SYNTHESIS OF LOW PERFLUOROALKANES AT HIGH-TEMPERATURE INTERACTION BETWEEN GRAPHITE AND FLUORINE

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INDUSTRIAL APPLICATIONS OF PERFLUOROALKANES

Low perfluoroalkanes CF_4, C_2F_6, C_3F_8, C_4F_{10} :

Gaseous fluorine carriers used for silicon, silicon oxide and silicon nitride etching in semiconductor industry

$Si_{solid} + C_nF_{2n+2\ gas} \rightarrow SiF_{4\ gas} + C_nF_{m\ gas}$

$SiO_{2\ solid} + C_nF_{2n+2\ gas} \rightarrow SiF_{4\ gas} + C_nF_{m\ gas} + O_{2\ gas}$

$SiN_{solid} + C_nF_{2n+2\ gas} \rightarrow SiF_{4\ gas} + C_nF_{m\ gas} + N_{2\ gas}$

Also C_2F_6, C_3F_8 used as non-ozone-depleting freons

The global industrial consumption of perfluoroalkanes is up to 5000 tons per year

TRADITIONAL INDUSTRIAL PROCESSES FOR PERFLUOROALKANES SYNTHESIS

1. Tetrafluoromethane CF_4

   $C_{solid} + F_{2\ gas} \rightarrow CF_{4\ gas}$

2. Hexafluoroethane C_2F_6

   $C_2F_mCl_{n\ gas} + HF_{gas} \xrightarrow{cat} C_2F_{6\ gas} + HCl_{gas}$

3. Octafluoropropane C_3F_8

   $C_3F_{6\ gas} + CoF_{3\ solid} \rightarrow C_3F_{8\ gas} + CoF_{2\ solid}$

4. Decafluorobutane C_4F_{10}

   anode process:

   $(C_4H_9)_3N_{liq} + F^{\cdot} \rightarrow (C_4F_9)_3N_{liq} + C_4F_{10\ gas} + NF_{3\ gas} + HF_{liq}$

INDUSTRIAL CARBON FLUORINATION

1. Tetrafluoromethane synthesis

   $C_{solid} + 2F_{2\ gas} \rightarrow CF_{4\ gas} + 931\ kJ$

   Sub products: absent

   Fixed graphite bed, Inverse wave of filtration combustion

   T ~ 2000 K, reaction heat removal – radiation

   Typical capacity of reactor unit – several hundred tons per year

2. Carbon fluoride synthesis

   $2C_{solid} + F_{2\ gas} \rightarrow (CF)_{n\ solid} + 198\ kJ$

   Sub products: CF_4, $C_nF_{m\ gas}$

   Fixed carbon bed

   T ~ 300-450^oC, reaction heat removal – natural convection

   Typical capacity of reactor unit – till to ten tons per year

THE MAIN GOAL OF INVESTIGATION

To study the possibility of commercial synthesis of perfluoroalkanes from elements:

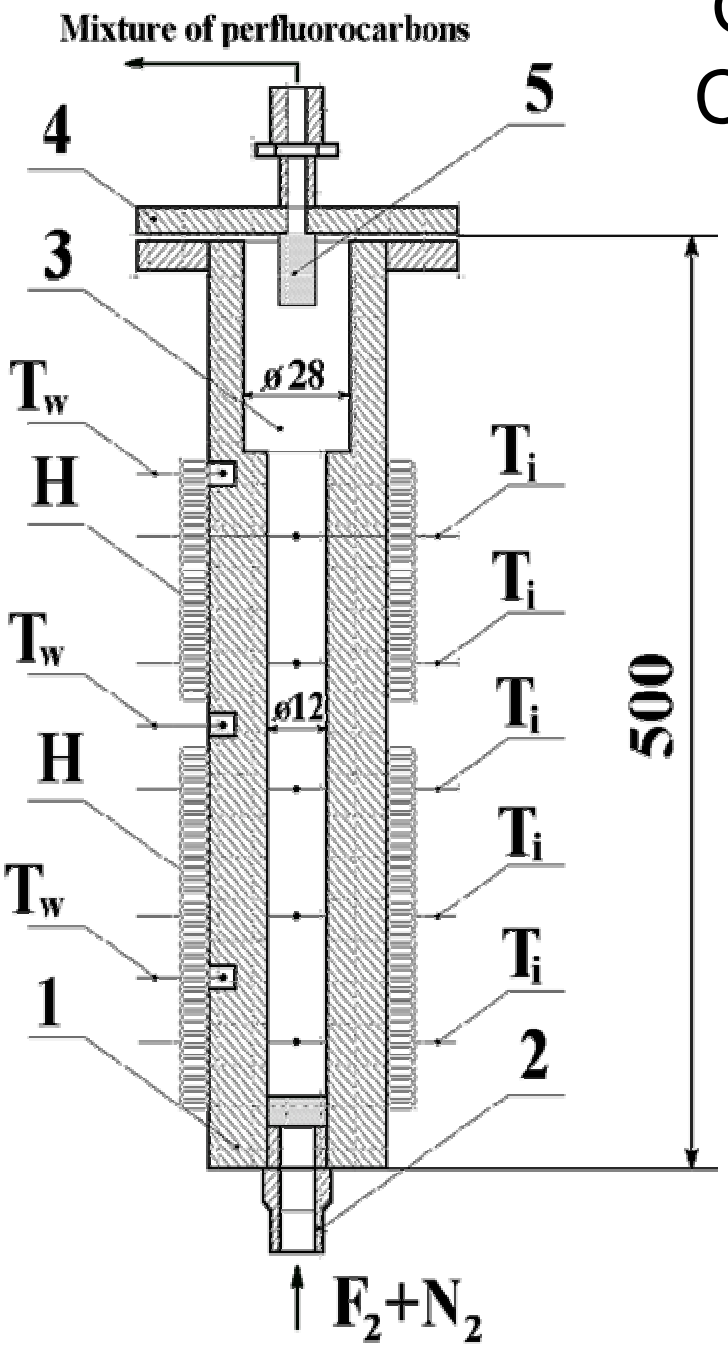
$$C_{solid} + F_{2\ gas} \rightarrow CF_{4\ gas} + C_2F_{6\ gas} + C_3F_{8\ gas} + C_4F_{10\ gas}$$

<u>Technical approach and methodology</u>

To provide thermo stabilization of the reaction zone we applied dynamic (mixed, movable) carbon powder beds

As a raw carbon we used classified graphite powder as a friable material, non-susceptible of lumping and bridging

GRAPHITE FLUORINATION IN CIRCULATING FLUIDIZED BED



Laboratory reactor

1 – the body of the reactor;

2 – connecting pipe for feed fluorinating mix;

3 – the flash box for dust separation;

4 – the cover of the reactor;

5 – the filter;

H – the electroheaters;

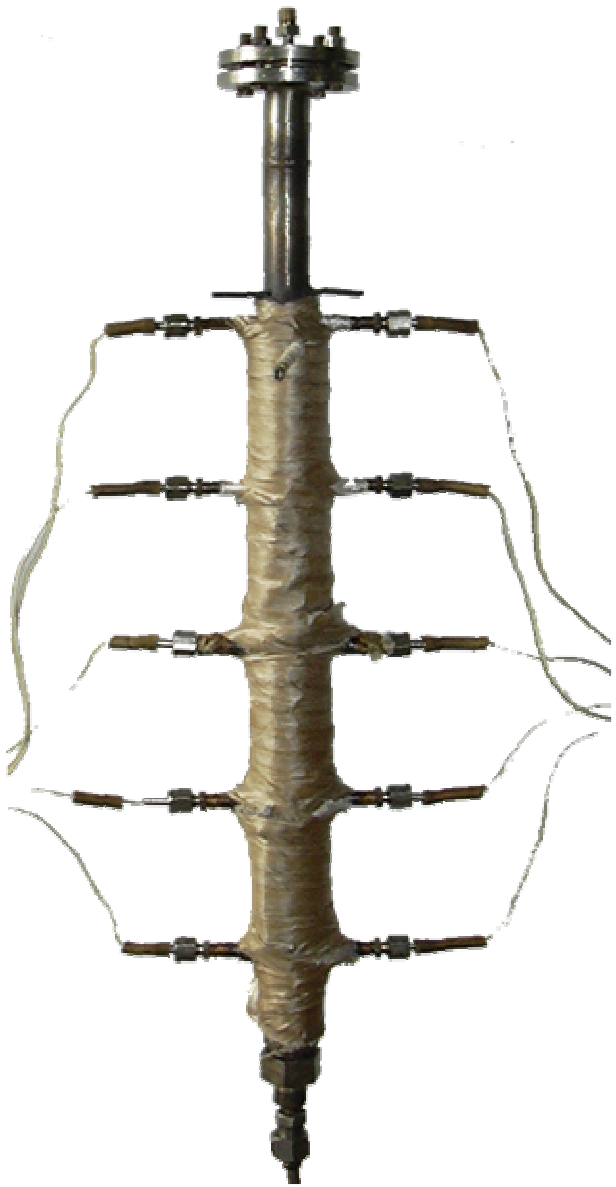
T_i – the inside thermocouples;

T_w – the wall thermocouple.

$l_{REACTOR}$ = 500 mm;

W_{MIX} = 6,5 ml/sec;

$t_{CONTACT}$ = 3 sec



Results of experiments

- At the temperature from 580 to 600^{0}C average composition of products of the reaction:

  CF_4 - 40-45 wt.%,

  C_2F_6 - 20-25 wt.%,

  C_3F_8 - 20-25 wt.%,

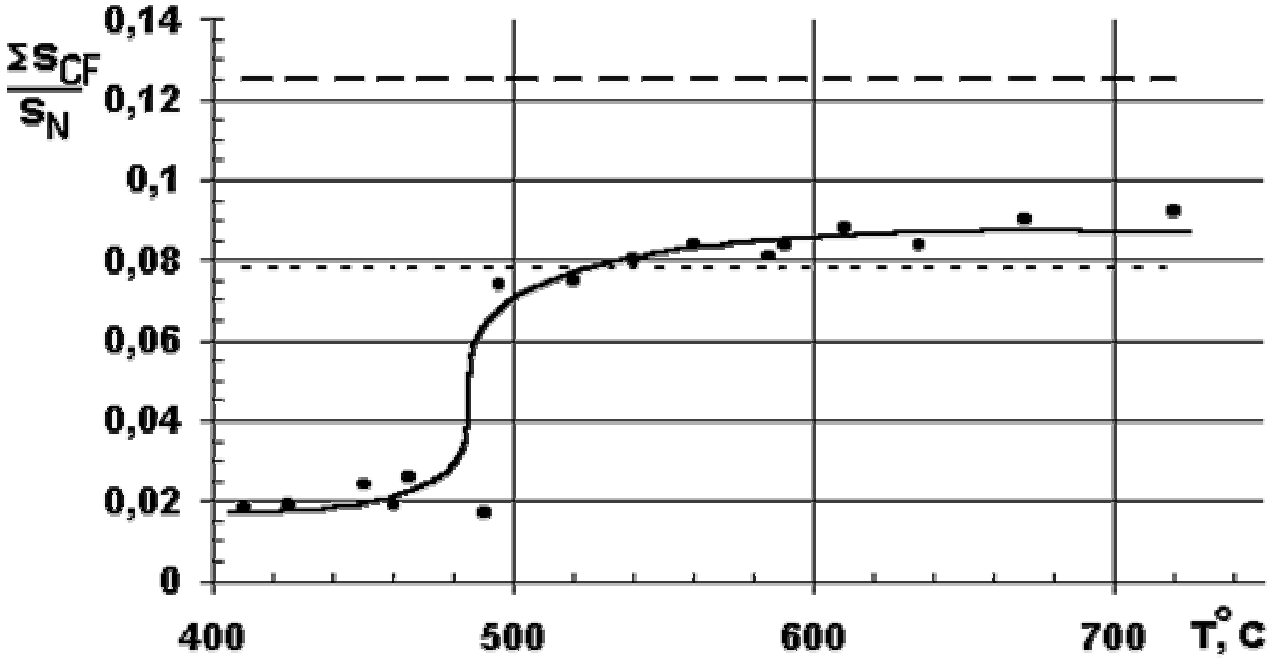
  C_4F_{10} - 10-15 wt.%.

- At the temperature is higher then 550^{0}C in the laboratory reactor there is no accumulation carbon polyfluorid $(CF_x)_{n\ sol}$.

- Synthesis CF_4, C_2F_6, C_3F_8, C_4F_{10} proceeds under the circuit: “synthesis $(CF_x)_n$ at $x \sim 10^{-3}$ - thermal decomposition $(CF_x)_n$ ”.

MACROKINETIC MODEL OF PERFLUOROALKANES SYNTHESIS

$\Sigma S_{CF}/S_N$ - the relation of the sum of the areas of chromatographic peaks of perfluorocarbons and area of chromatographic peak of nitrogen



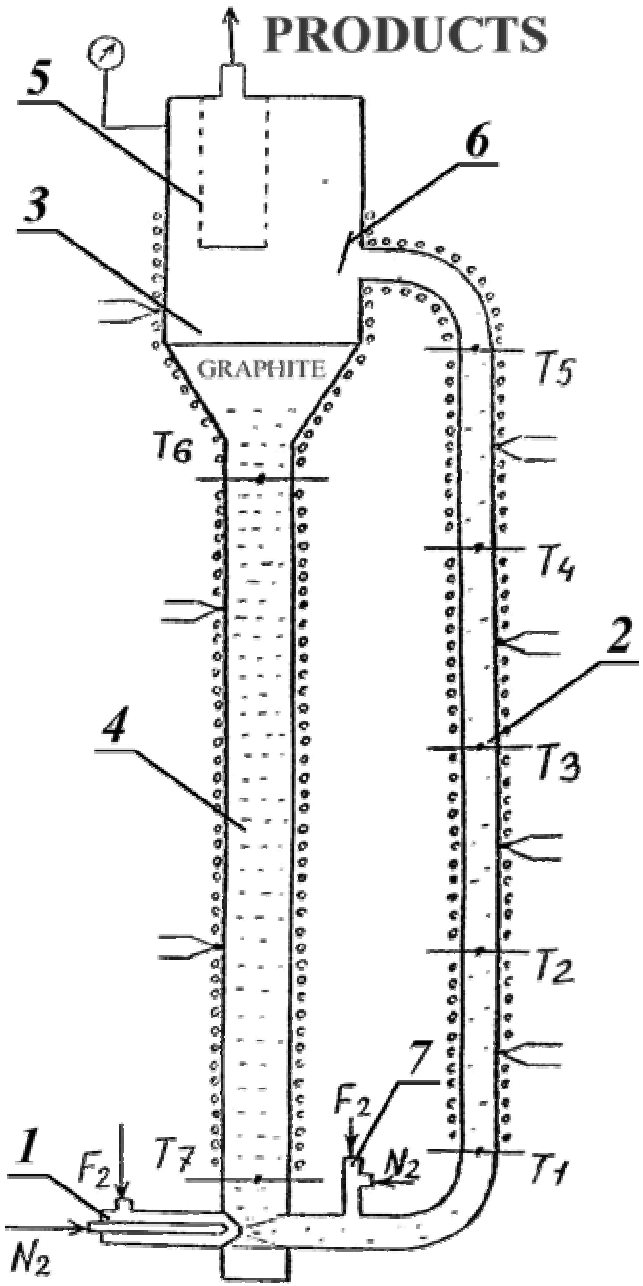
— the experimental dependence

– – – the theoretical value $\Sigma S_{CF}/S_N$ at preparing CF_4 only

---- the theoretical value $\Sigma S_{CF}/S_N$ at preparing of mixture with the average formula $CF_{3,2}$, corresponding to composition of products at the temperature of synthesis from 580 to 600 ^0C

SYNTHESIS AND DECOMPOSITION OF GRAPHITE FLUORIDE

Process	Characteristics	CF_4	C_2F_6	C_2F_4	C_3F_8	C_3F_6	C_4F_{10}
		Vol. %					
Synthesis	T=470 ^{0}C , Boiling bed, 20 vol.% F_2	44	26	0.1	14	–	15
Decomposition	T=550 ^{0}C, Boiling bed, N_2, $(CF_{0.35})_n$	73	16	–	7	2	2
	T=500 ^{0}C, He, $(CF_{0.9})_n$, τ=5 h	33	30	–	20	–	17
	T>600 ^{0}C , He, $(CF_{0.9})_n$	27	67	0.1	3	1	2



PERFLUOROALKANES SYNTHESIS IN ASCENDING GAS-DUST FLOW

Laboratory reactor

1 – ejector;

2 – lifting pipe, D=9 mm, L=1200 mm;

3 – separator;

4 – down-take pipe, D=20 mm;

5 – filter;

6 – sensor for solid phase discharge;

7 – injector;

T_1-T_7 – are thermocouples for the reaction medium.

Results of experiments

An approximate composition of gaseous products of the graphite fluorination according to the scheme «synthesis of $(CF_x)_n$ in gas-dust flow at $x \sim 10^{-3}$ - thermal decomposition of $(CF_x)_n$ in stationary bed» is as follows:

CF_4 - 35-40 wt.%

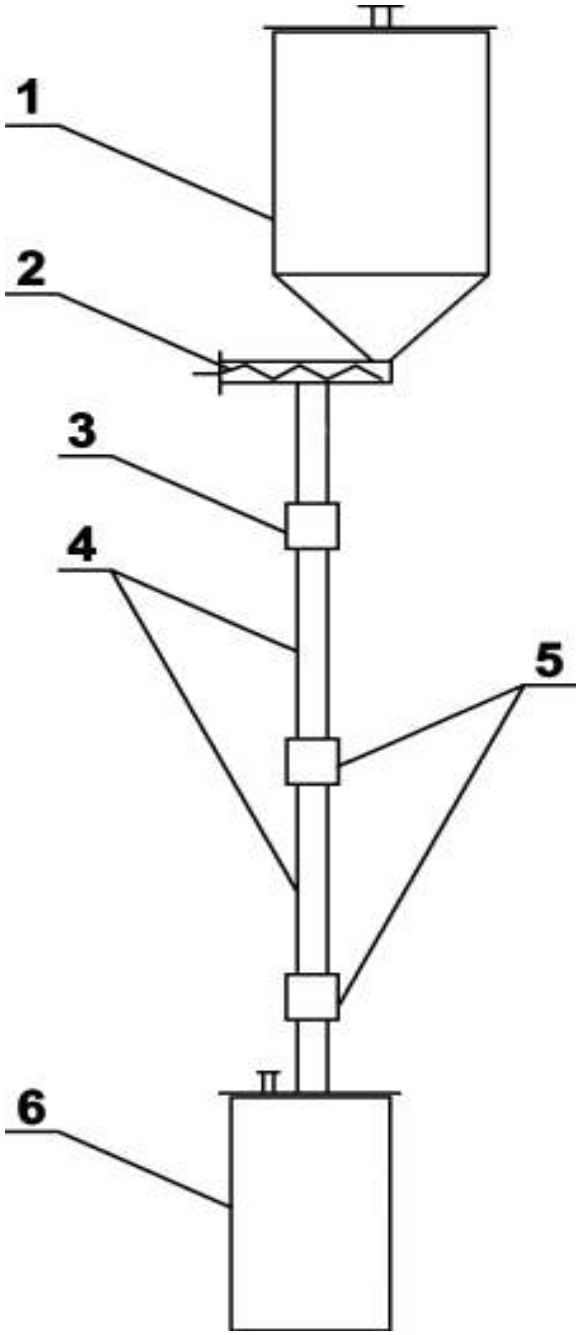
C_2F_6 - 25-30 wt.%

C_3F_8 - 15-20 wt.%

C_4F_{10} - 15-20 wt.%

By-products: C_2F_4 – 10^{-1}%, C_3F_6 – 10^{-1}%, cycle C_6F_{12} - 10^{-2}-10^{-3}%, perflurodecaline – 10^{-3}% etc.

The synthesis of $(CF_x)_n$ was carried out at 500-550^{0}C, while its thermal decomposition was carried out at 550-600^{0}C



PERFLUOROALKANES SYNTHESIS IN FREE-FALLING GRAPHITE POWDER BED

Laboratory reactor

1 – service bunker, V=1400 cm^3

2 – auger dozer

3 – fluorine input

4 – reaction tube, D=12 mm, L=300 mm

5 – controller

6 – receiving bin, V=1700 cm^3

Composition of gaseous products

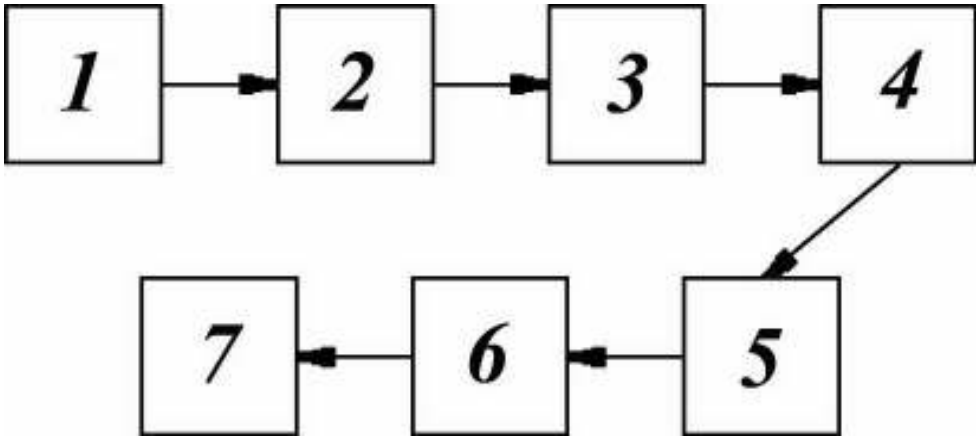
CF_4 - 38-40 wt%

C_2F_6 - 24-26 wt%

C_3F_8 - 19-21 wt%

C_4F_{10} - 10-12 wt%

PRINCIPAL TECHNOLOGICAL DIAGRAM OF PERFLUOROALKANES SYNTHESIS



1 – unit for preparation of initial components

2 – reactor unit (free falling bed reactor)

3 – unit for fluorination of unsaturated fluorocarbons (C_2F_4, C_3F_6) by CoF_3

4 – unit for separation of high-boiling admixtures (cycle C_6F_{12}, $C_{10}F_{18}$ etc.)

5 – alkali neutralization unit (F_2, HF)

6 – dehydration unit

7 – unit of separation of the desired products by rectification

CONCLUSION

- The reaction system carbon-fluorine was investigated with a dynamic powder bed using under nearly isothermal conditions close with the aim to produce CF_4, C_2F_6, C_3F_8 and C_4F_{10}. At a temperature of 550-600^{0}C the composition of fluorination products is as follows: 35-40 wt.% CF_4, 25-30 wt.% C_2F_6, 15-20 wt.% C_3F_8, 10-15 wt.% C_4F_{10}
- A macro kinetic process model was suggested, which means that the synthesis of gas perfluoroalkanes proceeds according to the following scheme: "synthesis of carbon polyfluoride $(CF_x)_n$ at x value of a 10^{-3} order - thermal decomposition of carbon polyfluoride"
- As a result of the conducted work there has been created a scientific basis for industrial technology to synthesize lower perfluoroalkanes (CF_4, C_2F_6, C_3F_8, C_4F_{10}) from graphite and fluorine