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Features of Chemical Kinetics of Concrete Fillers Production from Industrial Waste

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ABSTACT

The main environmental problem of the city of Kentau of the Southern Kazakhstan area is connected with industrial wastes as a part of which there are compounds of metals. Special danger to environment is constituted by slag waste of CHPP (combined heat and power plant). Heavy metals as a part of ash-slag waste of CHPP-5 rise by a wind to the air pool mix up with a dust and other connections and make harmful effects on environment and population health. Unfortunately, any program on such technology isn't entered into the industry till today therefore the solution of the problem of environmental pollution by heavy metals is all the more difficult. But possibilities of production of fillers of porous light concrete with simultaneous extraction of valuable components by processing of such industrial wastes are revealed.

Keywords: chemical kinetics, bituminous concrete fillers, industrial wastes, slag, ash-slag, ecology, Kentau, metal compounds

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INTRODUCTION

The most part of the porous fillers which are making in the Republic of Kazakhstan, now represent the ceramsite gravel burned in circular pipe furnaces. Production of the agloporit (sintered porous filler) in comparison with production of expanded clay has some advantages, for example, expansion of a source of raw materials by application of industrial wastes and by-products; reduction or even phase-out of specially added technological fuel; reduction of mineral mass of a natural material from the general balance of the raw materials applied in production of concrete fillers; fall of quantity of the dust rising as a result of processes of preparation, heat treatment and by that to lower extent of pollution of atmospheric air. Besides the listed above merits the sintering technology is low-volume: instead of occupying the space in 3-4 hectares of the circular pipe furnace in production of agloporit there are used only 0,6-0,7 hectares of the area of the earth [1; 2].

In production of construction materials the method of agglomeration was applied in the 40th years in Russia to receiving the astringent material on the basis of clinker, limestone and the soil. The production technology of agloporit is based on raw materials production for ferrous metallurgy by a burning of mineral raw materials in the agglomerative machine. Early studies on ashes and slag roasting by agglomerative way were carried out in 1937-38 by S. D. Toporkov. Burning ash-slag mixes, he found out that as a result of process of agglomeration it is possible to receive the porous material suitable for receiving light concrete [3; 4].

Hydrocarbons and its derivatives, hydrogen sulfides, anhydride of sulfur, an oxide of carbon and a nitrogen oxide, toxic and exhousted gases and dust which are emitted from petrochemical and oil-processing industry belong to the main sources of pollution of atmospheric air [5; 6]. The only manufacturing enterprise in the Southern Kazakhstan which is engaged in processing of oil products, is JSC Petro Kazakhstan Oil Products which is located at distance of 4-5 km from the southeast residential district of the city of Shymkent, on the left bank of the Badam River. The distance between the enterprise and the closest houses makes about 1000 meters, and Karabastau's district lies at distance of 1500 m. According to sanitary and hygienic characteristics of JSC Petro Kazakhstan Oil Products belongs to the first class on harm for environment, its sanitary protection belt according to sanitary rules and norm requirements makes 1000 meters. The area of this manufacturing enterprise makes 335,05 hectares and only 10 hectares of which are planted by trees and shrubs.

Oil processing in the integrated device promotes connection of scattered sources of pollution in a whole and facilitates definition of extent of distribution in the atmosphere of oxides of sulfur, hydrogen sulfide, oxides of nitrogen, an oxide of carbon, phenol, fuel oil and ashes [7; 8; 9].

For definition of level of pollution of the atmosphere of air, by means of application of an index of pollution of the atmosphere and identification of a class of danger of harmful substances, the quality standards and level of impurity of air, as a result of the carried-out research works the index of pollution of the atmosphere (IPA)in the course of work of manufacturing enterprise was calculated [10; 11; 12; 13]. It is as a result found out that only Shymkent oil processing production throws out in environment in the form of gases oxides of nitrogen and compounds of sulfur, and also unsaturated vapors of hydrocarbons and black oil ashes, polluting at life-threatening level the air atmosphere, also to this list it is possible to add compounds of sulfur, the flavored hydrocarbons and phenol as level of danger of these substances is also high.

MATERIALS AND METHODS

Acceptable method of restriction of harmful effects of harmful waste on environment is their agglomerative burning for what it is necessary to study kinetics of roasting [14]. For this purpose, as a result of work according to the literary review, it is revealed that till today the kinetics of burning of fuel wasn't investigated when receiving very easy porous filler agloporit from ashes, as raw materials and an organic additive, and oil slime, as fuels[15]. This work is directed on development of agglomerative technology of receiving a construction material which is aimed at the intensive development of construction of housing and environment clarification from ashes and oil waste [16]. Feature of this technology in viability, in an acceptability of a burning of all types of waste and receiving a high-quality and very easy porous filler from furnace charge and oil slime[17; 18]. Results of layer-by-layer roasting of particles depends on physical and chemical properties of industrial wastes of which these particles consist, from dimensional structures of particles, roasting temperature, etc. For example, studies have shown that for the burning of the coke waste in the composition of the ash of heat power industry, affect soil water molecules included in the composition of the particles.

It should be noted that processing by the method of layer-by-layer burning, which is considered to be ecologically and economically beneficial, using as the main raw material ashes, and as solid fuel for firing, particles from industrial waste with oilslime, there should be careful investigation of the kinetics of combustion of the fuel in the composition of these particles, as till to this time, the researchers did not pay proper attention on this problem.

Research of kinetics of burning of oil slime as a part of particles from ashes was conducted in 2 stages. If the first stage of research was carried out in the laboratory thermal furnace, the second stage of work was carried out on the increased agglomerative device (Fig. 1 and Fig. 2).

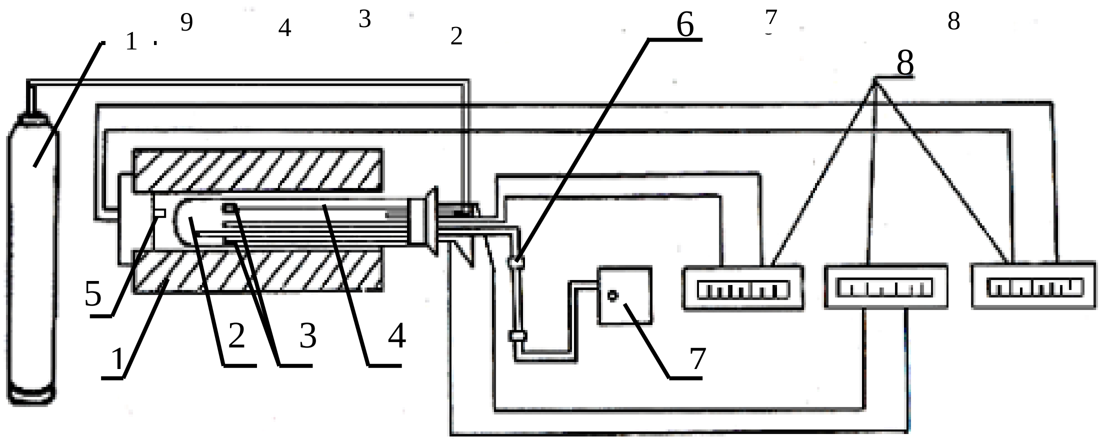
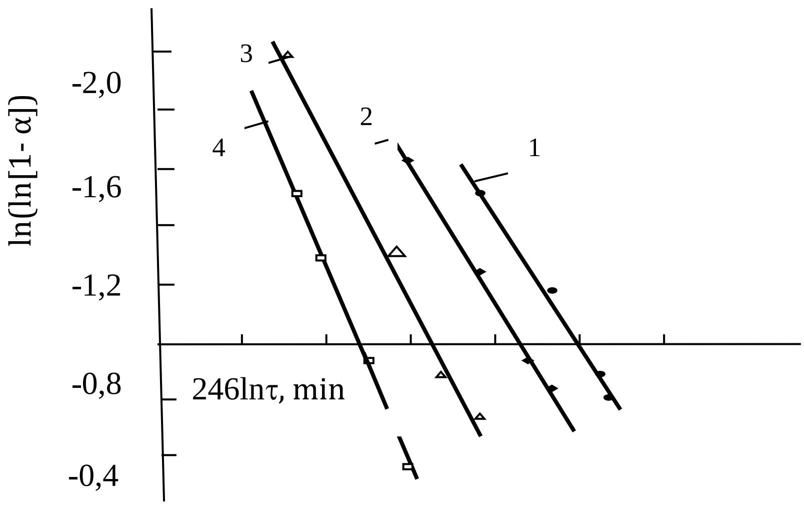


Fig. 1. The scheme of the laboratory device for studying of kinetics

1– tubular electric furnace; 2 – quartz tube; 3 – copies; 4 – thermal measuring wire; 5 – the wire intended for measurement of temperature of the furnace; 6 – rotameter; 7 – microcompressor; 8 – millivoltmeters; 9 – the cylinder filled with nitrogen.



1 – 600 ⁰C; 2– 700 ⁰C; 3– 800 ⁰C; 4– 900 ⁰C.

Fig. 2. Dependence of external diffusion $f(\ln(\ln\frac{1}{1-\alpha})$ from $\ln\tau$ **(without preliminary heating in the inert medium)**

In research works the kinetics of burning of oil slime as a part of ashes was calculated on the basis of processing of the equation of Kolmogorov-Yerofeyev, features of internal and external diffusion at kinetic burning of fuel were defined by Holt's method.

For clarification of accessory of burning of coal particles to an internal and external mode of diffusion, kinetic curves were brought by a method of Holt to the following equation:

$$(1-\alpha)\ \ln(1-\alpha) + \alpha = K\tau \qquad (8)$$

$$\ln\frac{1}{1-\alpha} = K\tau^{m} \qquad (9)$$

The equation (8) gives the chance to determine the diffusion of tension by carbon of a particle of oxygen of air (internal diffusion), and the equation (9) characterizes diffusion of an exit of educated oxides of carbon from within particles outside (external diffusion).

RESULTS AND DISCUSSION

Results of the researches defining external diffusion are shown in tables 1-6. But determination of parameter K in the equations (1) and (2) is possible only when scheduling on values in tables.

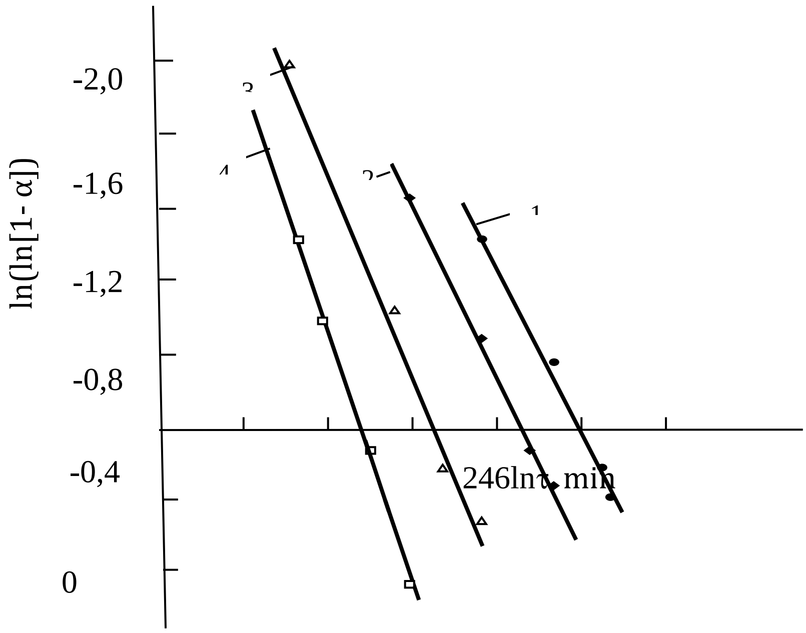
Table 1. Values of researches of external diffusion (without preliminary heating)

Sequence No.	α, %	1-α	$\frac{1}{1-\alpha}$	$\ln\frac{1}{1-\alpha}$	$(\ln(\ln\frac{1}{1-\alpha})$	τ
600 ^{0}C						
1	0,31	0,69	1,449	0,371	-0,991	3,64
2	0,52	0,48	2,088	0,734	-0,309	4,70
3	0,73	0,27	3,704	1,309	0,269	5,16
	0,79	0,21	4,761	1,560	0,445	5,35
700 ^{0}C						
1	0,25	0,75	1,333	-0,287	-1,248	2,99
2	0,47	0,53	1,887	-0,635	-0,454	3,64
3	0,65	0,35	2,857	1,050	0,049	4,38
4	0,76	0,24	4,167	1,427	0,356	4,61
800 ^{0}C						
1	0,18	0,82	1,219	0,198	-1,619	1,95
2	0,42	0,58	1,724	0,545	-0,607	3,13
3	0,72	0,28	3,571	1,273	0,241	4,09
4	0,85	0,15	6,667	1,897	0,640	4,32
900 ^{0}C						
1	0,29	0,71	1,408	0,342	-1,073	1,61
2	0,42	0,58	1,724	0,545	-0,607	2,08
3	0,64	0,36	2,778	1,022	0,021	3,22

Table 2. Values of researches of external diffusion (with preliminary heating)

Sequence No.	α, %	1-α	$\frac{1}{1-\alpha}$	$\ln\frac{1}{1-\alpha}$	$(\ln(\ln\frac{1}{1-\alpha})$	ln τ
600 ^{0}C						
1	0,21	0,79	1,266	0,236	-1,444	5,0
2	0,38	0,62	1,613	0,478	-0,738	5,35
3	0,51	0,49	2,041	0,713	-0,338	5,63
4	0,80	0,20	0,2	-1,609	0,476	6,17
700 ^{0}C						
1	0,22	0,78	1,282	0,248	-1,392	3,1

2	**0,38**	**0,62**	**1,613**	**0,478**	**-0,738**	**3,61**
3	**0,59**	**0,41**	**2,439**	**0,892**	**-0,115**	**3,87**
4	**0,65**	**0,35**	**2,857**	**1,050**	**0,048**	**4,0**
			800 ^{0}C			
1	**0,30**	**0,70**	**1,428**	**0,356**	**-1,033**	**2,48**
2	**0,42**	**0,58**	**1,724**	**0,545**	**-0,607**	**2,89**
3	**0,62**	**0,38**	**2,631**	**0,967**	**-0,034**	**3,22**
4	**0,72**	**0,285**	**3,571**	**1,273**	**0,241**	**3,40**
			900 ^{0}C			
1	**0,40**	**0,60**	**1,667**	**0,511**	**-0,672**	**1,609**
2	**0,63**	**0,37**	**2,703**	**0,994**	**-0,006**	**2,485**
3	**0,78**	**0,22**	**4,545**	**1,514**	**0,415**	**2,890**
4	**0,98**	**0,02**	**50**	**3,912**	**1,364**	**3,637**



1 – 600 ^{0}C; 2– 700 ^{0}C; 3– 800 ^{0}C; 4– 900 ^{0}C.

Fig. 2. Dependence of external diffusion $f(\ln(\ln\frac{1}{1-\alpha})$ from $\ln\tau$ **(without preliminary heating in the inert medium)**

#	T, ^{0}C	m	k	lnk	K	lnK
1	600	0,6	3,8	1,34	1,71	0,54
2	700	0,67	3,6	1,28	1,51	0,41
3	800	0,79	3,3	1,19	1,27	0,24
4	900	0,8	2,45	0,90	0,89	-0,12

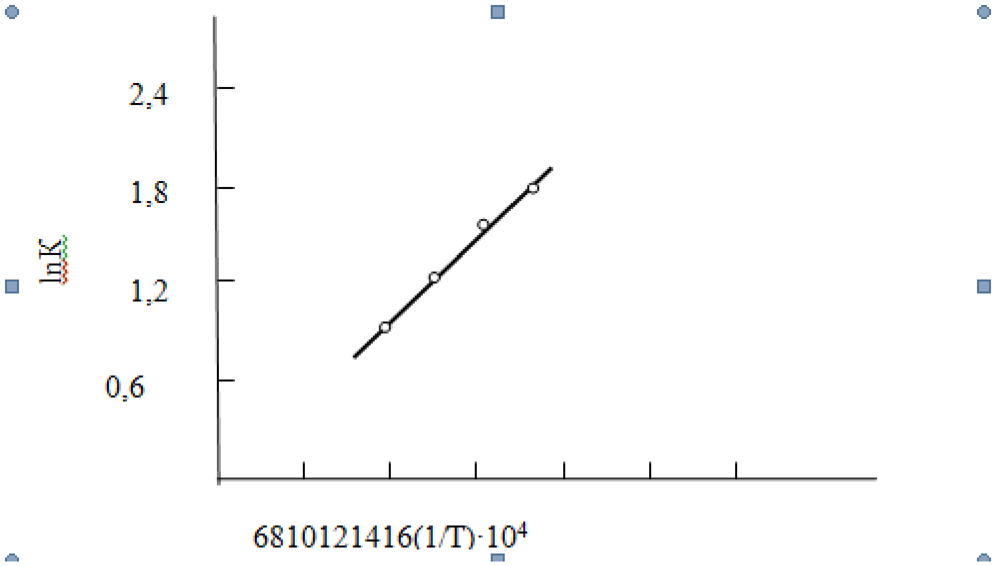
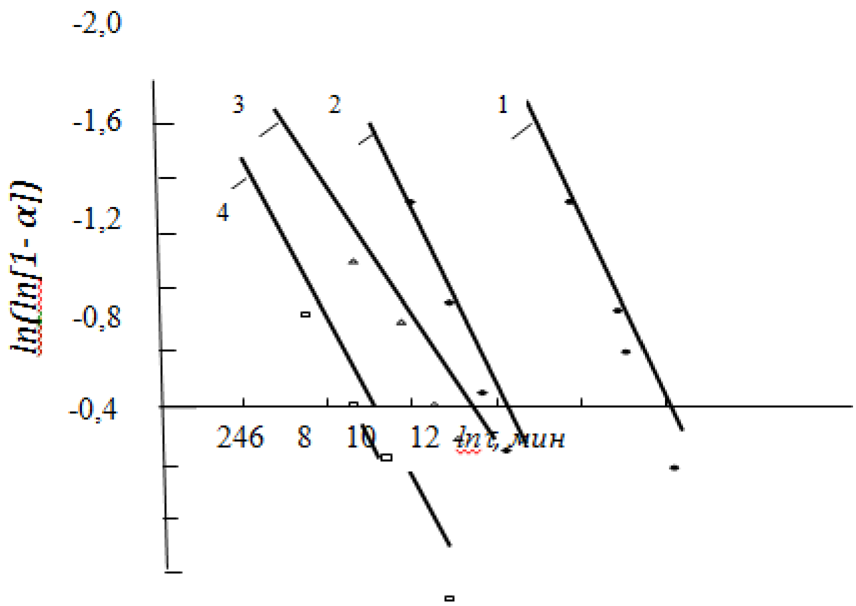


Fig 3. The dependence between the temperature and the constant speed of the effect of the inverse diffusion (without preheating)



1 – 600 ^{0}C; 2– 700 ^{0}C; 3– 800 ^{0}C; 4– 900 ^{0}C.

Fig. 4. Dependence of external diffusion $f(\ln(\ln\frac{1}{1-\alpha}),\tau$ **fromlnτ (with preliminary heating of the inert medium)**

	T, ^{0}C	m	k	lnk	K	lnK
1	600	1,47	8,1	2,09	1,8	0,59
2	700	2,27	7,3	1,98	1,7	0,53
3	800	1,0	4,8	1,57	1,56	0,44
4	900	0,79	1,92	0,65	0,58	-0,58

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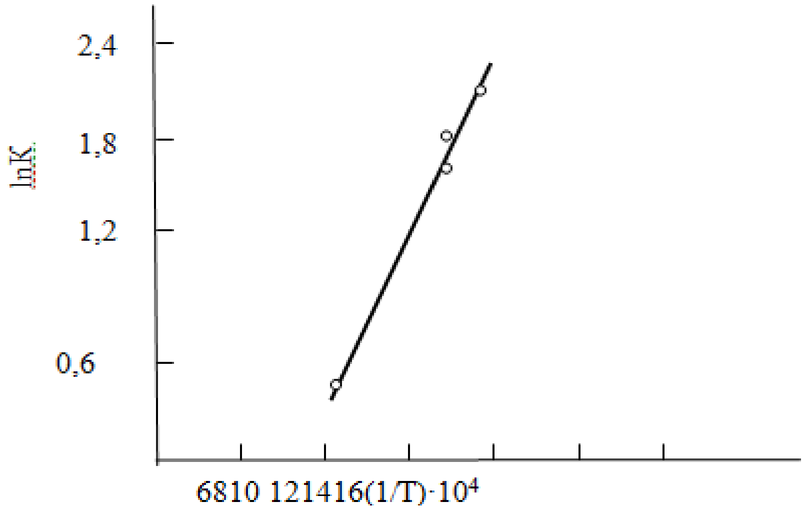


Fig. 4. The dependence between the temperature and the constant speed of the effect of the inverse diffusion (with preliminary heating)

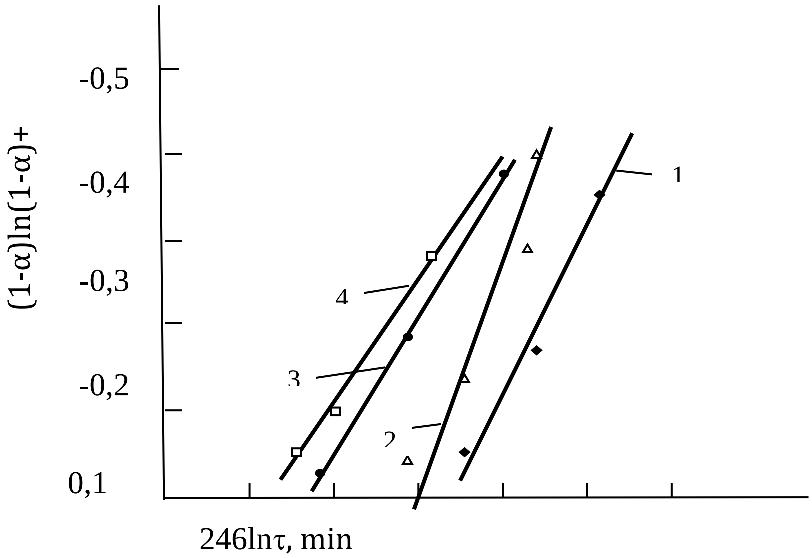
Table 3. Values of researches of internal diffusion (without preliminary heating)

Sequence No.	600 ^{0}C				
	α, %	1-α	ln(1-α)	(1-α)ln(1-α)	lnτ
1	0,31	0,69	-0,372	0,054	3,64
2	0,52	0,48	-0,734	0,168	4,70
3	0,73	0,27	-1,309	0,376	5,16
4	0,79	0,21	-1,561	0,462	5,35
700 ^{0}C					
1	0,25	0,75	-0,288	0,034	2,99
2	0,47	0,53	-0,635	0,134	3,64
3	0,65	0,35	-1,050	0,283	4,38
4	0,76	0,24	-1,427	0,417	4,61
800 ^{0}C					
1	0,18	0,82	-0,198	0,017	1,95
2	0,42	0,58	0,544	0,104	3,13
3	0,72	0,28	-1,273	0,364	4,09
4	0,85	0,15	-1,897	0,565	4,32
900 ^{0}C					
1	0,29	0,71	-0,342	0,047	1,61
2	0,42	0,58	-0,545	0,104	2,08
3	0,64	0,36	-1,022	0,272	3,22

Table 4. Values of researches of internal diffusion (with preliminary heating)

Sequence No.	600 ^{0}C				
	α, %	1-α	ln(1-α)	(1-α)ln(1-α)	lnτ
1	0,21	0,79	-0,236	0,024	5,0
2	0,38	0,62	-0,478	0,084	5,35
3	0,51	0,49	-0,713	0,160	5,63
4	0,80	0,20	-1,609	0,478	6,17
700 ^{0}C					
1	0,22	0,78	-0,248	0,026	3,1
2	0,38	0,62	-0,478	0,084	3,61
3	0,59	0,41	-0,891	0,224	3,87
4	0,65	0,35	-1,050	0,282	4,0
800 ^{0}C					
1	0,30	0,70	-0,357	0,050	2,48

2	0,42	0,58	-0,545	0,104	2,89
3	0,62	0,38	-0,967	0,252	3,22
4	0,72	0,28	-1,273	0,363	3,40
900 ^{0}C					
1	0,40	0,60	-0,511	0,093	1,609
2	0,63	0,37	-0,994	0,262	2,485
3	0,78	0,22	-1,514	0,447	2,890
4	0,98	0,02	-3,912	0,902	3,637



1 – 600 ^{0}C; 2– 700 ^{0}C; 3– 800 ^{0}C; 4– 900 ^{0}C.

Fig 5. Dependence of internal diffusion (without preliminary heating)

Table 5. Values of processing of schedules on 1 drawing (without preliminary heating)

#	T, ^{0}C	n	k	lnk	K	lnK
1	600	0,23	0,67	-0,400	-3,24	1,18
2	700	0,25	0,7	-0,357	-2,81	1,03
3	800	0,16	0,27	-1,309	-10,01	2,30
4	900	0,16	-0,2	-1,609	-11,9	2,47

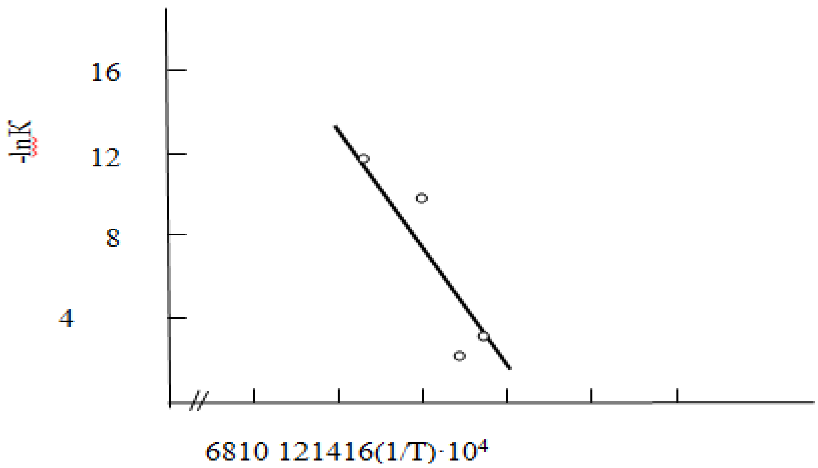
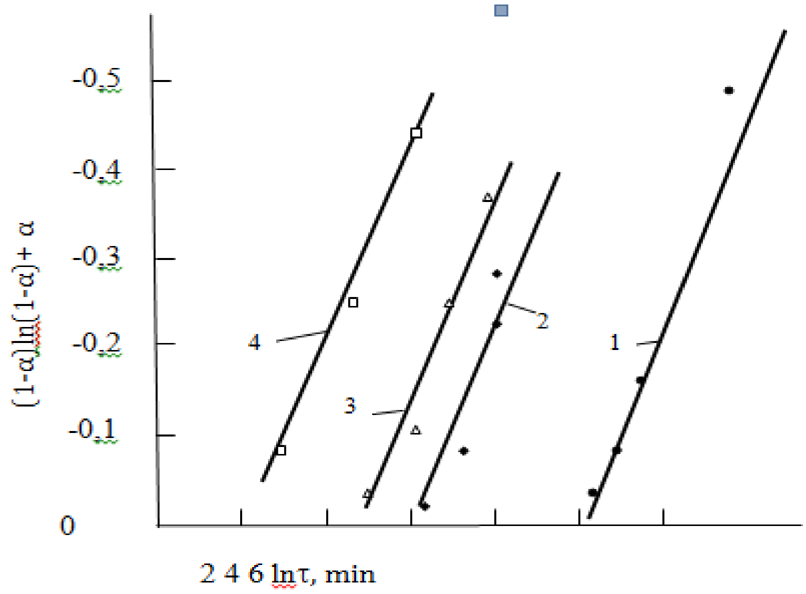


Fig 6. Dependence of influence of internal diffusion (without preliminary heating)

Table 6. Values of processing on Fig 1 (with preliminary heating)

#	T, ^0C	n	k	lnk	K	lnK
1	600	0,21	1,14	0,16	0,94	-0,06
2	700	0,69	0,6	-0,51	-1,11	0,10
3	800	0,2	0,48	-0,73	-5,26	1,66
4	900	0,28	0,35	-1,05	-5,0	1,61



1 – 600 ^{0}C; 2– 700 ^{0}C; 3– 800 ^{0}C; 4– 900 ^{0}C.

Fig 7. Dependence of influence of internal diffusion (with preliminary heating)

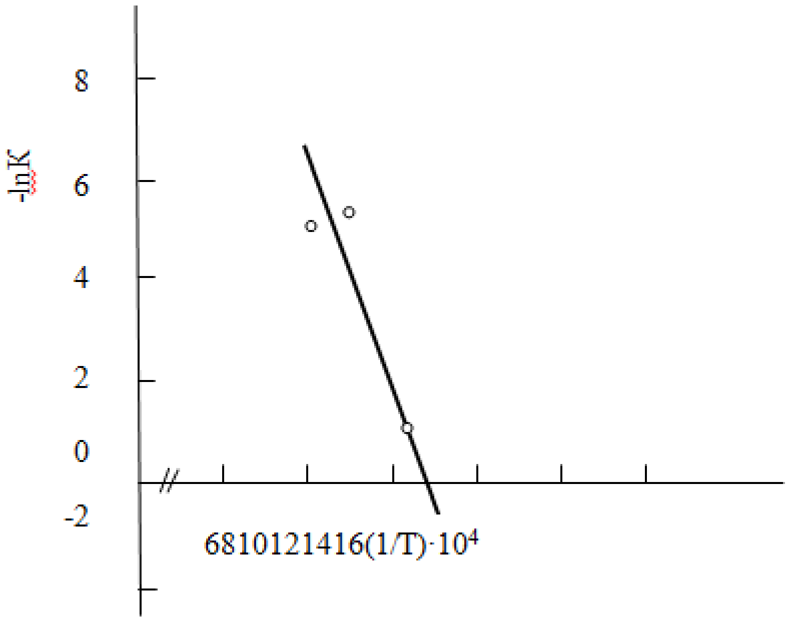


Fig 8. Dependence of influence of internal diffusion (with preliminary heating)

For the characteristic of energy of activation when passing oxygen through a layer of particles and a carbon tention, at first the constants of reaction peculiar to those temperatures, are characterized by corners between direct f (ά,τ) in fig. 5 on the plane of abscissae and equal to these values, lnk1 = 1,34; lnk2 = 1,28; lnk3 = 1,19; by lnk4 = 0,9 thus, tg calculation ϕ between constants of reaction and 1/T•104 it is possible to determine energy of activation. Such dependence is shown in fig. 6. According to this schedule of tgϕ = (1,71-0,89) / (11,45-8,53)=0,28, E=8,314 • 0,28 • 104 = =2,33¬äª/mol.

Considering influence of external return diffusion, for determination of energy of activation graphic these 3 fig. where from the equation, ln shows value of points of intersection of graphic straight lines with the plane of ordinates are used. Here m defines value of corners of tg m between straight lines and the plane of abscissae, and shows regularities of burning of carbon depending on temperature level in fig. 4.

Therefore, energy of activation depending on the return diffusion is revealed according to fig. 4 of dependences between a constant of speed of reaction of burning and the return temperature.

If value of energy of activation of reaction between the oxygen of air directed on inside layers of particles, and carbon it is equal 23,6 kJ/mol, energy of activation of an exit of the formed oxide of carbon on a surface of a particle is 6 times less, makes only 2,33 kJ/mol.

CONCLUSION

It follows from this that the diffusion directed in inside is limiting factor of burning of small coal as a part of particles.

So, first, the kinetics of burning of oil slime as a part of ashes was defined on the basis of Holt's equation, and values of internal and external diffusion are calculated.

Secondly, if value of activation of energy of reaction of oxidation between carbon and oxygen of the air directed on inside layers of particles, is equal 23,6 kJ/mol, energy of activation of an exit of the formed oxide of carbon on a surface of a particle is 6 times less, i. e. makes 2,33 kJ/mol. From this it is visible that the diffusion directed in inside is limiting factor of burning of small coal as a part of particles.

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