THE INVESTIGATION OF HTGR FUEL REGENERATION PROCESS

L.N. Lazarev, L.E. Bertina, V.P. Popik, V.P. Isakov,
N.B. Alkhimov, Yu.A. Pokhitonov

USSR

During fabrication and operation of uranium-graphite fuel elements of high-temperature gas-cooled reactors (HTGR) waste and rejects on the one hand and exhausted fuel elements,regeneration of which is advisable taking into consideration economical and eccological reasons on the other hand are formed. The aim of this report is the investigation of HTGR fuel regeneration process.

The determinative operation in the technological scheme of uranium extraction from such fuel elements is separation fuel from graphite. Available methods of graphite matrix destruction may be divided into three main groups:

- mechanical destruction;
- chemical destruction;
- burning.

Mechanical destruction is supposed in combination with processes of leaching or chlorination. Dustformation during graphite grinding and formation of slowly filtered graphite masses,sorbing uranium, cause considerable labour consuming of "grinding - leaching" process.

The use of chloration for regeneration of rejected and irradiated fuel requires great amount of energy (process temperature is 1200-1400°K) and causes apparatus corrosion. Methods of chemical destruction of graphite matrix are not studied sufficiently. Selective graphite destruction without fuel solution may be obtained by electrochemical solution

or using reactions of bromine or sulphuric acid with oxidizing additions on graphite. These methods possess the following defects: high specific chemical agent consumptions, difficulties of constructions materials choice for reactor-

Nowadays most of the investigators prefer to remove graphite by burning it. The main advantages are: essential decrease the amounts of materials to be reprocessed, later on, low quantity of secondary waste to be buried, minimal consumption of energy and minimal expenditures for reagents (air, oxigen).

There is much information concerning furnace construction development for burning. As a rule, furnaces of shaft type [1] and furnaces with fluidized bed [2] are considered. However, general approach to the furnace construction is not developed because of complexity of calculation and experimental determination of temperature and concentrations fields in apparatus of complex geometry and specificity of nuclear safety requirements. Burning of ground graphite allows to increase greatly the furnace output, however, grinding is attended by dustformation and essential apparatus complication.

We recommend the following succession of technological operations: burning of spherical fuel element graphite shell and outer layer of pyrocarbon (PyC), CFP shells unsealing with subsequent their treatment with nitric acid, uranium extraction from acidic solution with standard methods.

Burning is the most labourious operation and it limits all regeneration process as matrix graphite and pyrocarbon part amounts to about 98% of fuel element mass.

We studied the possibility to use the furnaces of shaft type for graphite spheres (without previous grinding) burning. Advantange of such apparatus is simplicity of fabrication and operation. The method based on separate study of graphite and pyrocarbon oxidation kinetics and reactor space conditions of furnace in dependence upon gasdynamic factors is used to choose furnace profile and burning regime. Interaction of artificial soviet graphite of trade marks МПГ-6, АРВ,3 ОЛГ, matrix graphite and oxygen in mixture with nitrogen was studied using model cylindrical specimens 10 mm in diameter and 4-5 mm high. PyC specimens were plates 10×10×1 mm. The treatment of experimental data (determination of activation energy, reaction order,preexponential factor) in experiments with PyC was carried out graphically by means of plotting dependence of reaction rate upon reciprocal temperature and oxygen concentration,while graphite oxidation kinetics investigation results were treated using special computer program, according to this program the rate constant of reaction was found applying the method of subsequent approximations with putting arbitrarily chosen values of rate constant into two equations system

$$K(T) \cdot C_s^n(x,y) = \beta(x,y) \cdot \left[C - C_s(x,y) \right]$$

$$\frac{\Delta m}{\tau} = K(T) \cdot \rho \cdot \int_S C_s^n(x,y) \, dx \cdot dy \qquad (1)$$

where K(T) - rate constant of reaction;

C, C_s - oxygen concentrations in bulk and near the specimen surface correspondingly;

$\beta(x,y)$ - mass transfer rate near specimen surface;

$\frac{\Delta m}{\tau}$ - time variation of specimen mass;

ρ - specimen density;

n - reaction order.

As follows from the system (1) two-dimensional problem
is solved , that is, radial symmetry in the cylindrical coor-
dinates is supposed. The specimen geometry is chosen in con-
nection with above-mentioned. The experimental dependences
of materials oxidation rate in air upon temperature (1a) and
upon oxigen concentration at T=11170 K (1b) are presented in
Fig.1, and kinetics parameters of graphite and PyC interac-
tion with oxigen are given in table 1.

Table 1

Kinetics parameters of graphite and PyC interaction
with oxygen (specimens density is 1.80-1.82 g/cm^3)

Trade marks of graphite	Oxygen concentration vol. %	Temperature, range, K					
		1070-1270			1270-1470		
APB	12-40	160	0.9	4.0×10^6	164	0.5	4.6×10^6
	40-60	162	1.0	5.0×10^6	168	0.6	7.5×10^6
	60-100	162	1.0	5.0×10^6	176	0.6	2.2×10^7
МПГ-6	12-40	160	0.9	3.8×10^6	162	0.5	2.6×10^6
	40-60	164	1.0	5.7×10^6	164	0.6	3.8×10^6
	60-100	164	1.0	5.7×10^6	168	0.6	6.2×10^6
3 ОПГ	12-40	162	0.9	4.5×10^6	166	0.5	4.1×10^6
	40-60	166	1.0	6.6×10^6	170	0.6	7.4×10^6
	60-100	166	1.0	6.6×10^6	174	0.6	1.3×10^7
Matrix graphite	12-50	160	0.9	6.0×10^6	164	0.5	5.5×10^6
	50-100	160	1.0	5.7×10^6	164	0.6	6.0×10^6
PyC	12-60	170	0.9	1.0×10^7	174	0.5	1.1×10^7
	60-100	174	1.0	1.6×10^7	178	0.6	1.4×10^7

As follows from the data presented in Fig.1 when temperature rises the difference of oxidation rates between the most resistable (PyC) and the least resistable (matrix graphite) decreases. The results given in Table 1 show that in temperature ranges 1070-1270 K and 1270-1470 K dependence of oxidation rate upon oxygen concentration may be described by various decree functions. It follows from stoichiometric relations that preferable carbon dioxide formation corresponds to reaction order 0.9-1.0 and carbon oxyde formation corresponds to reaction order 0.5-0.6.

Thus we consider to be advisable to carry out gasification of matrix graphite and PyC at 1100-1300 K that provides accetable rates of reaction (0.1-0.5 g/m^2s) and allows to prevent oxide carbon formation.

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Mass transfer constants necessary to calculate kinetics parameters were determined with modelling oxygen mass transfer to reacting surface by means of indicator mass transfer to the surface sorbing the indicator. Sodium carbonate dissolved in water was used as an indicator, ion-exchang resins were used as sorbent. Sodium content in sorbent grains was determined by flame photometry method. Such an approach permitted to determine local mass transfer parameters not only for single graphite specimens but for graphite balls filling as well. Dependence of Nusselt (Nu) number upon flow Reynolds (Re) number at various number (N) of layers in cylindrical filling of resin grains 1 mm in diameter is shown in Fig.2. Height of filling is 12 mm, its diameter is 10 mm, porosity is 0.48. Similarity of oxygen flow to graphite and sodium ion flow to resin grains was provided by accomplishing the condition:

$$\frac{Nu}{Sc^{1/3}} = const$$

(2)

where $Sc=\frac{\nu}{D}$ - Schmidt number;

ν - kinematic viscosity;

D - diffusion coefficient.

From the data presented in Fig.2 it follows that when $N<13$ an unstabilized oxidizer flow at an inlet and outlet sections of cylindrical filling of spheres plays an essential role in mass transfer. When $N>13$ mass transfer in such a filling may be calculated according to known dependences [3]. The described approach permitted to show that optimal regime of mass transfer corresponding to minimal temperature gradient in furnace volume and maximum oxygen use was realized in furnace for burning fabricated as turned over cone with oxidizer inlet on a perforated foundation, and outlet at the top of a cone. Maximum mass transfer corresponding to Re_{max} (Fig.2) was ensured at the outlet furnace section with minimum oxygen concentration in a gas phase in the furnace for burning of the mentioned geometry. When gas velocity at the inlet was 1-2 m/s kinetic regime of reaction was realized in 12-20 cm high fuel elements layer and oxidation rate obeyed to regularities of Fig.1 and Table1; in the next 20-30 cm high layer oxidation rate was limited by oxygen mass transfer to graphite surface.

The constant of mass transfer was determined from dependence $\beta = \dfrac{N_u D}{d}$, where d - characteristic fuel element size in a layer and corresponding value of Nusselt number was chosen according to the data presented in Fig.2. Kinetic regime of reacting was again set up at the outlet furnace section because of considerable oxidizer flow turbulization. Operation regime (T=1200-1300 K) in a furnace was provided by setting on fire finely disperred cellulose seeding and soot placed

in an upper zone of a furnace in a flow of pure oxygen, after this air with flow rate 10-20 m^3/h was supplied to a reaction volume.

Experiments on graphite fuel elements gasification in different regimes were carried out in the described furnace for burning with operative volume 10 l. 20 kg of fuel elements were loaded in one of the experiments on burning. Output was 1 kg/h. Matrix graphite was gasified completely, outer PyC on CFP was 96% gasified.

After burning of graphite matrix and outer PyC - coating of CFP, they were subjected to shock destruction in gas flow, accelerated to 100-200 m/s. The advantage of such a method of CFP unsealing in comparision with drinding in a mill is minimum dusting with highly effective unsealing and low energetic consumption. CFP velocity providing SiC-coatings destruction was calculated according to formula:

$$V = \left(\frac{15\, 6max}{4 \rho R} \cdot \frac{1-y}{2-y} \right)^{5/6} \cdot m^{1/3} \cdot R_0^{-1/6} \cdot E^{-1/3} \qquad (3)$$

where 6_{max}, E, Y - tensile strength, elastic modulus and Poisson coefficient of silicon carbide respectively;

R_0 , R — CFP and SiC layer radii respectively;

m — CFP mass;

ρ — density.

Necessary CFP velocity in a pipeline was provided by 0.5-0.7 MPa pressure drop. Such a pressure drop provides complete CFP unsealing, preserving most of fuel kernels (Fig.3) integrity. During CFP shock destruction dust quantity was not more than 0.1% CFP mass. Further fuel regeneration included

pyrolitic carbon burning in air in muffle furnaces at 1100 K, treatment with nitric acid and ammonia or peroxide purification. As a regeneration result we obtained uranium dioxide of purity providing possibility to use it for microspherical HTGR fuel fabrication.

We investigated above mentioned methods of fuel element fabrication, waste regeneration concerning irradiated fuel. Technological scheme of fuel element regeneration is added by several operations. Cooling of releasing gases, filtration and trapping of radioactive noble gases (RNG) are carried out during graphite balls burning. Nitric acid solutions are subjected to radiochemical tretment. Extraction schemes of uranium, plutonium and fission products re'zover. are investigated in detail when regenerating fuel of thermal reactors [4] and their use concerning HTGR fuel doesn't cause difficulties.

Nitric acid solutions were used to solute uranium dioxide post silicon carbide shells unsealing. Ratio S:L and acid concentration are chosen taking into consideration requirements to uranium and acid concentratins in a final solution to be extracted.

When fuel burnup is 100 MW days/kg slime is forming; slime contains molybdenum, palladium, ruthenium, plutonium and uranium [5,6]. Slime is treated with concentrated acid, which may be used to solute the following fuel lot. To increase slime dissolution rate fluorine ion is introduced. Obtained uranylnitrate solutions are directed to extraction retreatment. Investigations on choice of nuclear fuel regeneration regimes were carried out in "hot" cells of Radium Insti-

tute named after V.G.Khlopin on experimental device CU -2 permitting to carry out various investigations [4].

Extraction stand consists of the following parts:

- assembly of extraction purification of uranium, plutonium, neptunium and separation of plutonium and neptunium from uranium;
- assembly of extraction additional purification of uranium;
- assembly of extraction additional purification and separation plutonium and neptunium.

Thus each of final components (uranium, plutonium and neptunium) passes two extraction purification cycles (30% tributylphosphate in hydrocarbon diluent is used as extragent).

When the scheme of fuel element reprocessing is chosen it's necessary to take into consideration the following:

- initial enrichment and strict maintenance of nuclear safety conditions;
- burnup value, cooling time and necessary degree of uranium and plutonium purification;
- requirements on chemical composition of final products;
- ratio of fission fragments, corrosion products and trans-uranium elements present in macroquantities in liquid and solid waste.

When fuel elements with low exposure are delivered for reprocessing it is necessary to carry out three cycles of uranium and plutonium purification. In this case plutonium may be extracted jointly with uranium during the first and the second cycles, and during the second cycle plutonium is separated using reducing reextraction and is delivered to the third cycle of purification [5,6].

For successful process realization taking into consideration features of HTGR fuel careful development and checking of the following operations is carried out:

- effectiveness of cooling system and gas filtration at the outlet of furnace for burning;

- initial solutions clarification for removal of any origin suspensions (some influence may have presence of water-soluble organic compounds in the case of incomplete removal of graphite and pyrolitic carbon of protective coatings);

- extraction of final products when high concentrations of fission products being present, use of agentless (for example, electrochemical) methods of macroquantities separation of plutonium and uranium;

- reprocessing of highly active refinates, determination of their resistance point at the stage of concentration by evaporation and during the subsequent storage.

The described technological scheme of fuel regeneration and its apparatus realization meet main requirements of nuclear fuel regeneration technology:

- ensuring minimum uranium and plutonium losses (0.1% and less);

- obtaining of chemical composition of nitricacid solutions meeting requirements of subsequent extraction reprocessing of these solutions using tributylphosphate;

- minimum quantity of radioactive waste;

- ensuring of equipment nuclear safity, its high output and possibility of remote maintenance.

Our investigations show the principal possibility to realize regeneration of HTGR rejected and irradiated fuel.

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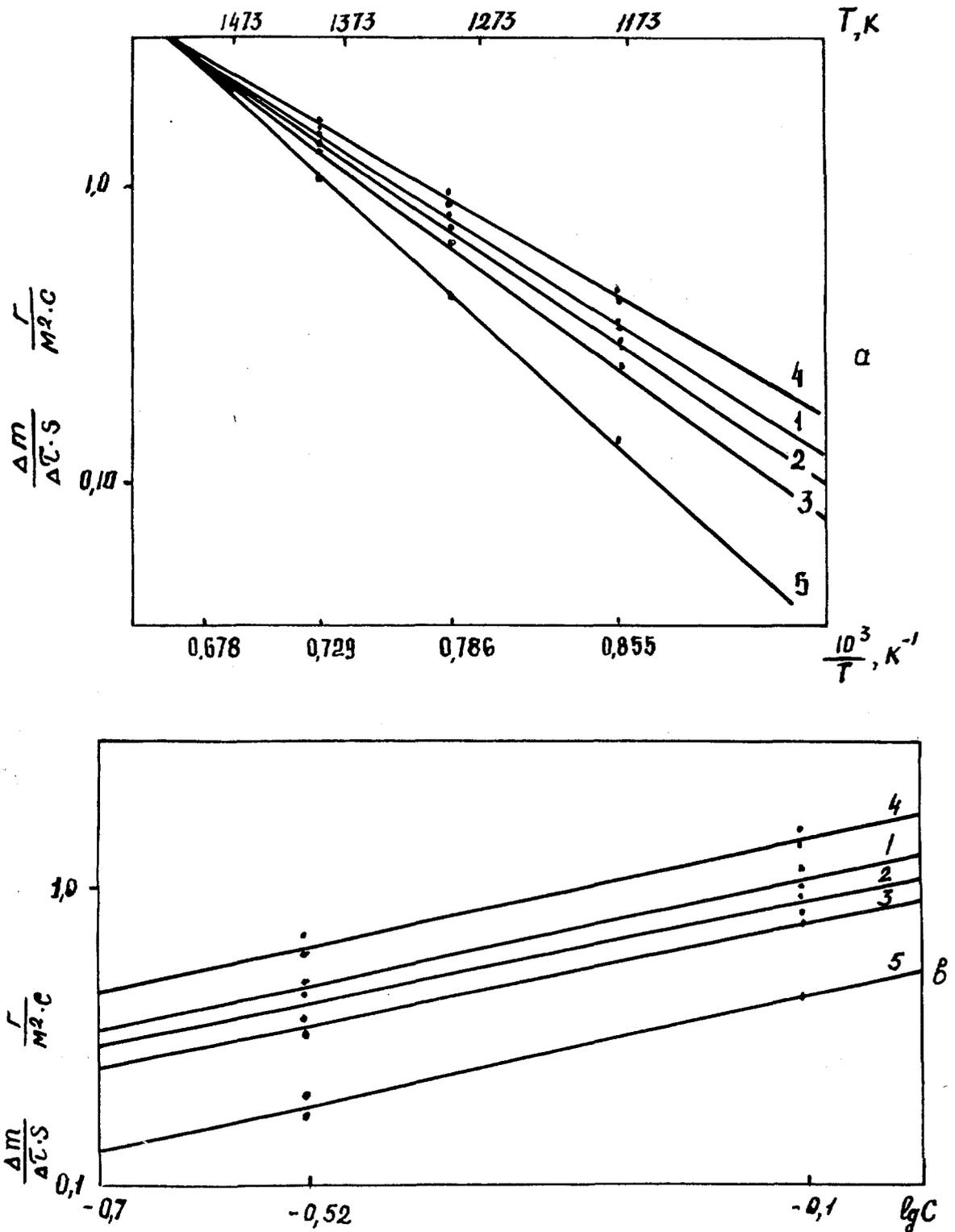
Fig.1. Dependence of Gasification rate of APB(1), МПГ-6(2),
ЗОПГ(3) Graphites, Matrix Graphite (4) and PyC(5)
upon Temperature (1a) when Oxigen Concentration is
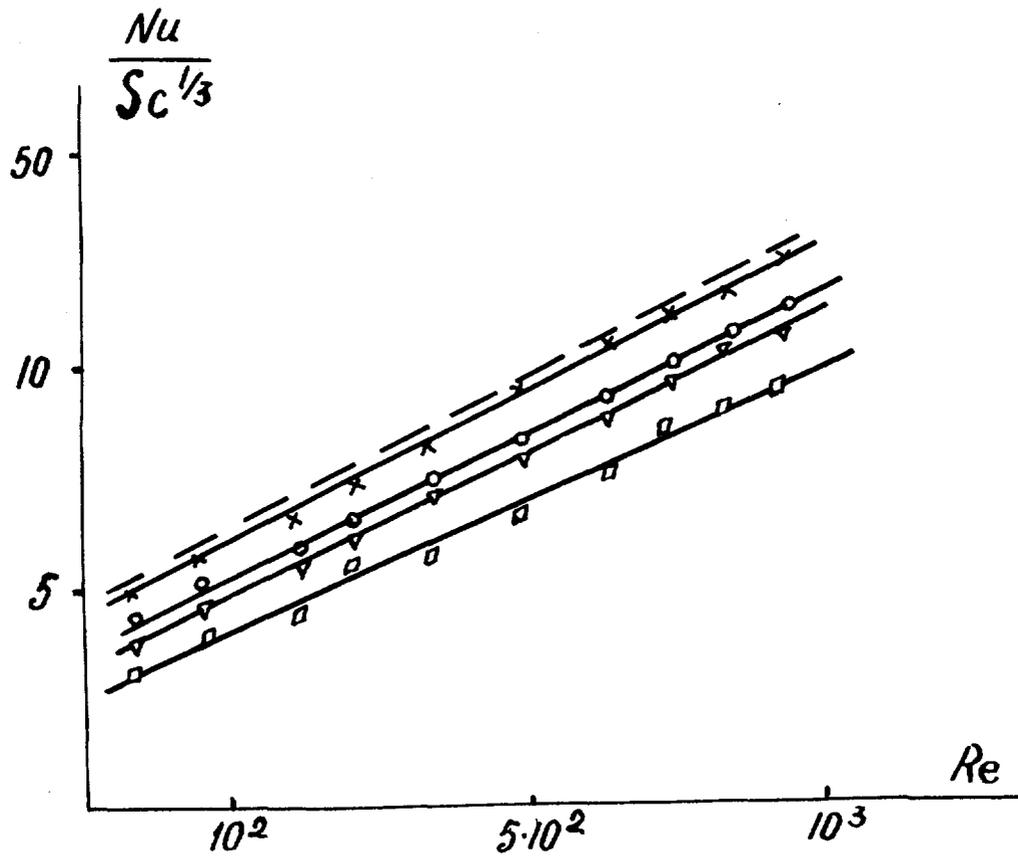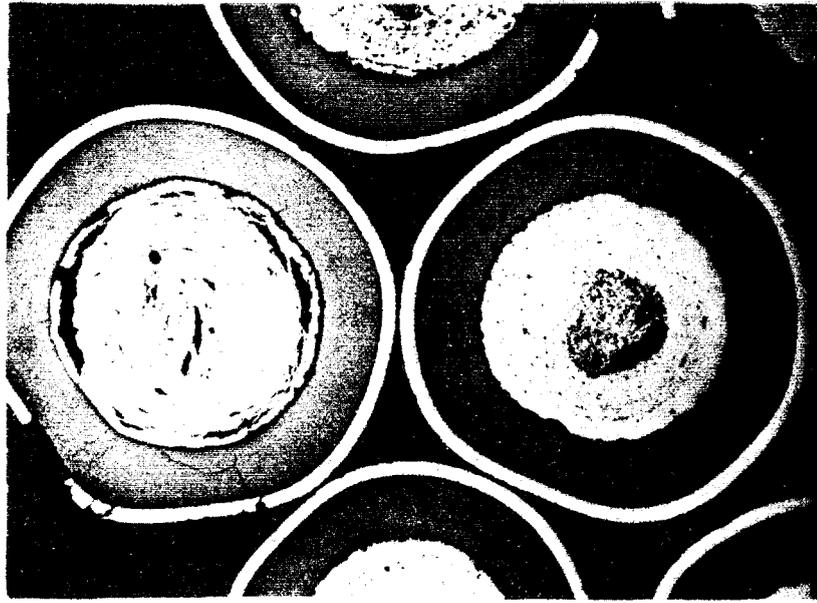21vol.% and upon Oxigen Concentration (1b) when Tem-
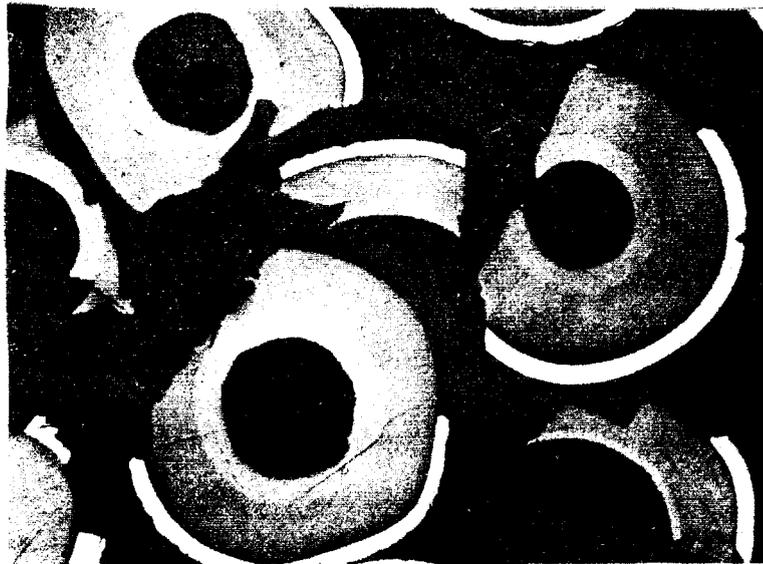perature is 1170 K.

$$\frac{Nu}{Sc^{1/3}}$$

Fig.2. Dependence of Mass Transfer upon Layers Number (N)

of Cylindrical Spheres Filling: $-\square-$ N =1, $-\triangledown-$ N=3,

$-o-$ N =5, $-x-$ N=13, $---$ data [3].

Fig.3. Coated Fuel Particles post Shock Destruction under
Effect of Pressure Drop. 0.2 MPa (a, x 80), 0.5 MPa
(b, x 30).