PLASMA WASTELESS PROCESSING OF SILICON TETRAFLUORIDE

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SUMMARY

Plasma (H-O-H) chemical process for conversion of silicon tetrafluoride – a voluminous by-product in HF and UF_6 production - to silica and hydrogen fluoride has been studied and demonstrated in the bench-scale plant. The process is tested on a large scale to utilize SiF_4 from the off-gas of a hydrofluoric plant. The SiF_4 - conversion rate reaches 99.5 %, the concentration of resulted HF-acid is in range 42 - 45 %. Silica is produced in the form of γ-tridymite having specific surface area of 200 m^2/g and particle mean size of 9 μ.
During the long-time testing in the ARRICT there a few tons of SiF_4 were reprocessed. The experimental results are based upon representative statistic material.

INTRODUCTION

The silicon tetrafluoride (SiF_4) is a by-product of the hydrometallurgical processes where silicate or siliceous ores containing fluorine are subjected to acidic treatment. The process of hydrogen fluoride production by dissolution of fluorospar in sulfuric acid is shown schematically in Figure 1.

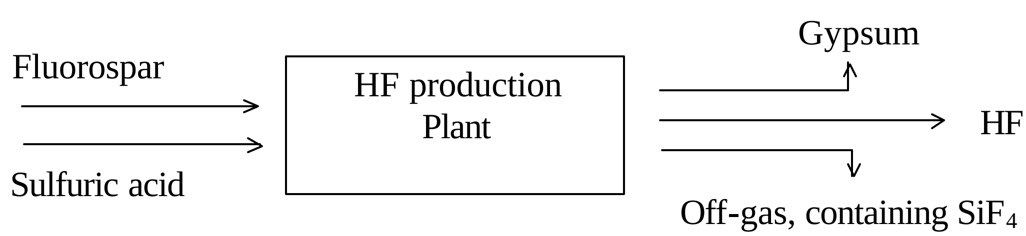

Figure 1. General scheme for production of hydrogen fluoride from fluorospar.

As a result of this process, up to 4 % of fluorine initially containing in fluorospar is lost in the from of SiF_4 polluting the environment of area of hydrofluoric plants. It is very difficult to utilize fluorine from SiF_4 because of its extremely high thermal stability. The problem grows more complicated when SiF_4 is a component of gas mixture containing air and other components.

Off-gas after hydrofluoric plants contains silicon tetrafluoride because of presence of silica in a raw material called fluorospar. As result, there are at least four economical, technical and social problems at these plants:

1. Incomplete extraction of fluorine from fluorospar.
2. Harmful action of fluorine-containing substances to environment.
3. Very complicated utilization of SiF_4 because of its extremely high chemical and thermal stability.
4. Silicon tetrafluoride is diluted with air and other gases.

The plasma process was worked out to convert silicon tetrafluoride (pure and containing in off-gas of a hydrofluoric plant) to disperse silica and hydrogen fluoride using an arc water plasma generator [1]. Total process is described by the following reaction:

SiF_4 (g) + 2 H-O-H (plasma) ® SiO_2 (c) + 4 HF (g), $\Delta H \sim 87$ kJ/mole

The results presented below are the large-scale follow-up of the previous R&D stage published earlier (1).

EXPERUMENTAL

According to the selected scheme, a gas mixture containing 15 - 30 % silicon tetraftoride in a quantity of 12 - 15 nm^3/h are compressed to the pressures of 107-127 kPa and fed to the plasma reactor where these gases are mixed with the (H-O-H) plasma generated by arc plasma generator. Silica and gaseous mixture consisting of hydrogen fluoride, superfluous water vapor and air are separated with help of fine metalloceramic filters. Hydrofluoric acid is condensed from gas flow in the condenser, collected in transport containers and directed to the following processing. When a hydrofluoric acid is concentrated enough we used rectification for producing waterless hydrogen fluoride returning azeotrope mixture HF-HOH to the plasma reactor.

SiF_4 in the plasma reactor converts stoichiometrically. Hereby the yield of hydrogen fluoride is a function of temperature of chemically reacting system. But when SiF_4 contains in a mixture with air one must use an excess of water plasma to realize quantitative conversion of SiF_4.
Below are shown the apparatus scheme (Figure 2) and the appropriate flow sheet (Figure 3). A rectification column was not used in this variant: concentrated hydrofluoric acid was reused for treatment a fluorospar to produce gaseous HF. The apparatus consists of the following primary units: SiF_4 - supply; plasma reactor combined with filtration system and device for discharging silica; condenser and HF-acid collector; HF - desorption unit.

The plasma apparatus has the following operation parameters:

- power of arc plasma generator, kW 120-140;
- water plasma supply, kg/h 25-30;
- gas exhaust supply, nm /h up to 35;
- concentration of SiF_4, % 15-30;
- specific expenditure of energy, kW*h/T 2,0-2,5;
- productivity on SiO_2, kg up to 25;
- productivity on HF, kg/h up to 35;
- concentration of HF acid, % 50-55.

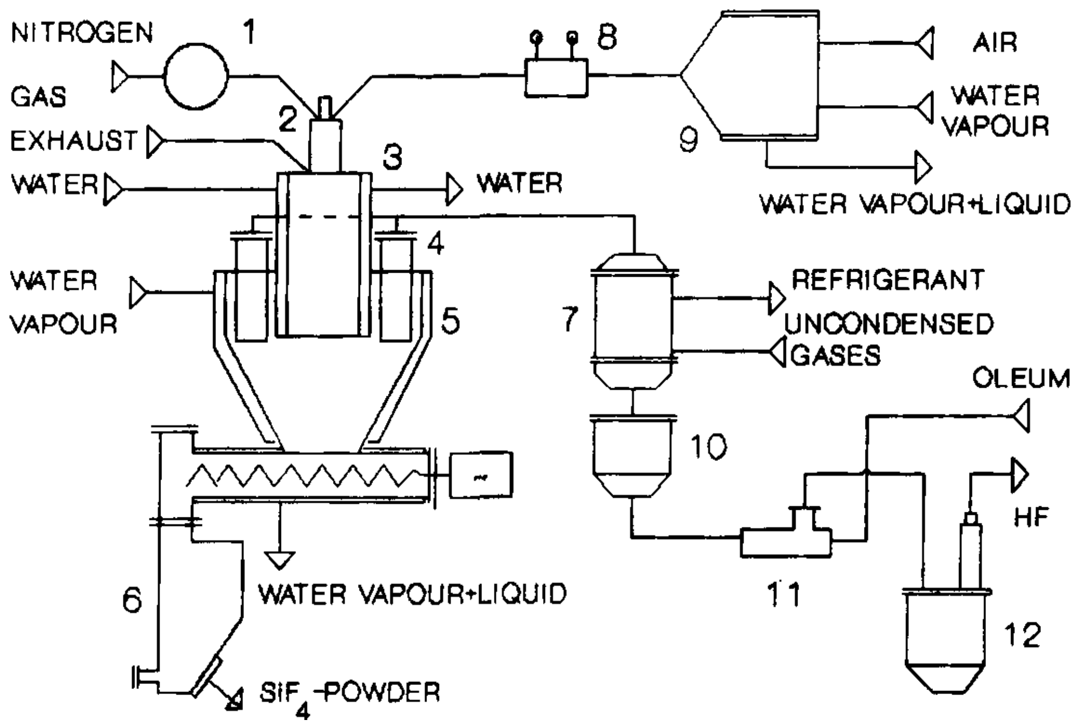

Figure 2. The apparatus scheme of a pilot plant for conversion of silicon tetrafluoride in (H-OH)-plasma: 1-compressor; 2-plasmatron; 3-reactor; 4-filter; 5-intermediate container; 6-container; 7-condenser; 8-steam heater; 9-collector; 10-vessel; 11-mixer; 12-desorber.

A distillation column is not used in this scheme: we produced concentrated hydrofluoric acid was recycled back to the apparatus for producing hydrogen fluoride from fluorospar. Additionally, the apparatus includes a plasma generator and instruments for control and regulation.

Technological parameters of the process are shown in Table 1. Table 2 presents the composition of source and final gas mixtures in large scale experiments. One can see that the initial gas mixture contains 8-18 '/. SiF_4. So far as SiF_4, is very diluted one must use large excess of steam. Therefore the hydrofluoric acid obtained is diluted and application of rectification is unprofitable. That is why the scheme of conversion of SiF_4 was simplified: we returned the hydrofluoric acid obtained to the apparatus for producing HF from fluorospar.

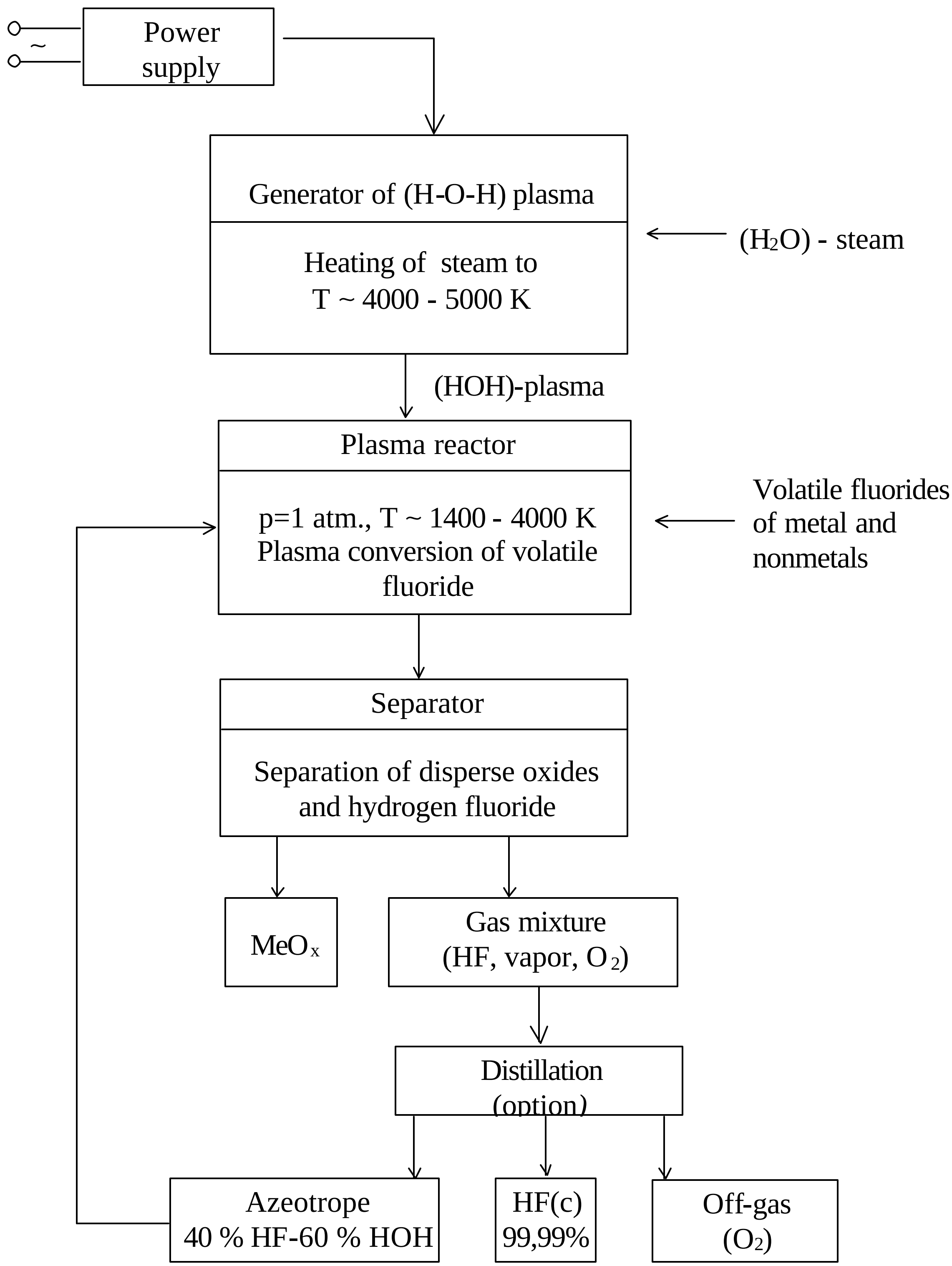

Figure 3. Flow sheet for plasma conversion of volatile fluorides.

Table 1. Parameters of industrial plasma conversion of SiF_4 in off-gas of a hydrofluoric plant

N exp	Plasma Torch Power, *kW*	Steam supply, *kg/h*	Gas flow, *nm³/h*	H_2O/SiF_4 ratio	Mixing Zone temp., *K*	Full conversion time, *s**	SiF_4 conversion rate, *%*	[HF] , % mass.
1	120	30	28	8,0	2600	0.01	99,5	42.2
2	120	30	36	13,0	2100	0,01	94,0	26,3

**) Time of conversion was determined using mathematical modeling (to be published later)*

Table 2. Gas composition at the inlet and the outlet of the plasma reactor

N exp.	Gas probe location	Concentration of components, % vol.					
		SiF_4	POF_3	O_2	N_2	HF	Other gases
1	Inlet	18,8	0,2	10,2	54,1	0,0	16,7
	Outlet	0,1	0,0	6,4	67,2	0,0	26,3
2	Inlet	8,2	0,0	6.9	73,4	1,2	10,3
	Outlet	0,5	0,0	7.3	82,0	0,4	9.8

Composition of hydrofluoric acid produced from the off-gas of a hydrofluoric plant is presented in the Table 3. This product was recycled for treatment a fluorospar; as result, the yield of gaseous HF increased by 4 % .

Table 3. Composition of hydrofluoric acid produced by plasma hydrolysis of SiF_4 after hydrofluoric plant

N exp.	Content of the constituents, % mass.				Conversion efficiency ($SiF_4 \rightarrow HF$), %
	HF	H_2SiF_6	H_2SO_4	SO_2	
1	40,0	2,40	2,21	0.001	97,8
2	42,14	3.41	1,64	0,001	97,1
3	46,09	2,08	0,98	0,017	98,0

Some properties of second product - silica are presented in Table 4. The product has low bulk density, relatively large specific surface area; one can see that additional thermal treatment of the powder in a discharge from the reactor into a container results in decrease of a specific surface area.

As a rule, the values of specific surface area of SiO_2 powder is in the range from 120 to 212 m^2/g. Its bulk density is of 0,05-0,07 g/cm^3 without shaking, and of 0,09 g/cm^3 after shaking, the size of SiO_2-particles is near 0,08-0,1 μ.

Table 4. Properties of silica produced by plasma conversion of SiF_4 from the off-gas of a hydrofluoric plant

Location of the probe	Bulk density, *g/cm^3*	SiO_2 (powder), *% mass.*	Residual moisture, *% mass.*	Specific surface area, *m^2/ g*	Residual Fluorine, *% mass.*
Filter	0,07 - 0,096	93,5	0,19	212	3,1
Container	0,05 - 0,07	89,7	2,17	127	3,5

The silica produced here as a by-product can be used as a filler for rubber articles, as heat and electricity insulator. We studied the physical properties of the product. The values of specific surface area of SiO_2-powder were in the range from 120 to 212 m^2 /g, its bulk density was of 0,05-0,07g/cm^3 without shaking, and of 0,09 g/cm^3 after shaking, the size of SiO_2- particles were of 0,08-0,10u. X-ray analysis of disperse silica produced by SiF_4- plasma conversion reveals metastable form of γ-tridymite.

Heat conductivity of the pressed SiO_2 pellets was determined depending on temperature (Figure 4). It was found that heat conductivity of this material is lower that heat conductivity of the best high temperature heat insulator - natural quartz.

Moreover, it was found that silica obtained is very good insulator in spite of impurities of fluorine and other elements from the raw material used (Figure 5).

The method of a stationary uni-axial thermal flux was used for measurement the heat conductivity and specific resistance of the silica. During the reported here R&D a few metric tons of SiF_4 were treated. So, the presented results are based on a large statistic material on production of hydrofluoric acid and disperse silica.

CONCLUSIONS

From the results of research and development of the plasma process presented we found that at least three technical and social problems can be successfully solved:

- increasing liberation of fluorine from fluorospar up to 99,9 %;
- preventing pollution of environment by gaseous SiF_4;
- producing disperse silica in crystalline or amorphous form.

The conversion rate of SiF_4 increases with increasing the mole ratio H_2O/SiF_4 at constant temperature, reaching 99,9 % at T=3000 K and H_2O/SiF_4 ~ 6-8. However, when the mole ratio H_2O/SiF_4 is essentially more than stoichiometric value - 2, concentration of HF-acid is lowered. It was found, that main factor defining high conversion rate of SiF_4 to SiO_2 and HF-acid in combination with high concentration of HF-acid, is the temperature in the plasma reactor. Thus, to produce hydrofluoric acid of mass concentration near 45 %, at conversion step of SiF_4 of 95,7, one must have the temperature in the converter more than 2500 K and the mole ratio H_2O/SiF_4 = 5. The by-product of the process is a disperse silica which meets the market requirements as a filler in rubber articles and as a material for heat and electrical insulators.

REFERENCE

1. Y.N. TUMANOV, A.V. IVANOV, *et al*. "Plasma Conversion of Silicon Tetra-fluoride", In: Proceedings of 10-th International Symposium on Plasma Chemistry. Bochum (Germany).August,4-9,1991, p.1-6.