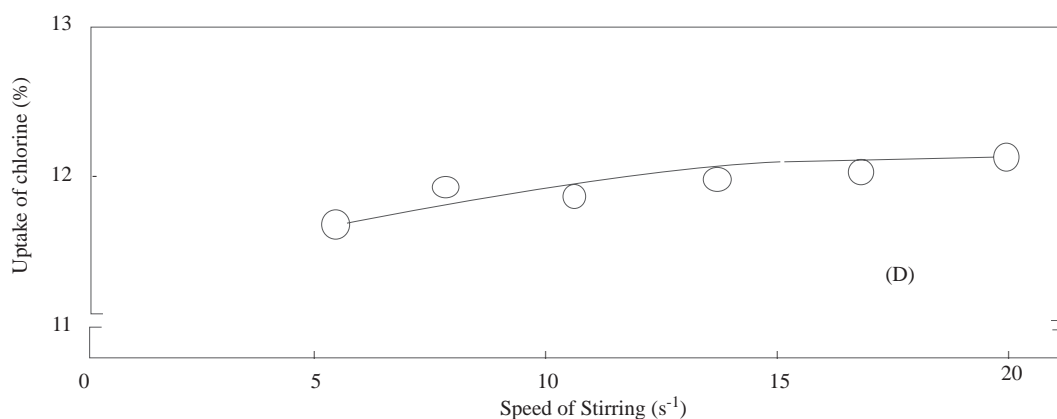
**a**



**b**



**c**



**d**

**Figure 1.** Effect of stirring speed on the rate of chlorine uptake of coal in water medium [Dadaği coal (A), Mengen coal (B) and water-carbon tetrachloride medium [Dadaği coal (C), Mengen coal (D)]. Particle size=250-425  $\mu\text{m}$ ; time=3600 s; temperature=40°C; gas flow rate=350 mL min<sup>-1</sup>; solid-to-liquid=1/25.

### Effect of Stirring Speed

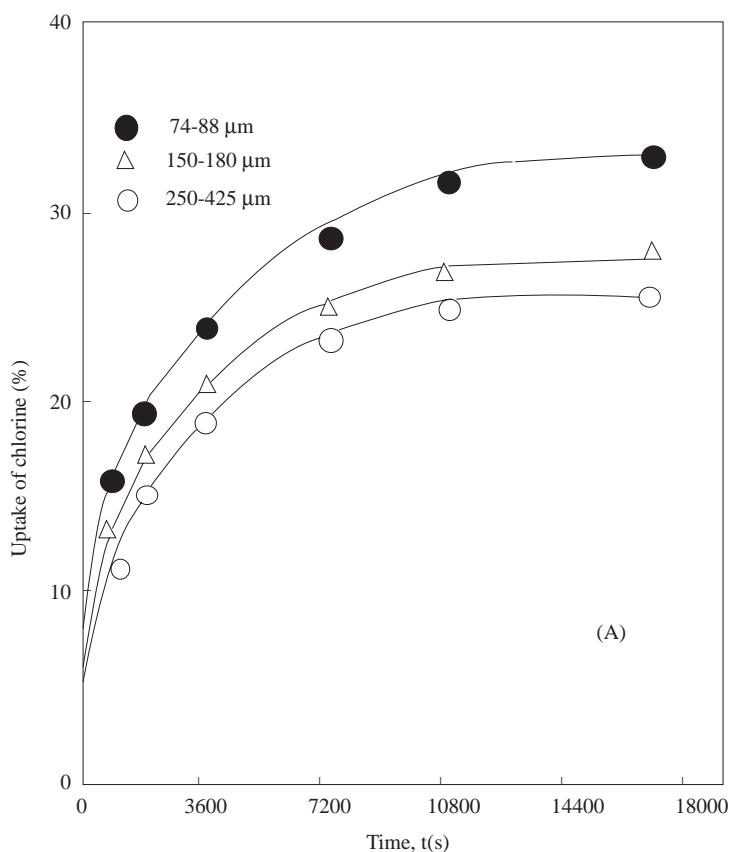
To study the effect of speed of stirring on the chlorine uptake rate of Dadaği and Mengen coals in water and water-carbon tetrachloride media the coal samples were chlorinated at controlled speeds between 5 to 20 s<sup>-1</sup> at 40°C for 1 hour. The results are shown in Fig.1 a-d. In both media, the rate of chlorine uptake of coals increased with the increase in speed of stirring up to 14s<sup>-1</sup>. From this, it may be concluded that the rate of chlorine uptake is a physically controlled processes, because, in general the rate of physical processes is considerably more sensitive to the change in stirring speed than that of chemical process<sup>15,16</sup>.

Any further increase in stirring speed had little or no effect on the rate of chlorine uptake of coal. Therefore, a speed of 14s<sup>-1</sup> was used for the rest of the experiments.

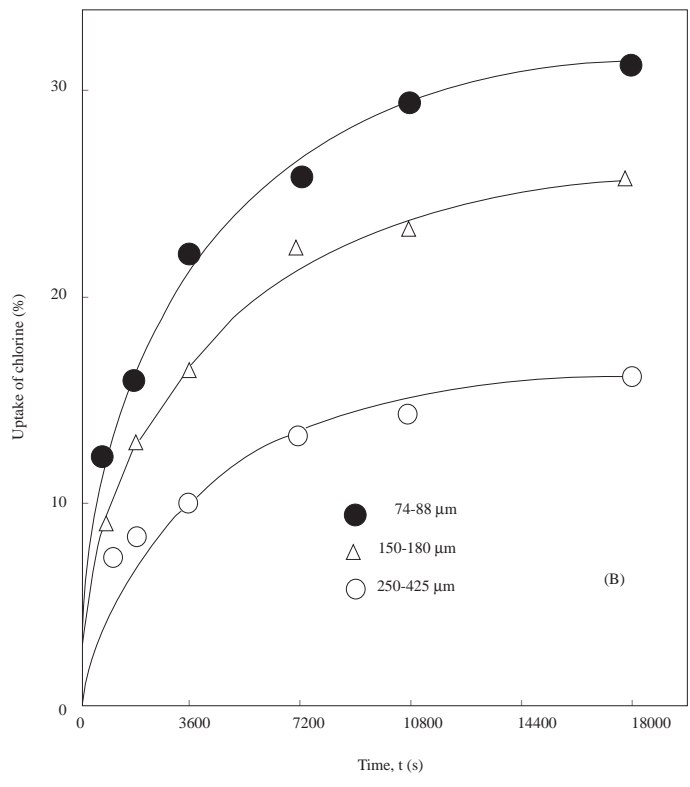
## Effect of Particle Size

The effect of particle size on the chlorine uptake of coals is given in Fig.2 a-d. As can be seen from these figures, in both media for both coals the amount of chlorine uptake increased with decreasing particle size. Decrease in coal particle size results in an increase in the reactive sites of the coal surface. There will not be any effect of particle size in the case of continuous reaction model. (In the case of the surface reaction the increase in surface area would increase the reaction rate<sup>15</sup>.)

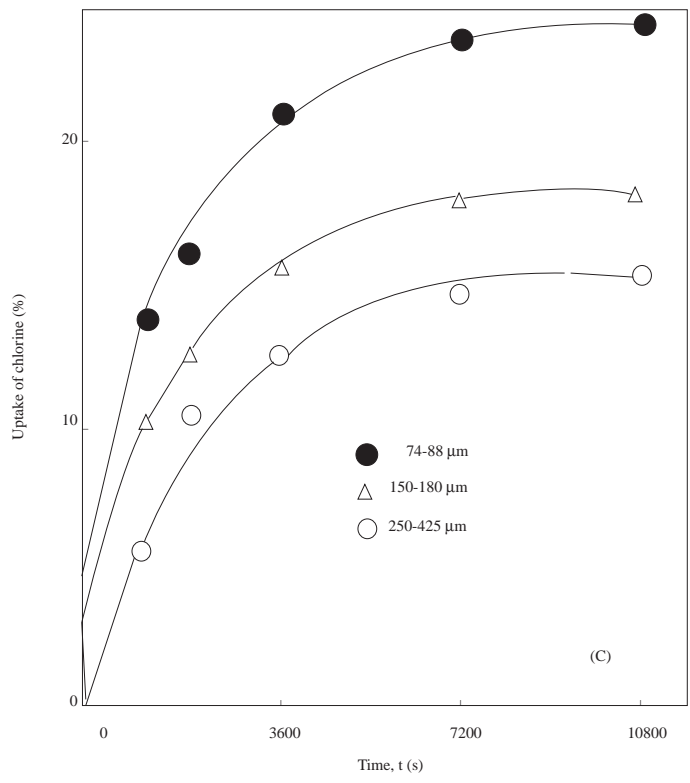
It was seen that the amount of chlorine uptake in Dadağı coal was substantially lower than in Mengen coal under similar reaction conditions in water-carbon tetrachloride medium. This situation may be attributed to differences in organic matrix of coals<sup>5,6</sup>. Coals probably contain aromatic, cyclic and aliphatic groups. These groups in coal are have different selectivities toward chlorine. The later removal of the chlorine bound to aromatic structures would be very difficult<sup>1,5</sup>. Chlorinolysis of the both coal in water-carbon tetrachloride media showed no significant differences in chlorine uptake when compared with the chlorinolysis of same coals in water alone under the same reaction conditions. Furthermore the uptake of chlorine by each of the coals within 7200 seconds (Figure 2a-d) tends to approach a constant value.



a

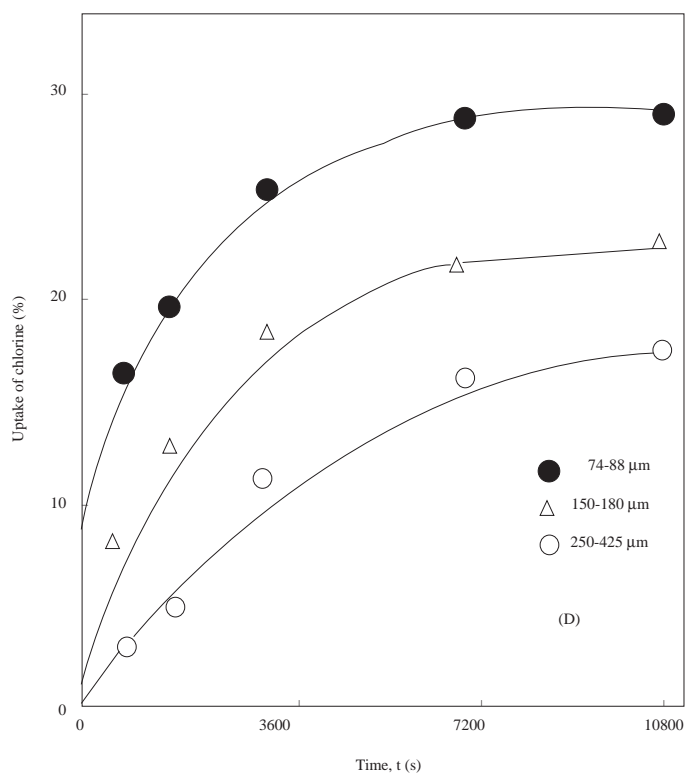


**b**



**c**





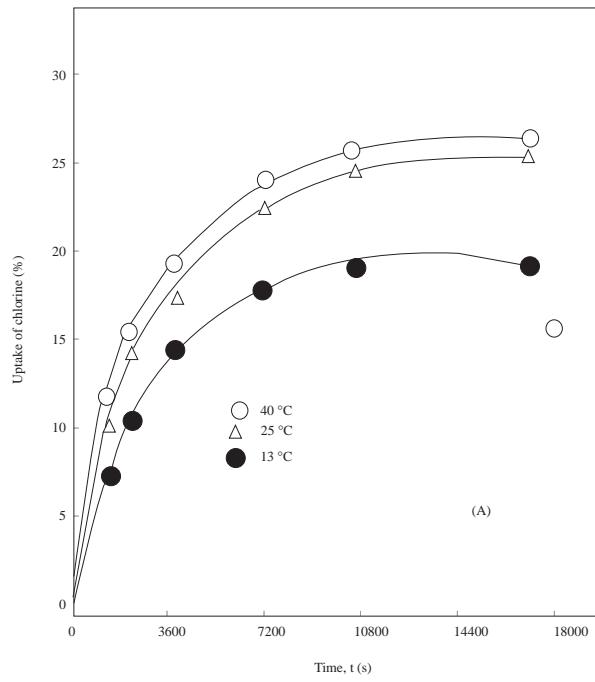
d

**Figure 2.** Effect of particle size on the rate of chlorine uptake of coal in water medium [Dadağı coal (A), Mengen coal (B) and water-carbon tetrachloride medium [Dadağı coal (C), Mengen coal (D)]. Temperature=40 °C; gas flow rate=350 mL min<sup>-1</sup>; stirring speed=14 s<sup>-1</sup>; solid-to-liquid=1/25.

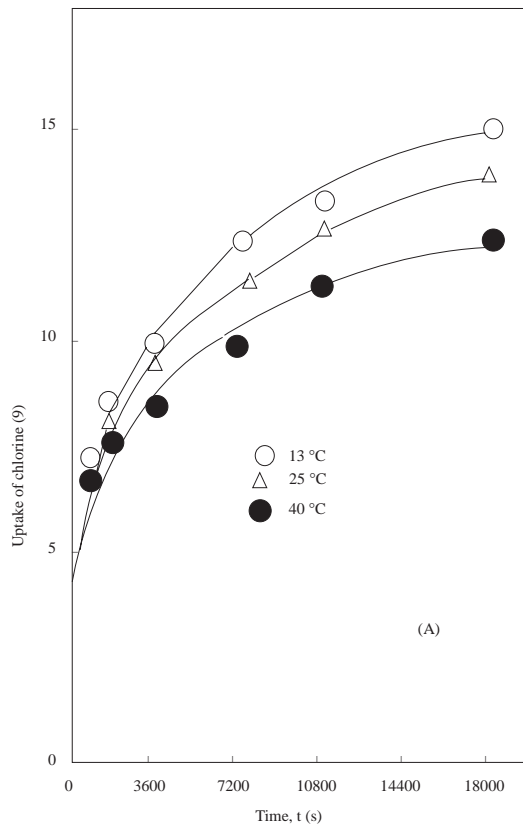
## Effect of Temperature

Experiments were conducted to investigate the effect of temperature on the chlorine uptake of Dadağı and Mengen Coal in water and water-carbon tetra-chloride media. The results are shown in Fig.3 a-d. As can be seen from these figures, the rate of chlorine uptake of coals increased with increasing temperature. Although the chlorine solubility was decreased with increasing temperature the rate of chlorine uptake of coals was increased. This situation has shown that the temperature have a marked effect on the rate of reaction.

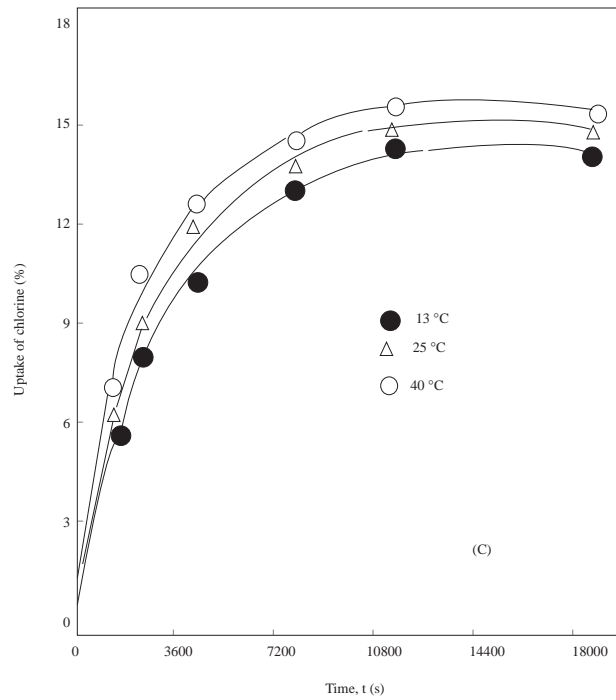
The amount of chlorine uptake of coal under similar reaction conditions was smaller in the water-carbon tetrachloride medium than that in the water medium. It is possible that the decrease might be due to a difference in reactive nature of coal or, alternatively, the aggregates of molecules in the coal may dissociate as chlorination proceeds, facilitating the uptake of chlorine by a sorption process or by an addition reaction<sup>9</sup>. Furthermore it was seen that the uptake of chlorine by each of the coals within 7200 seconds (figure 3 a-d) in both media tends to approach a constant value.



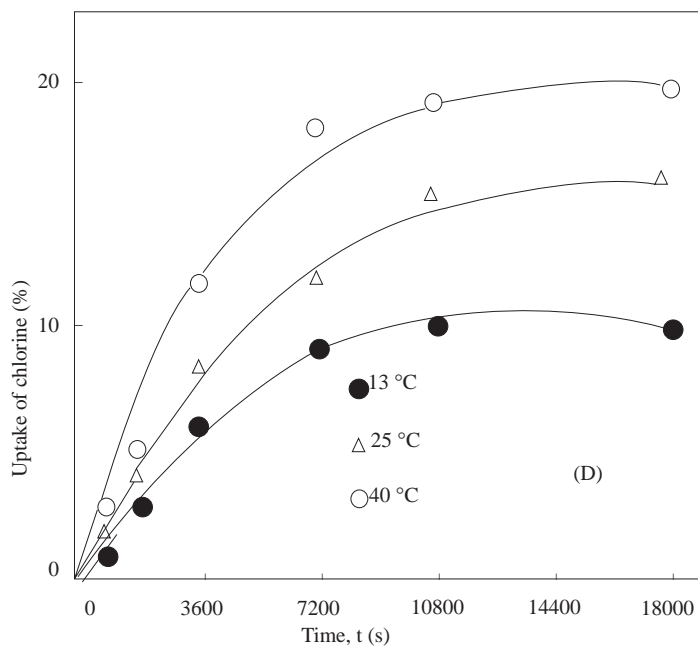
a



b



**c**



**d**

**Figure 3.** Effect of temperature on the rate of chlorine uptake of coal in water medium [Dadađı coal (A), Mengen coal (B) and water-carbon tetrachloride medium [Dadađı coal (C), Mengen coal (D)]. Particle size=250-425  $\mu\text{m}$ ; gas flow rate=350 mLmin<sup>-1</sup>; stirring speed=14 s<sup>-1</sup>; solid-to-liquid=1/25.

## Conclusion

The rate of chlorine uptake increased with decreasing particle size and increasing temperature in both media. Particle size have much less effect on the chlorine uptake of the both coal in water-carbon tetrachloride medium when compared with the chlorinolysis of same coals in water alone under the same reaction conditions. Otherwise the amount of chlorine uptake in Dadağı coal was substantially lower than that in Mengen coal under similar reaction conditions in water-carbon tetrachloride medium. It was seen that the amount of chlorine uptake in water-carbon tetrachloride medium are smaller than that in water medium with changing temperature. Furthermore, the amount of chlorine uptake by both coals in both media tends to approach to a constant value within 7200 seconds.

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