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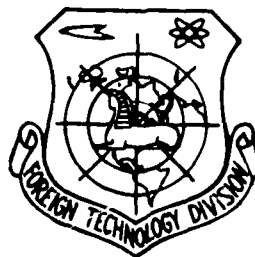
FOREIGN TECHNOLOGY DIVISION



THE EFFECT OF PHASE CHANGED IN THE MINERALOGICAL
COMPOSITION OF THE INORGANIC PART OF NATURAL
CARBONS ON THE ELECTRICAL CONDUCTIVITY OF
A COLLOIDAL PLASMA

by

N. A. Sinayskiy and I. A. Yavorskiy



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ABSTRACT *09 Title cont. - CONDUCTIVITY OF A COLLOIDAL PLASMA The thermal ionization of an aerosol with a disperse phase consisting of reacting ash particles of up to 10 μm in diameter were studied by measuring the electrical conductivity at a frequency of 3.77 mc/s, with X-ray analysis of the reaction products in the condensed phase. The aerosol, which formed a colloidal plasma with a particle diameter of up to 0.1 μm at high temperatures, was heated in a Tammann furnace. The dispersion medium was dry nitrogen and the gaseous products of dissociation of the original minerals (not more than 6%). All transformations of the minerals entering the disperse phase of the aerosol occurred between the measuring electrodes and were governed solely by the temperature of the gas in the furnace and the particle concentration. A systematic study of the combined effect on the conductivity of the colloidal plasma of such factors as initial mineral composition, temperature, concentration, phase transitions and aggregation into slag granules shows that: 1) In systems with a calcite base, with the beginning of crystallization from the liquid phase of $3\text{CaO} \cdot \text{SiO}_2$ in the post-eutectic temperature range and the subsequent reaction between the solid phases to form $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, a shift is observed in the ionization equilibrium of the plasma:				

$$\left(\frac{dn}{dt}\right)_{\text{emiss.}} + \left(\frac{dn}{dt}\right)_{\text{abs.}} - \left(\frac{dn_e}{dt}\right) > 0,$$

with a simultaneous curtailment of the coagulation and aggregation of particles into slag granules (gas temperature 1900°K and above, concentrations up to 1%); 2) The temperature dependence of the conductivity is closely approximated in the exponential range investigated both for heat-emission and chemical-emission ionization occurring when the phase composition of the seed varies; 3) The appearance of a liquid phase in the intermediate stages of the reaction or in the final reaction products leads to an increase in the rate of electron absorption and to a decrease in plasma conductivity. It is shown that calculations of the conductivity of coal combustion products (H. Rincer, S. Way - 1964) without allowance for the physico-chemical phenomena occurring in the mineral part of the coal clearly deviate from the experimental results. For an analytical solution of the problem, information obtained directly from the reacting colloidal plasma must be introduced into the algorithm.

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Я я	<i>Я я</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, б; e elsewhere.
 When written as ѣ in Russian, transliterate as yě or ě.
 The use of diacritical marks is preferred, but such marks
 may be omitted when expediency dictates.

THE EFFECT OF PHASE CHANGED IN THE MINERALOGICAL
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A COLLOIDAL PLASMA

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Introduction

The effectiveness of conversion of the thermal energy of coal into electrical (including the problems of conductivity, slag formation, drifts, erosion and corrosion of the MHD-duct) in considerable measure depends on the physical chemistry side of this question.

For appraisal of the role of phase changes of minerals in the process of ionization of particles an overall physical chemistry investigation was conducted of colloidal plasma forming during the heating of an aerosol with a dispersed phase from the mineral part of certain coals of Siberia. The principal characteristic of colloidal plasma - its conductivity was determined and the physical chemistry processes occurring in its dispersed phase were investigated.

In [1-3] it is shown that aerosols made in the appropriate way with dimension of solid particles of 10^{-7} - 10^{-4} cm with small work function of electrons, can in process of heating form a good-conducting colloidal plasma.

In the reacting colloidal plasma obtained on the basis of the mineral part of coal, the geometric dimensions of particles, their concentration and distance between them are by variable values. The process of ionization of solid particles with multicomponent mineralogical composition is complicated by internal reaction of the minerals among themselves and between particles, and also their external reaction with the gas phase. In examining the MHDG cycle on combustion products of coal, Bincher and Way [4-5] did not take into consideration the physical chemistry phenomena occurring in the ashes of the coal. Works on the investigation of the process of formation of reacting colloidal plasma are lacking.

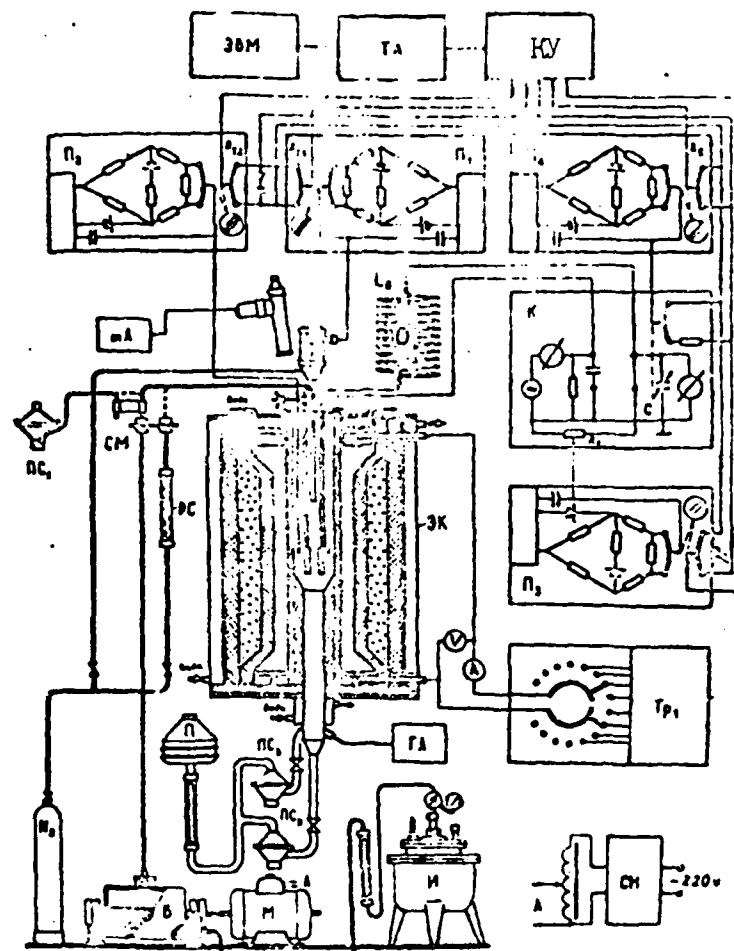
2. Experimental Installation and Method of Investigation

In order to trace the change of real (phase) composition of the mineral part of coal during its heating in a gas flow and to show that conductivity of colloidal plasma is directly connected with the character of reaction of the initial minerals, the installation in Fig. 1 was created, allowing us, simultaneously with measurement of conductivity of colloidal plasma, to produce sampling of the condensed phase, rapidly cooled to room temperature with subsequent separation of flux into roughly and thinly-dispersed. In the roughly-dispersed (coagulant) the particles of ashes coagulated and aggregated in granules of slag settled in the vertical section of the suction line. In the thinly-dispersed (aerosol) the particles of volatile ash followed from the running flow of gas to the dust dust collector.

In the furnace there was created an industrially pure neutral atmosphere (95-100% N_2 ; 0-0.5% O_2 ; 0-1% CO ; CO_2 - by means of dissociation of carbonates contained in the ash); imposition of the burning process of coal particles on the process of ionization of the mineral part was not produced. Into the furnace there was fed the mineral part of a given coal which was preliminarily decarbonized in a muffle at a temperature of 550-600°C, which permitted almost completely preserving the initial mineral composition, contained in the inorganic part of the coal. Thus, all transformations of minerals in particles of dust flow (aerosol), passing between measuring electrodes, were caused only by the temperature of gas in the furnace and their concentration in the flow.

The method of experiment ensured minimum possible gradient of temperature between particle and medium, medium and surface of measuring electrode, and also isothermality in the reaction zone of the dustgas mixture. These conditions were attained by carrying out the experiments in a Tammann furnace (3K in Fig. 1) with constant initial dimension of particles of 0-10 μm lifted by nitrogen from the vibrating mill B.

The length of stay of particles in the zone of maximum temperature was selected in accordance with the time of chemical reaction between solid phases of the aerosol with dimensions of particles up to 10 μm and amounted to 0.1-0.3 seconds.



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Fig. 1. Technological diagram of the experiment.

Determination of concentration by weight of the condensed phase in the zone of measurement of conductivity was produced indirectly according to the results of measurement of the initial concentration of dust in the supply tube by means of weighing the filter of upper dust collector ΠC_1 at defined intervals of time, and according to chemical analysis of the mineral part of a given coal. Error in determination was established by balance of weight of the condensed phase on line of supply and suction and did not exceed 5%. Measurement of temperature in conditions of thermal equilibrium $T_{st}/T_{sr} = 1$ was produced with a telescope with potentiometer Π_1 , thermocouple with potentiometer Π_2 and optical pyrometer MA with coordination of readings of the instruments on the section of temperatures of 1400-1600°C. Measurement of conductivity of colloidal plasma was performed according to the Q-meter method in a quasi-steady-state operation, with which on a time interval of 10-75 seconds there can be obtained no less than three close-value Q-factor signals of the measuring circuit loaded with plasma. Forced search of extremum of Q of the measuring circuit of Q-meter K was produced manually. The objectivity of the measurement of conductivity is due to the automatic recording of the readings of all instruments on tapes with subsequent functional conversion of Q values and capacity manually, and treatment of part of the experiments on an electronic computer [EVM]. To do this, readings indication of the measuring instruments were read by coder KY in eight-digit binary code with help of a telegraph apparatus TA. Punched tape was introduced into the working storage of the EVM through a transmitter. The block diagram of the program of formation of measured conductivity value included an operator for dispatching four codes and point separator, isolation of mantissa, and formation of number order, normalization of the number, calculation, and a printer. Analysis of functional measuring error of electrical conductivity by a method developed according to calculation and calibration on an aqueous solution of KCl , a fusion of $NaCl$ and molecular dispersed colloidal plasma $H_2 + K_2CO_3$, showed that the maximum relative measuring error of conductivity does not exceed 16%.

3. Characteristics of the Investigated Materials

The most interest from the point of view of use of the mineral part of coal in an MHD-generator is in the possibility of formation of newly fusing embryonic crystals of simple and complex oxides, and also ion-formation during the course of the reactions.

$$AB_{(mb)} = A_{(mb)} + B_{(mb)}$$

$$m A_{(mb)} + n S_{(mb)} = m A \cdot n S_{(mb)}$$

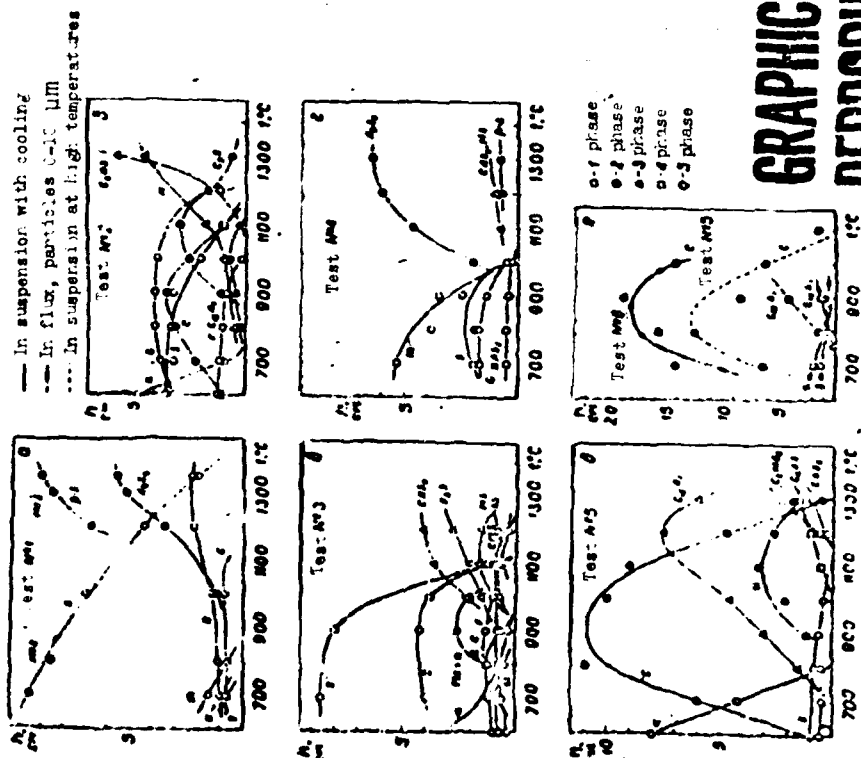
In Fig. 2 there is shown the mechanism of crystal formation of intermediate structures forming in powdery samples during heating in a crucible. Technical characteristics of samples of coal ashes of different deposits taken for physical chemistry analysis at a temperature of 800°C are given in Table 1.

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Number of sample		1	2	3	4	5	6
I	Rank of coal	CC	Brown	MP	CC	CC	Model
	$W^a, \%$	2,25	12,85	4,22	5,5	30,5	
	$A^c, \%$	44,5	6,11	4,58	9,85	15,6	
	$V^2, \%$	30,7	45,8	32,8	25,3	43,2	
	Q_f^2 , kcal/m	7750	6800	8200	7200	5140	
II	$SiO_2, \%$	63,18	10,68	40,45	45,42	8,15	12,7
	$Al_2O_3, \%$	29,48	7,70	19,3	35,67	21,55	5,56
	$Fe_2O_3, \%$	2,81	6,49	8,91	1,86	1,22	0,7
	$TiO_2, \%$	1,38	0,35	0,73	0,67	0,6	0,2
	$CaO, \%$	0,68	46,27	11,74	2,68	58,78	44,9
	$MgO, \%$	0,24	5,26	3,55	-	3,09	0,1
	$SO_3, \%$	0,14	11,90	2,00	2,09	1,7	0,1
	$K_2O, \%$	0,05	-	0,25	0,86	-	0,1
	$Na_2O, \%$	0,2	0,17	1,85	0,22	0,35	0,5
	Losses during heat treatment, %	0,88	11,9	3,34	2,2	3,3	3,5

CONVENTIONAL DESIGNATIONS OF MINERALS

ONE-COMPONENT	TWO-COMPONENT
Q - quartz - SiO_2	As - sillimanite - Al_2SiO_5
Tr - tridymite - SiO_2	Ms - mullite - Al_2SiO_5
Cr - cristobalite - SiO_2	Il - (illegible) - SiO_2
Co - corundum - Al_2O_3	W - wollastonite - CaSiO_3
He - hematite - Fe_2O_3	L - larnite - CaSO_4
Li - lime - CaO	Ol - olivine - $\text{SiMgSi}_2\text{O}_6$
M - magnetite - Fe_3O_4	Pl - plagioclase - $\text{NaAlSi}_3\text{O}_8$
An - anhydrite - CaSO_4	Fa - fayalite - FeSiO_3
Ca - calcite - CaCO_3	En - enstatite - MgSiO_3
C - carbon - C	Ca - calcium - CaO
	Al - alumina - Al_2O_3
	Sp - spinel - $\text{MgO} \cdot \text{Al}_2\text{O}_3$
THREE-COMPONENT	FOUR-COMPONENT
CaS - anorthite - $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	
CaF - gehlenite - $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	
AlS - ferroan cordierite - $\text{Fe}_2\text{Al}_2(\text{Al}, \text{Fe})_2\text{Si}_2\text{O}_{12}$	
AlF - almandine - $\text{Fe}_3\text{Al}_2(\text{Si}, \text{Al})_2\text{O}_{12}$	
KAS - orthoclase - $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	
MS - monticellite - $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$	
MS - diopside - $\text{CaMgSi}_2\text{O}_6$	
CaF - andradite - $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$	
MS - olivine - Mg_2SiO_4	
CaF - akermanite - $\text{Ca}_2\text{Mg}_2\text{Si}_2\text{O}_{10}$	
Al - grossularite - $\text{Ca}_3\text{Al}_2(\text{Si}, \text{Al})_2\text{O}_{12}$	
CaF - melilite - $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	
	MULTI-COMPONENT
	MS - fayalite - Fe_2SiO_3
	Al - haughtonite - $\text{Na}_2\text{Ca}_2(\text{Al}, \text{Fe})_2\text{Si}_2\text{O}_{10}$
	Il - ilite - $\text{Na}_2\text{Al}_2(\text{Si}, \text{Al})_2\text{O}_{10}$

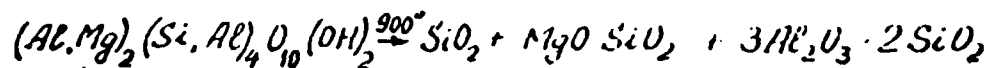


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Fig. 2. Mechanism of crystal formation in the mineral part of coal during heating of the powder in a muffle.

X-ray analysis of tests was performed on a URS-50M diffractometer under constant conditions of survey: $U = 35$ kV, $I = 10$ mA, $W = 2$ deg/min.

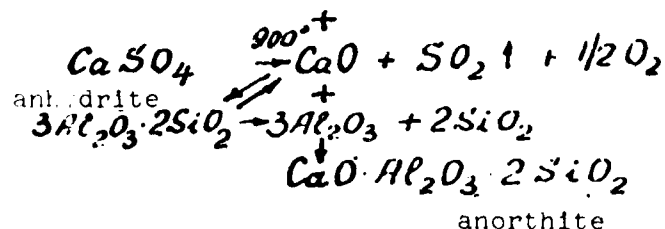
As can be seen from Fig. 2, the general property of reaction of minerals forming the inorganic part of coal is the multistage nature of the process. Products of dissociation of parent substances enter into reaction, forming metastable compounds crystallized with increase of the temperature of the system. Content of transition crystal structures grows to maximum, after which they are destroyed and in the X-ray amorphous state there will be formed the sequent more complex crystal compounds. Intermediate products of a single, binary, or ternary system can react with intermediate products of other systems, increasing the number of metastable structures in the ashes. The process of reaction can be described by constitution diagrams of two, three, and multicomponent systems. The mineralogical composition of intermediate and end products of reaction up to transition of the whole system into the liquid phase does not depend on conditions of reaction (in a piece or in a dustflow); sequence of formation of intermediate products does not depend on state of reagents in the initial ashes. Distinction is observed only in quantitative content of products of solid-phase reaction caused by distinction in chemical composition, time factor, ambient atmosphere, physical processes of heat and mass transfer. Thus, for example, depending upon content in the initial mixture of minerals with a calcium base, the reaction in tests 3 and 4 can go either in the direction of mullite, or in the direction of formation of anorthite due to the solid-phase reaction of calcium oxide with mullite:



montmorillonite

enstatite

mullite



The number of roentgenographically definable topochemical periods, in each of which, with an increase of temperature there appears, increases in content of crystals to maximum, and then vanishes, a group of solids which are intermediate metastable products of reaction of initial minerals, in tests 2 and 5 increases to 5. Simultaneously with the transformations of minerals reactions proceed in binary and ternary systems. Dissociation of calcite and anhydrite in the first stage leads to formation in the second stage of a large quantity of lime, distinguished by increased chemical activity. In accordance with this, in the third stage reaction of lime with quartz predominates, in the fourth gehlenite and akermanite will be formed, in the fifth - anorthite.

Growth of crystalline new formations occurs, as electron-microscopic examination showed, by microterraces from the X-ray amorphous phase of the same substance or their three-dimensional embryo new phase. Average dimension of a single lime crystal, forming during dissociation of calcite, in the case where it does not enter into further reaction, composes, under conditions of the experiment, 3000 Å, aggregates of particles of calcium oxide during photorraphing of the preparation on opening [text illegible] average dimension of 1.2 μm.

Thus, physical chemistry investigation of the reaction process in the mineral part of coal showed that the dispersed phase of a colloidal plasma obtained on the basis of mineral part of coal cannot be examined in the form of chemically neutral, solid, spherical particles of constant radius, concentration, and intercenter distance, possessing constant thermionic potential. Phase transitions inside particles of the aerosol, made under normal conditions from minerals, able to react, and subjected to the influence of high temperatures, predetermine the conductivity of the colloidal plasma. Facts established during investigation of exoelectron emission [6] show that the work of going into an unstable state of surface of particles is very small, is almost equal to zero, and the process of crystallization during phase transition corresponds to the increase of intensity of exoemission of electrons. This permits assuming that in a region of high temperatures under conditions noted above, along with effect of

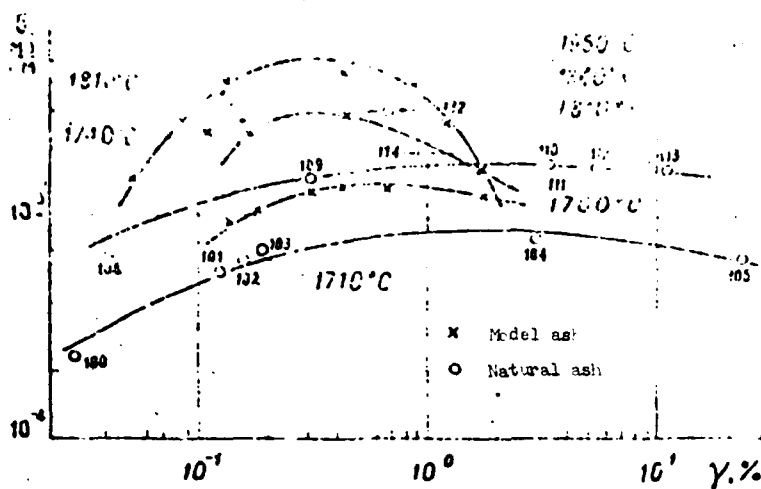
thermoemission of electrons from particles, there will appear a chemoemission effect which will lead to growth of conductivity in the reacting colloidal plasma at the same cross section of collision.

4. Specific Electrical Conductivity of Colloidal Plasma with the Presence of Changes in Phase Composition of Ionized Additive

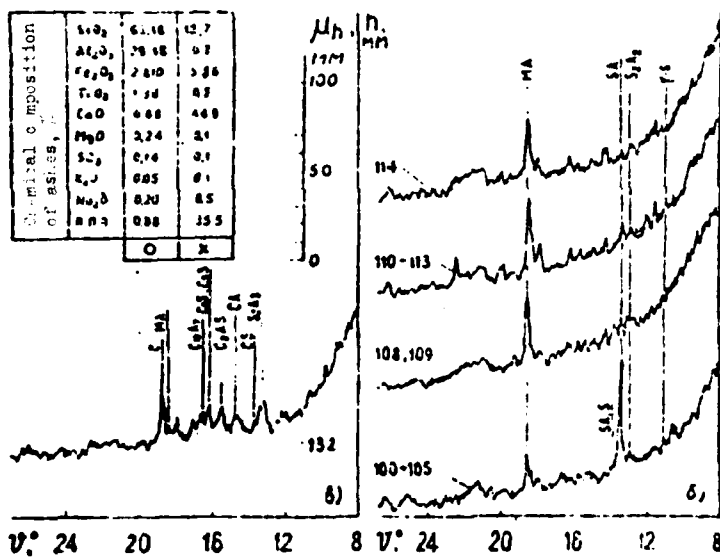
Electrical conductivity of colloidal plasma is detected as in ordinary plasma, by losses of pulse during contact collisions, distant interactions of electrons with charged particles, and collisions of electrons with neutral phase components [1] and can be considered as the total kinetic characteristic of processes of emission and absorption of electrons in the presence of reaction and change of collision cross section according to increase of concentration and aggregation of the condensed phase.

In Fig. 3a there is shown the temperature-concentration dependence of conductivity of colloidal plasma, the ionized additive to which, according to chemical analysis at 800°C consists of 63% SiO_2 and 29% Al_2O_3 with a small quantity of other impurities (Test 1). Its mineralogical composition in Fig. 2 is represented basically by quartz, of which only an insignificant part is combined with aluminum oxide, liberated during dissociation of clayey minerals, in compounds such as mullite, sillimanite (Fig. 3b), and basically undergoes only thermal transformations prior to transition to liquid phase. Work of electron yield from quartz is comparatively high (5 eV) and inasmuch as in increase of concentration of electrons in a given system mainly the mechanism of thermionic emission participates, the degree of ionization is small and almost does not depend on concentration of the additive.

At a temperature of gas of 1700°C quartz and sillimanite are revealed in the ashes in Fig. 3b (curves 100-105). Optimum concentration of additive composes 3% and further increasing it insignificantly lowers conductivity of the plasma, obviously, only due to the growth of collision cross section of electrons with neutral particles. Increasing the temperature of the gas to 1950°C increases conductivity of the colloidal plasma to $3 \cdot 10^{-3}$ MO/cm in Fig. 3a, which can be considered maximum for concentration of sample 1 of 0.1-10%, inasmuch



Chemical composition of ashes, %			
SiO_2	62.18	12.7	
Al_2O_3	29.18	9.7	
Fe_2O_3	2.610	3.36	
TiO_2	1.34	0.7	
CaO	0.68	4.68	
MgO	2.24	2.1	
ZnO	0.74	0.1	
K_2O	0.05	0.1	
Na_2O	0.20	0.5	
H_2O	0.98	15.5	
	O	X	



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Fig. 3. Physical chemistry characterization of reacting colloidal plasma: a) concentration-temperature dependence of conductivity; b) diffractograms of products of reaction of the disperse phase (Test 1); c) - in same (Test 6).

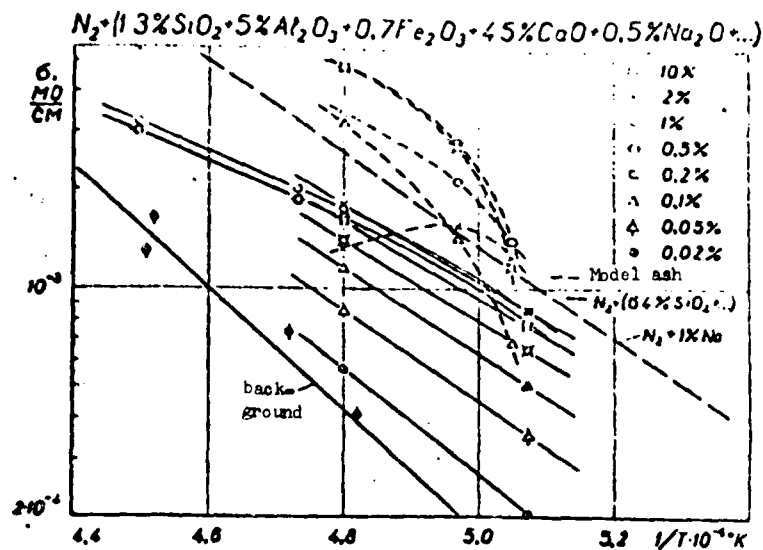
as during these temperatures and a length of stay in the furnace of 0.1-0.3 s in the condensed phase all reactions are finished and it passes into liquid phase. Transition to liquid phase is seen distinctly by diffractogram, Fig. 3b (curves 108-114), on which the intensity of lines of mullite and sillimanite decreases with increase of temperature.

Equiconcentration lines of temperature dependence of conductivity in Fig. 4 are constructed on curves of temperature-concentration dependence of Fig. 3. They permit characterizing the kinetics of the ionization process in colloidal plasma and permit introducing the idea of apparent activation energy of the system in the presence of reactions occurring on borders of phases of solids and accompanied by rebuilding the crystal lattice the substance, that is, by changes in phase composition.

Under weak reaction in test 1 apparent activation energy does not exceed 5 eV of Fig. 4 and decreases with increase of concentration and temperature, leading to formation of the liquid phase.

On the whole, with any concentrations, test 1 does not ensure a conductivity of colloidal plasma greater than that from the presence of 1% vapors of sodium in nitrogen (calculated dependence is plotted in Fig. 4, broken line).

The addition of calcite to test 1 in a 4-1 ratio essentially changes the temperature-concentration dependence of electrical conductivity of colloidal plasma of Fig. 3a (model ash). Formation in particles of the additive of chemically active calcium oxide and its multistage reaction with the remaining components of additive displaces the value of optimum concentration of the condensed phase up to 0.2-0.5% with increase of maximum electrical conductivity by 40%. In the reaction products in Fig. 3c lime, wollastonite, calcium aluminates, larnite, alite, and gehlenite appear in addition to mullite. The sharp increase of electrical conductivity of the system to optimum concentrations is connected with the high apparent activation energy of this system in the region of a temperature of 1700°C in Fig. 3 (model ash). This permits making an assumption about the presence



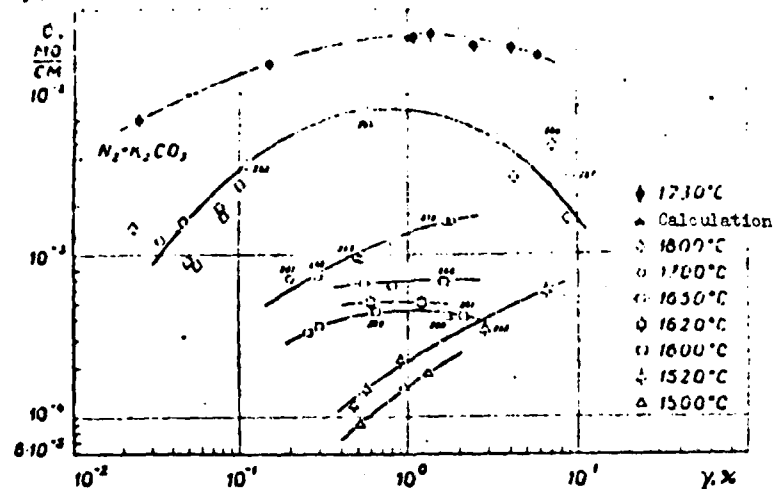
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Fig. 4. Dependence of electrical conductivity on inverse temperature in the dispersed phase from test 1 and with addition of calcite (test 6).

of an additional source of ionization in colloidal plasma with reacting ionized additive. Apparently, the shift of ionization equilibrium on the solid-phase section of the reaction is explained by an increase in the formation rate of electrons by means of an addition to the thermoemission yield of electrons from particles in the gas during construction of the crystal lattice of forming metastable compounds of calcium oxide with aluminum and silicon oxides. The increase in concentration of the condensed phase to 2% leads to a lowering of electrical conductivity with a temperature after maximum, which is observed at 1750°C. Such a movement of the sum of exponentials is connected with the fact that the rate of electron absorption, which can be expressed by its exponential, during growth of forces of adhesion exceeds the rate of emission of electrons and the process of ion-formation is delayed.

The noted characteristic of increase of formation rate of electrons in a colloidal plasma during intensification of the process of reaction of ash due to introduction of calcite was confirmed by investigation of the kinetics of ionization of a number of minerals

N_2 15.5% SiO_2 15.7% Al_2O_3 1% Fe_2O_3 45.9% CaO 2% CO_2 0.5% KN_2O_3 ...)



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Fig. 5. Concentration-temperature dependence of conductivity of a reacting colloidal plasma during dispersed phase from test 5.

coals (tests 2, 3, 4, and 5).

In Fig. 5 concentration-temperature dependence of conductivity of colloidal plasma is shown, the ionized additive of which consists, according to the roentgenographic analysis in Fig. 2, of calcite with an admixture of clay and quartz, or according to chemical analysis at 800°C, of 59% CaO , 21% Al_2O_3 , 8% SiO_2 (test 5). As can be seen from Fig. 5, at gas temperatures of 1500-1520°C conductivity of the colloidal plasma rapidly and monotonically increases with increase of concentration, not reaching maximum even with concentrations of condensed phase near 10% (experiments 249-258). In the precipitation of aerosol and coagulant, which constitute a white powder with aggregated, clumps, macrosigns of slag formation are absent. X-ray analysis of these tests, Fig. 6a, b (curves 255) shows that in the system an intense solid-phase reaction goes on, and in it predominate metastable intermediate products: lime, 12 CaO , 7 Al_2O_3 , silicates and aluminates of calcium (CA , CS , C_2S , C_3S), entering into further reaction with the formation of gehlenite and anorthite; sillimanite; almandine;

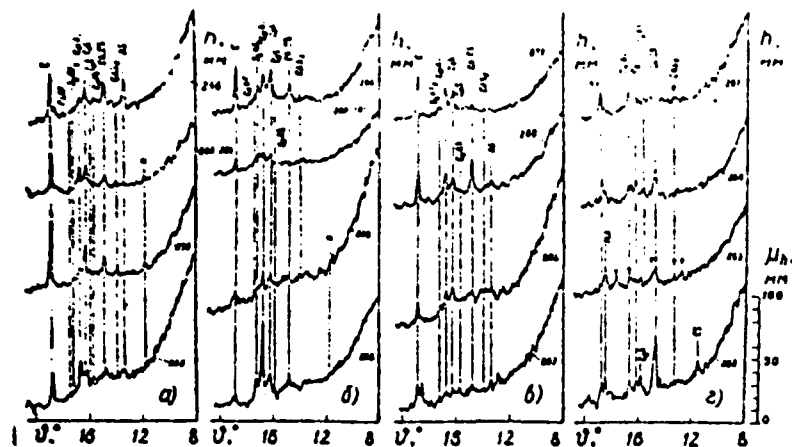


Fig. 6. Diffractograms of products of reaction of the dispersed phase of test 5: a) aerosol deposit; b) coagulant deposit; c) without separation 1700°C; d) without separation 1800°C.

$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and hauynite. From curve 255 it is possible to judge regarding the high dispersiveness of the aerosol, in the particles of which crystals of calcium oxide predominate, whereas the heavier particles of the coagulant are enriched by crystals of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, almandine, and alite, forming as a result of the solid-phase reaction. Lime is almost absent in the coagulant inasmuch as it follows with remaining particles of aerosol after carrying its molecules of gas flow, reversing in the by-pass tube with a velocity of ~ 0.2 m/s.

From the point of view of kinetics of the process (Fig. 7) this section with solid-phase reaction in particles of ash of all concentrations of the condensed phase is characterized by high values of apparent activation energy of the process equal approximately to 9 eV.

At gas temperatures of 1520-1550°C in particles of ash there appears a liquid phase due to formation of eutectic in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system, which with concentration of additive of more than 2% delays speed of ion-formation. Increasing the temperature of the gas to 1600°C permits the liquid phase to begin to render a

$N_2O \cdot 0.5XSiO_2 \cdot 1.57XAFe_2O_3 \cdot 1XFe_2O_3 \cdot 45.9XCuO \cdot 4XMgO \cdot 0.5XN_2O$

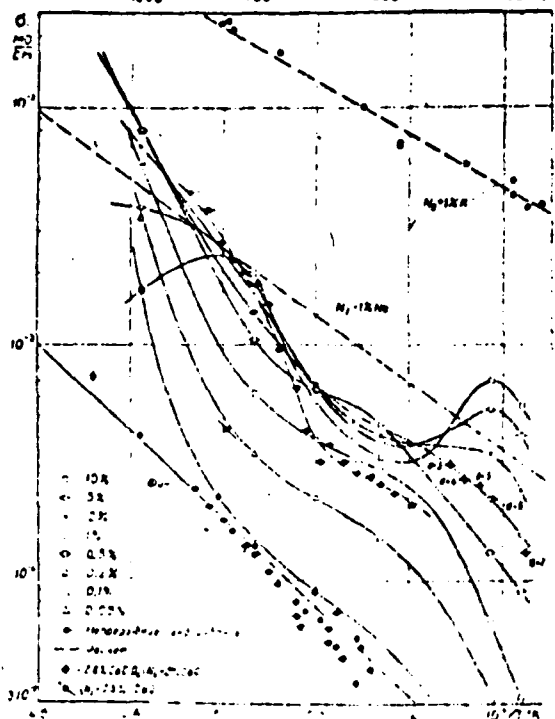


Fig. 7. Dependence of electrical conductivity on inverse temperature during dispersed phase in test 5. [Designations not legible].

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perceptible influence on lowering the conductivity of the plasma even at concentrations of condensed phase in the flow of 0.1%. In experiments 257-266 the conductivity of colloidal plasma almost did not depend on the concentration of the condensed phase. In the deposit of coagulant there appeared macroscopic granules of slag, in Fig. 6b (curves 259-261), and in aerosol deposit, in Fig. 6a (curves 259-261) a measured content of nonreacting lime. Figure 7 shows that in this way the rate of ion-formation is minimal. It is obvious that the increase in concentration of electrons (conductivity) due to thermoemission from crystals of lime and other products of solid-phase reaction was compensated by absorption of electrons of aggregating particles of slag, therefore the resultant conductivity of plasma remains constant or diminishes. Together with electrons from the plasma, the aggregating drops of slag seized the solid particles of lime, therefore their content in the deposit of coagulant turned out to be somewhat greater than in the deposit of aerosol in Fig. 6a, b (curves 260).

A temperature of gas of 1650°C corresponds to the beginning of an abrupt growth of lime in Fig. 6b (curve 266), crystallized in the liquid phase at temperatures of particles of 1480-1500°C, and further transition to reaction in solid phases. The apparent activation energy of the process at concentrations up to 2% again increases to 9 eV (Fig. 7). Excess of formation rate of electrons over their absorption rate is characterized by monotonic growth of conductivity of plasma with increase of temperature and concentration (experiments 267-272) 1700°C curve in Fig. 5 and Fig. 7, where the content of lime, $C_{12}A_7$, C_3S increases to optimum concentration of the additive, and wollastonite at great concentrations almost vanishes, entering into reaction with the calcium aluminates. The solid-phase reaction with great apparent activation energy is preserved in this system up to temperatures of 1800°C at concentrations of condensed phase of 0.05-1%. Optimum concentration of the additive in colloidal plasma composes 0.8-0.9%.

An increase in concentration of the condensed phase of more than 5% at 1700°C and more than 1% at 1800°C (Fig. 5) leads a sharp reduction of conductivity of the plasma. In the reaction products there appears a large quantity of nonreacting lime, increases in content of calcium silicates and aluminates due to incompleteness of the reaction and background is increased on the diffractograms (a great number of peaks of small intensity and hollows), indicating the appearance of the liquid phase of Fig. 6d (curves 286-287). Increasing the absorption rate of electrons permits that sum of exponentials characterizing the process again passes through maximum (Fig. 7) at concentration of condensed phase of 10%.

Value of maximum specific conductivity of colloidal plasma, formed in test 5 at gas temperatures near 1800°C and optimum concentrations approach values characteristic for colloidal plasma of N_2 -1%K with molecular disperse dimension of potassium ions of Fig. 7 (exponential N_2 -1%K). Concerning the high dispersiveness and completeness of reaction in test 5 at this temperature it is possible to judge from curves 282-287 Fig. 6c, d. At concentrations of 0.1% in the ash are formed lime, silicates and aluminates of calcium, almost completely reacting at optimum concentration to anorthite.

Intensity of the peak of lime on curve 283 is less than on all the remaining diffractograms which testifies to the almost complete reaction of lime with formation in the fifth stage of reaction of highly-dispersed particles of anorthite.

The role of chemical reaction in ash is confirmed also by experiments with determination of conductivity of colloidal plasma, obtained on a base of lime. The dimension of lime particles in Fig. 7 ($N_2 + 3,5\% CaO$) was taken the same as in experiments with test 5, but conductivity of the colloidal plasma with nonreacting calcium oxide, ionizing the system by thermoemission of electrons from particles, turned out to be on an order less than with those same concentrations in the condensed phase of the ash.

A long-range appraisal of the kinetics of the ionization process and maximum attainable conductivity of combustion products of minerals of coals in the absence of a burning process, but with the use of reaction in the mineral part, was performed by interpolation of the graphs of dependence of conductivity on inverse temperature for a mixture of nitrogen with the mineral part of investigated coals. From this it was considered that smoke gases, just as nitrogen, are an equivalent neutral component, inasmuch as potentials of their ionization have a value of 14-15.6 eV respectively, and the degree of ionization of mineral part of coal in each gas is identical at equal concentrations by weight.

Results of calculation of the concentration of ash in smoke gases by average composition of combustible mass of coal and average ash content are given in Table 2.

According to the value of concentration by weight of ashes in smoke gases, taking into account losses during heat treatment, in the family of equiconcentration curves characterizing the kinetics of process for a given ash, there was imposed an interpolation curve.

Results of interpolation are shown in Fig. 8, from which it follows that the most promising ashes for an open cycle MHD-generator are those for which in region of high temperatures, starting at 1800°C,

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Table 2.

Test			1	2	3	4	5
Characteristics of combustible mass of fuel	C ²	%	41,0	42,0	42,0	40,4	40,5
	H ²	%	5,2	5,0	5,0	5,2	5,7
	N ²	%	1,5	1,5	2,7	1,0	1,6
	O ²	%	11,8	10,6	8,0	11,4	27,1
	S ²	%	1,2	0,0	0,7	1,2	1,3
Technical characteristics of fuel	A ^c	%	40,0	15,0	12,0	0,7	10,1
	W ^u	%	1,5	11,0	2,0	0,8	19,1
	A ^p	%	36,8	10,2	10,8	8,4	9,6
	W ^p	%	8,0	12,0	0,0	4,9	40,1
Characteristics of smoke gases	V _{C2}	$\frac{\text{г}}{\text{г}} \cdot \frac{\text{м}^3}{\text{г}}$	0,8	0,8	1,2	0,9	3,0
	V _{H2O}	$\frac{\text{г}}{\text{г}} \cdot \frac{\text{м}^3}{\text{г}}$	0,5	0,6	0,7	0,4	0,7
	$\sim \text{min}$	$\frac{\text{г}}{\text{г}} \cdot \frac{\text{м}^3}{\text{г}}$	4,6	4,1	6,0	0,2	3,0
	V ₀	$\frac{\text{г}}{\text{г}} \cdot \frac{\text{м}^3}{\text{г}}$	5,0	4,8	7,4	7,3	4,5
	G	$\frac{\text{г}}{\text{г}} \cdot \frac{\text{м}^3}{\text{г}}$	6,1	6,3	6,0	0,0	4,8
	γ	$\frac{\text{г}}{\text{г}} \cdot \frac{\text{м}^3}{\text{г}}$	74,0	7,3	0,0	10,2	20,5
	δ	%	6,2	0,0	0,45	0,95	2,0

[$\text{г}/\text{м}^3/\text{кг} = \text{м}^3(\text{NTP})/\text{кг}$, $\text{г}/\text{г} = \text{г}/\text{м}^3(\text{NTP})$].

there increases, due to solid-phase reaction in particles of ashes, the apparent activation energy of the system. This property is possessed by coals 2 and 5 with calcite base in the mineral part, which can ensure a conductivity of colloidal plasma greater than that for a mixture of $\text{N}_2 + 1\% \text{Na}$, approaching, with further increase of temperature, the conductivity of a system of $\text{N}_2 + 1\% \text{K}$. Formation of the liquid phase in the posteutectic interval of temperatures (1520-1600°C for gas) lowers in them the ion-formation rate, but with the beginning of crystallization of alite from melt, the solid phase in particles is reestablished, the index of exponential grows, and the charge of solid particle is increased, that is

$$\left(\frac{dn}{dt}\right)_{\text{solid}} + \left(\frac{dn}{dt}\right)_{\text{gas}} = \left(\frac{dn}{dt}\right) > 0$$

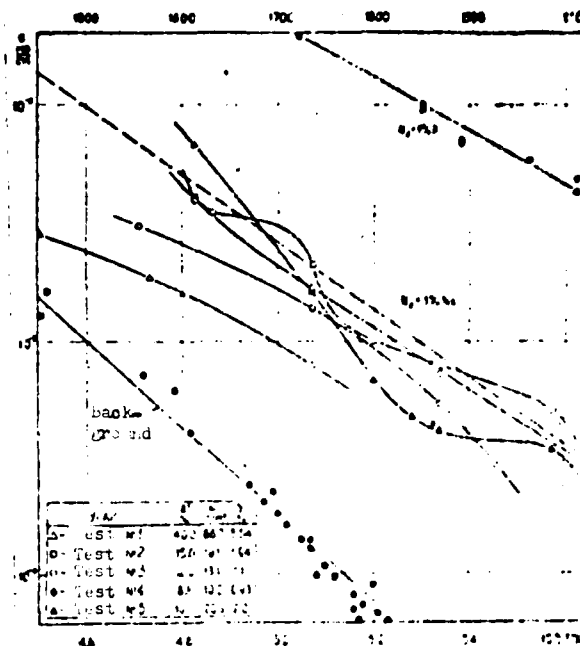


Fig. 8. Dependence of electrical conductivity on inverse temperature for colloidal plasma forming during heating of the aerosol with disperency phase from mineral part of certain Siberian coals.

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The mineral part of coals 1 and 3, due to the large content of quartz, cannot be considered promising. At first there will be formed the liquid phase due to fusion of the quartz, but in the second place, besides this, there will be formed, as a result of reaction of low-temperature eutectic which still more increases the absorption rate and leads to a decrease in apparent activation energy of the system in a region of temperatures of 1900°C more sharply than for sample 1.

In the mineral part of coal 4, despite the large content of quartz, there occurs intense reaction in solid phases with the formation of mullite, which increases overall the degree of ionization of the colloidal plasma to a level of conductivity of a mixture of $N_2 + 1\% Na$.

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