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Chloration of coals of different oxygenation degree in an electrolytic system

Process of electrochemical chlorination of coals and humic acids of Shubarkol and Oykaragay fields is investigated. Results of researches of products of electrochemical chlorination of coals are given. Optimum conditions of chlorination of coals are revealed. Dependence of extent of chlorination of coal on density of current, time, temperature and ratio T: J is shown. It is established that values of total and chemically connected chlorine differ in coals of Shubarkol and Oykaragay fields, exactly, dependence of amount of the attached chlorine on petrographic composition of coals is observed. The content of chlorine is more in the products received at chlorination of Oykaragay oxidized coals.

Key words: coal, humic acid, chlorated coal, fulvic acids, polycondensation.

Huge resorts of brown and coals of a different stage of a metamorphism are concentrated on the territory of Kazakhstan which are widely used, generally for receiving the coke that applied in metallurgical industry and to the power purposes. Nevertheless, processes of receiving of motor and boiler liquid fuel, power and technological gases [1, 2] from coals are developed now.

Coal as the high-carbonaceous raw materials containing to 70 % of carbon, represents one of alternative sources of receiving hydrocarbonic raw materials which can compete with oil. Effective resource-saving and ecologically safe technologies of chemical processing of coals are developed, the structure and reactionary ability of coal are investigated, the assessment of power chemical potential of various coals is carried out, search of new scopes of chemical products from coals is carried out.

Research of process of chlorination of coals is perspective in the meaning of increasing their chemical activity. Introducing of reactive atom of chlorine in the organic mass of coal increases solubility it in organic solvents to 60–80 %. At the same time there is an decalcification and coal [3, 4] desulphuration.

Therefore the purpose of our researches was studying processes of electrochemical chlorination Shubarkol and Oykaragay's coals' field, optimum conditions of chlorination of coals are revealed. The received derivatives of coals are of interest as the available complex founders of binding, bactericides, as initial connections in synthesis of polymers [5, 6].

Nowadays one of the most intensively developing branches of organic chemistry is development of technologically feasible methods of synthesizing substances with given properties. An inexhaustible and accessible source of obtaining them is brown coals and coals oxidized within the formation utilizing of which is an important problem in the region. Considering this researches in the field of synthesizing functional derivatives of coals and humic acids is extremely important, which is explained by their synthetic potential and wide practical application range [1, 2].

One of the most effective and accessible ways of modification is the method of electrochemical chloration of coals, which allows us to combine processes of obtaining chlorine and coal chloration in one electrochemical system. Studying chloration of organic mass of coals (OMC) is a prospective way of increasing its chemical activity. Injecting chlorine allows us to widen the range of chemical conversions of coals. Obtained chloroderivatives can act as initial compounds in synthesis of dyes, bactericides, film-forming substances, plant growth stimulators, polyfunctional cations and polyampholites [3, 4].

Humic acids which are found in oxidized coals have a complex of valuable properties: catalytic and biological activity, ability to absorb metal ions and etc. their production is economically profitable and ecologically safe. However application of humic acids is limited due to low performance characteristics (chemical, hydrolytic and oxidational instability, peptization and others), which makes it necessary to chemically modify them.

Experimental part

Humic coals with different oxidation degree of Shubarkol and Oykaragay coal fields was used as initial material for electrochemical chloration. 20 % water solution of sodium chloride was used as catolyte and anolyte. Following conditions for chloration process have been selected: S:L (Solid:Liquid ratio = 1:25, temperature of reaction mixture 60 ºC, current density on the anode — 0.2 A/cm^2, duration — 4 hours.

Chloration has been conducted in an electrolyser with cation-exchanging diaphragm, graphite rod was used as anode and steel plate as cathode.

Chlorine content has been determined according to Scheniger method, by means of combustion of the substance in oxygen atmosphere. Chlorine was absorbed by H_2O_2 solution and titrated by 0.1 N solution of mercury (II) nitrate in the presence of diphenylcarbazone until solution color turned from yellow to light purple. Amount of chemically bonded chlorine was calculated according to the results of analysis of samples of chlorated coal before and after desorption.

Results and discussion

Studying the process of electrochemical chloration of different coal types has shown that in this process chloration products are different by structure and by dissolving in anolyte and water solutions with different pH values. Characteristics of chlorated coals insoluble in anolyte are presented in Table 1.

Table 1

Chloration of coals with different oxidation levels

№	Mother coal substances	Cl, %		W_a, %	A_a^{daf}, %	ΣCOOH + OH, mg-eq/g
		ΣCl	Chem.bond			
1	Shubarkol oxidized	0,15	–	13,10	8,3	4,3
2	Shubarkol chlor. coals (oxidized)	23,2	18,5	4,30	6,9	4,5
3	Shubarkol run-of-mine	0,07	–	10,2	8,0	3,4
4	CCSh (run-of-mine)*	19,3	18,2	6,16	4,6	4,6
5	Oykaragaysky run-of-mine	–	–	7,80	12,5	1,2
6	CCO (run-of-mine)*	30,6	29,2	4,35	7,2	3,6
7	Oykaragaysky (oxidized)	–	–	14,31	13,4	3,09
8	CCO (oxidized)	22,4	22,6	5,65	6,03	3,4

Note. *CCSh — chlorated coal Shubarkol deposit; CCO — chlorated coal Oykaragaysky deposit.

According to presented results it is obvious that amount of bonded chlorine depends on the nature of coal matter. During electrochemical chloration of ordinary coals increasing number of oxidized groups is observed due to electrochemical oxidation of OMC. Values of total amount and chemically bonded amount of chorine in chlorated products are close. It was supposed that chlorine formed in anode environment is fully chemically bonded and not absorbed on coal surface. Amount of bonded chlorine in ordinary coals is higher than in oxidized coals. Obtained results are explained by structural features of ordinary coals. Aromatic packing of coal contains a lot of unsubstituted places in the nucleus compared to oxidized coals. Under conditions of electrochemical synthesis electrophilic substitution of chlorine in aromatic nucleus takes place.

In oxidized coals number of acidic groups stays unchanged. Probably, under given conditions of electrochemical synthesis reactions of oxidizing destruction of coal mass, which form new acidic groups and reactions of decarboxylation of coal matter take place in parallel. In this case, number of acidic groups should stay unchanged.

Values of total and chemically bonded chlorine differ in coals from Shubarkol and Oykaragay coal fields, i.e. dependence of amount of bonded chlorine from petrographic composition of coals is observed. Chlorine content is higher in products obtained during chloration of Oykaragay oxidized coals.

Results of study show that oxidized coals having complex structure, which is determined by variety of functional groups and chemical bonds between OMC fragments, during electrochemical chloration form chlorated products with different molecular weight (table 2). Mechanisms of formation of these products are different.

Humic acids, which are basic components of organic mass of humic coals are composed of fulvic acids, himatomelanic, humic acids and gummites (residual coal). Each of these components has complex chemical structure with different types of bonds between its fragments. Under conditions of electrochemical chloration hydrolytic decomposition of esters and unsaturated bonds with formation of new oxygen-containing groups and chloration of decomposition products takes place. Chlorated substances have differentiated solubility in water solutions with pH 2–3.

Table 2

Products of electrochemical chloration of oxidized coal

№	Chlorated substances	Ways of extracting from reaction mixture	Chlorine content, %	Efficiency, %
1	Chlorated coal	From anolyte by filtration	23	2
2	Chlorated fulvic acids (1)	Anolyte methylethylketone (MEK) extraction	14–17	8,2
3	Chlorated polyaromatic acids	Anolyte ether or ethyl acetate extraction	5	2,5
4	Low molecular chlorated humic acids	From scouring water at pH 2–3 by jumping	5–7	7,5
5	Chlorated fulvic acids (2)	Scouring water MEK extraction after jumping	14–17	4,8

During the process of electrolysis and following flushing with cold distilled water most of the mass of chlorated coal (up to 28 % of initial amount) passes to the solution. Fulvic and polyaromatic acids are extracted from anolyte and low molecular chlorated humic acids and chlorated fulvic acids, which were absorbed on the surface of chlorated coals, are extracted from flushing water. According to table data, degree of extraction of soluble chlorated substances is around 78 % from total dissolved matter.

Solubility of chlorated ordinary coals under these conditions is much lower — 6 %, which is explained by chemical structure and composition of humic acids in initial brown coal.

A study of electrochemical chloration of coals under varying different process parameters has been conducted. In order to determine optimal conditions of coal chloration effect of these factors on chlorine bonding degree has been studied (figure 1 *a, b, c, d*).

Effect of anode current density on coal chloration process. Current density (D, A/cm^2) was altered from 0.05 A/cm^2 till 0.25 A/cm^2, with increasing it in every following test series by 0.05 A/cm^2. Test results are presented in figure 1*a*.

This dependence shows that current density has an effect on chloration degree only at initial stage of the process. Amount of bonded chlorine increases from 20 % at D = 0.05 A/cm^2 current density till 29 % at D = 0.15 A/cm^2. Then at D = 0.2 A/cm^2 amount of bonded chlorine increases slightly and makes 30 %. Because of this optimal current density for further tests was selected as D = 0.2 A/cm^2.

Process duration effect. Coal chloration process has been conducted with duration from 1 to 5 hours. Dependence of coal chloration degree on process duration is shown on figure 1(b).

Following tendency was recorded with the studied duration interval: chloration degree which increases suddenly in the beginning after first two hours of synthesis decreases till 25 %. Decreasing amount of chlorine bonded to OMC with increasing duration is explained by destructive processes. According to results of the research optimal duration of the process is 3–4 hours.

Effect of temperature. Synthesis for chloration of coals have been conducted under 20–80 ºC temperature interval with 20 ºC increment. Obtained data is presented in figure 1*c*. Coal chloration degree increases from 15.5 to 32 % with increasing temperature from 20 to 60 ºC. Further temperature increase leads to decreasing amount of bonded chlorine. According to test data optimal temperature of the process is 60 ºC.

Effect of coal:electrolyte ratio. Changing of coal chloration degree depending on weight ratio of coal:electrolyte has been determined at S:L ratio of 1:35; 1:25; 1:16; 1:13; 1:10. On figure 1*d* dependence of chloration degree on this parameter is presented. The best value of chloration degree 30 % has been obtained at S:L ratio = 1:25.

Therefore, it was determined that as a result of electrochemical chloration a mixture of chlorated products with different molecular weight, chlorine content in the structure and solubility in organic and water solutions is formed. Ways of extracting chlorated coals from reaction mixture have been studied. Optimal conditions of coal chloration process have been determined: temperature 60 ºC, duration 3 hours, current density 0.15 — 0.20 A/cm^2, S: L ratio=1:25.

On IK — a spectrometer with Fourier transformation (fig. 2), changes in structure of the oxidized coal are visible. At chlorination of coal there are profound changes, as in aromatic system, and aliphatic fragments of coal. The chlorine which entered into an aromatic kernel, reduces degree of its associativity, there are new carboxyl, phenolic groups (cm^{-1} area 1700–1730), chlorine in aliphatic part leads to emergence of hydroxyl, radio and other oxygen-containing groups (area of 1200–1300 cm^{-1}).

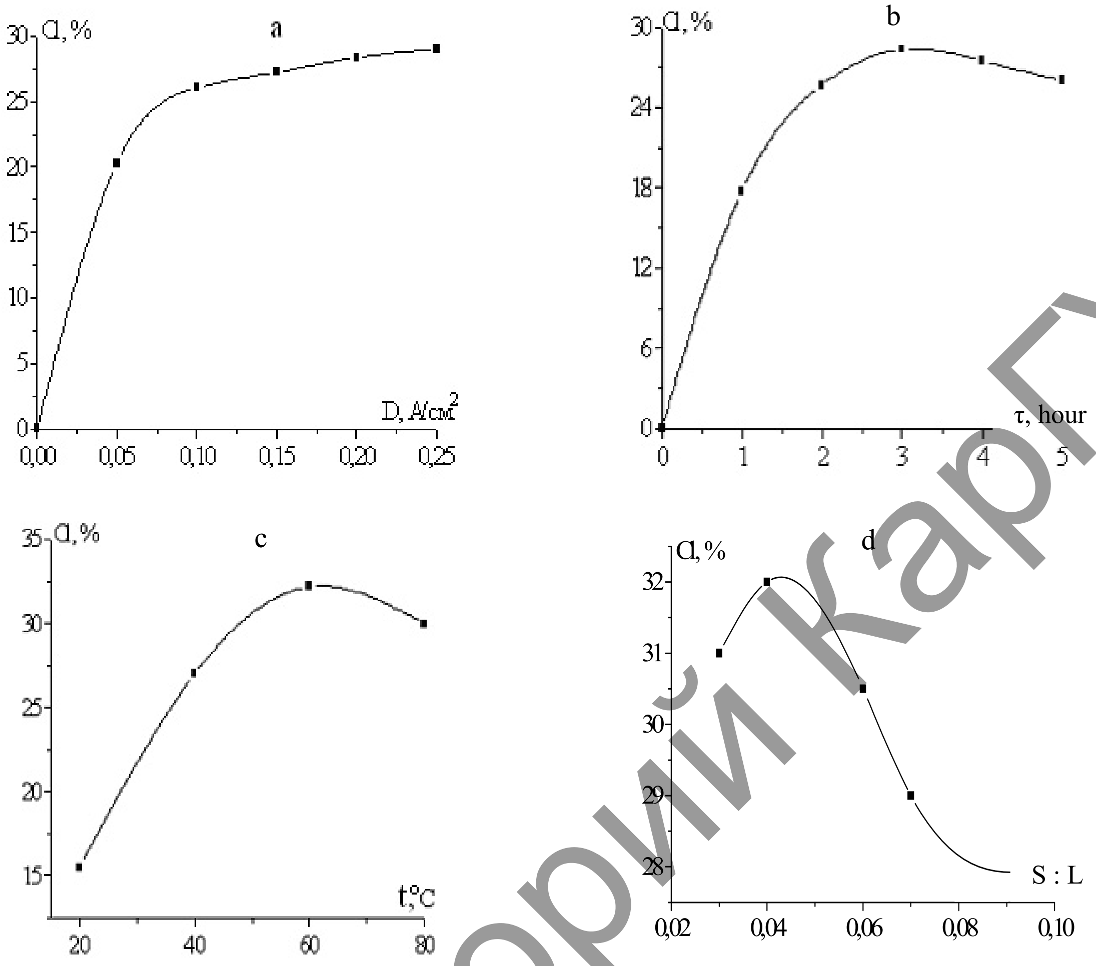

Figure 1. Dependence of coal chloration degree on current density (*a*), duration (*b*), temperature (*c*) and S:L ratio (*d*)

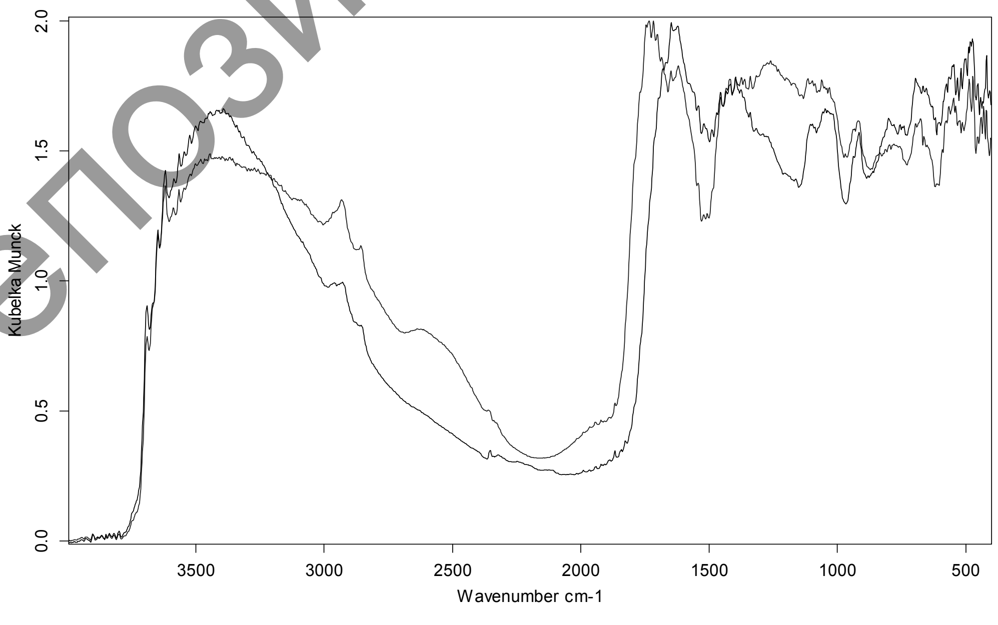

Figure 2. Comparison of IR spectrums with Fourier transformation of the oxidized coal and its derivatives

The research of electrochemical chlorination of the oxidized and ordinary coals of Shubarkol and Oykaragay fields is conducted. Ability of coals to reactions of electrochemical chlorination is shown and optimum conditions of process of chlorination are defined: temperature 60°C, duration is 3 hours, density of current 0,15–0,20 A/cm^2, T:J ratio = 1:25. Synthesized new chlorinated coals have the increased solubility in organic solvents, are of interest as initial monomers in synthesis of polycondensation polymers, possess bactericidal properties.

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Әр түрлі дәрежеде тотыққан көмірлерді электрохимиялық жүйеде хлорлау

Шұбаркөл және Ойқарағай тотыққан көмірлерінің электрохимиялық хлорлау процесі зерттелді. Көмірлерді электрохимиялық хлорлау өнімдерін зерттеу нәтижелері келтірілген. Көмірді хлорлаудың оңтайлы жағдайлары анықталды. Көмірдің хлорлау дәрежесінің ток тығыздығынан, уақыттан, температурадан және Т:Ж қатынасынан тәуелділігі көрсетілген. Шұбаркөл және Ойқарағай көмірлеріндегі жалпы және химиялық байланысқан хлордың мөлшерлері әр түрлі, бұл қосылған хлор мөлшері көмірдің петрографикалық құрамына байланысты екенін білдіреді. Хлордың мөлшері Ойқарағайдың тотыққан көмірлерін хлорлау нәтижесіндегі өнімдерде көбірек.

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Хлорирование углей разной степени окисленности в электрохимической системе

Исследован процесс электрохимического хлорирования рядовых и окисленных углей Шубаркольского и Ойкарагайского месторождений. Приведены результаты исследований продуктов электрохимического хлорирования углей. Выявлены оптимальные условия хлорирования углей. Показана зависимость степени хлорирования угля от плотности тока, времени, температуры и соотношения Т:Ж. Установлено, что значения суммарного и химически связанного хлора отличаются в углях Шубаркольского и Ойкарагайского месторождений, т.е. наблюдается зависимость количества присоединенного хлора от петрографического состава углей. Содержание хлора больше в продуктах, полученных при хлорировании ойкарагайских окисленных углей.

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