Water plasma plant for halogenated hydrocarbon decomposition

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Abstract: PlasmaAir has designed and built a testing plant to investigate the performance in CFC decomposition for two different applications: typical exhaust gases from the semiconductor industry and high concentrated waste streams from the chemical industry. The plasma source used for a parameter study is an arc-heated plasma torch with various plasma gases. The decomposition performance was tested in two different types of reactors, a water-film-cooled system as well as a radiation-cooled system.

Keywords: plasma plant, hazardous waste, steam plasma, thermal decomposition.

1. Introduction

CFC (fluorinated and chlorinated hydrocarbons) and perfluorinated compounds (PFCs) like CF_4, C_2F_6, C_3F_8, C_4F_8, NF_3 or SF_6 are still used for etching and cleaning processes as well as insulation gas during quality control of the wafers in the semiconductor industries, even though their use is strongly regulated by the Kyoto Protocol and subsequent international contracts. However, PFCs cannot be substituted easily in this field of application due to their unique characteristics. Conventional post combustion techniques show poor treatment efficiencies for PFC containing waste gases, especially in case of CF_4.

Exhaust gases in semiconductor industry are typically characterised by concentration levels of several thousand ppm of e.g. CF_4 in nitrogen.

In the production of CFCs in chemical industry small flow rates of CFCs are emitted as waste air compounds.

For the disintegration of CFC materials the use of a water plasma may be favourised due to the high energy density and the presence of oxygen and hydrogen, which are necessary to produce the desired final products after the high temperature zone: CO, CO_2, HF and HCl. Using a steam plasma the waste in chemical industry can either be depolluted or the CFC can be converted to reuseable producs like HF.

2. Process description

The technical plant consists of an arc heated plasma unit followed by a combustion chamber and a quench-scrubber system. The multi gas plasma torch of PlasmaAir is used as plasma source. The torch can be operated at electrical input levels from 5 – 25 kW and with various plasma gases like water steam, air and nitrogen, which were investigated in this study. The PlasmaAir torch was also designed to

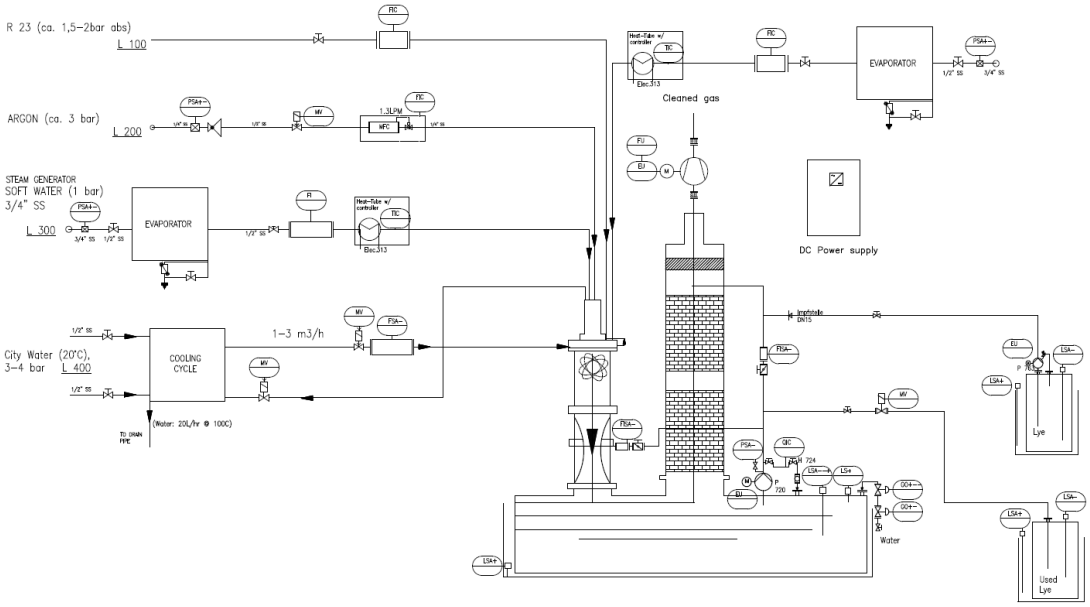

Fig. 1: Scheme of the plasma plant.

achieve a long lifetime of the electrodes. CFC gas was injected into the plasma plume in a subsequent mixing unit directly installed between the torch and the reactor itself. Two different reactor types were investigated. A radiation-cooled reactor as it is presently used in industrial plants and an inner water-film-cooled reactor as it is installed at different sites of the semiconductor industry. Downstream of the reactor the process gas is quenched with a low concentrated lye to scrub out the HF and the HCl.

After the quench the process gas is finally treated by a packed column scrubber to eliminate residual acidic waste air compounds by an aqueous lye. Between the quench and the scrubber the process gas was analysed using both a GC-MS system and a FTIR.

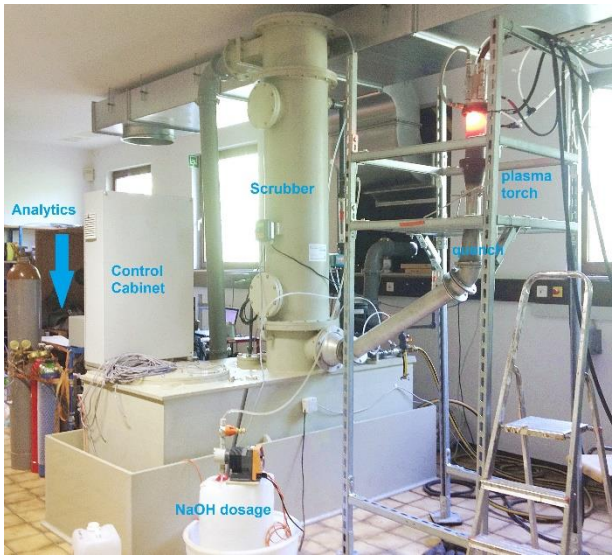

Fig. 2: Picture of the test plant with the radiation-cooled reactor.

3. Results with CF_4 in Nitrogen

In a first pilot batch the decomposition rate of CF_4 in nitrogen was investigated. A typical exhaust gas contribution known from the semiconductor industry was selected. Tests were performed at 50 l/min and 100 l/min with both reactor systems. Table 1 shows the comparison of the CF4 concentrations in the gas after the reactor, on the one hand for the water-cooled reactor, on the other hand for the radiation-cooled reactor at 100 l/min waste gas flow. In both cases the decomposition efficiency increases with increasing power. A very high degree was found with the 20 kW radiation-cooled configuration.

	Fall-film-cooled reactor			Radiation-cooled reactor		
Steam [kg/h]	13 kW	15 kW	20 kW	13 kW	15 kW	20 kW
1.5	1726	777	395	1293	1020	543
2.0	1210	661	214	689	398	9.4

Table 1: CF_4 concentration in ppm in the clean gas Operation conditions: 100 l/min N_2, 5890 ppm CF_4 (fall film) or 5389 ppm radiation-cooled.

Using the fall film reactor the dependency of the plasma gas on the decomposition rate was investigated. The system was set to 50 l/min nitrogen as carrier gas and a CF_4 concentration of 5300 ppm (steam plasma) and 3200 – 3800 ppm (nitrogen or air plasma) as operational point. The measurement results for these three plasma gases at three different electrical power levels are shown in table 2.

Steam mass flow 2.0 kg/h Fall film reactor			
Power	13 kW	15 kW	20 kW
CF_4 in ppm	204	108	29.6
NO in ppm	39830	33428	44127
Nitrogen plasma; flow 2.0 kg/h Fall film reactor			
Power	13 kW	15 kW	20 kW
CF_4 in ppm	469	233	125
NO in ppm	37556	38140	48005
Air plasma; flow 2.0 kg/h Fall film reactor			
Power	13 kW	15 kW	20 kW
CF4 in ppm	361	302	165
NO in ppm	74100	79600	92400

Table 2: CF_4 and NO concentrations in clean gas operation conditions: 50 l/min N_2, 5890 ppm CF_4 (steam plasma) and 3200 – 3800 ppm CF_4 (nitrogen or air plasma).

The results demonstrate, that with all three kinds of plasma gases high decomposition rates are achieved. Considering higher crude gas levels of CF_4 in case of the steam plasma, the performance level of the steam plasma is even higher than for nitrogen or air. Operating the system with steam plasma, the NO concentration after the reactor is the lowest concentration observed in this study. This concentration severly influences the lye consumption of the system. Due to the performance in CF_4 degradation and lye consumption, steam therefore is the best suitable plasma gas for this process.

The effect of the total nitrogen flow on the decomposion of CF_4 is shown in Table 3. It was found, that the degree of decomposition is strongly affected by the nitrogen flow and the initial concentration of the CF_4. The higher the nitrogen flow, the lower the treatment efficiency. This is an indication, that the specific energy, directly affecting the temperature of the system, is too low for the high carrier gas flows to achieve high decomposition rates.

CF_4 con-centration	N_2 flow radiation-cooled reactor			
ppm	50 l/min	100 l/min	150 l/min	300 l/min
2790	100%	100%	94.4%	68.7%
5500	100%	99.8%	95.5%	65.9%
11000	100%	99.2%	94.6%	67.0%
22000	100%	96.3%	94.5%	-

Table 3: The CF_4 deposition rate in % for different exhaust gas volume flows for fixed plasma conditions: 20 kW, 2.0 kg/h water plasma stream

4. Results with R23 in high concentrations

Using the equipment of the radiation cooled reactor as described, the decomposition of R23 in a water steam plasma was investigated. During the tests the plasma parameters were kept constant and the flow of the R23 was varied.

El. input power of the plasma torch	13.6 – 13.94 kW
Argon flow	1.8 slm
Water steam plasma	1.0 kg/h

Table 4: Plasma parameters for the R23 decomposition tests.

The decomposition efficency of the steam plasma towards R23 is shown in table 5. Besides the steam as plasma gas additional steam was fed into the mixing chamber to supply reaction partners for the R23 in a substoichiometrical, stoichiometrical, or hyperstoichiometrical way. It can be seen, that the efficiency is very high using the water plasma at stoicheometric conditions. During degradation of R23 other VOCs, formed by plasma exposure, were detected in the exhaust gas and identified as low amounts of CF_4 and CF_3OH. The plasma conditions were kept constant during the whole process (13.4 kW plasma input power, 1 kg steam in plasma). Decomposition rates of more than 99.99% were achieved and thus very high. Consequently, the consumption of lye in the scrubber was very high. This is an significant indication that HF was nearly stoichiometrically formed during this process.

Input into the reactor in kg/h		Concentration measured after the quench in ppm		
R23	H_2O	R23	CF_4	CF_3OH
4.0	2.0	7.2	0.5	0.1
5.0	2.0	5.4	1.2	0.3
7.5	2.0	111.6	1.7	4.6
10.0	3.0	108.8	3.1	3.7
12.0	1.5	232.5	45	2.5

Table 5: R23 concentrations and byproducts in the clean gas. Mass flows of R23 and H_2O were varied. Operation conditions: 1.8 l/min argon, 13.77 ± 0.17 kW.

5. Summary

Investigations of the decomposition of CFCs with CF_4 and R23 as exemplary compounds were conducted in two different plasma reactors. The decompositional behaviour of a typical waste gas stream of the semiconductor industry was determined. The effect of initial concentrations, carrier gas flows, electrical power, specific energy, plasma gas, and the configuration of the plasma reactor were intensively tested and quantified by gas. The water plasma in combination with the radiation cooled reactor was identified as the best suitable system for this application. The decomposition rates strongly depend on the specific energy supply. Rates up to 99.99% in case of CF_4 degradation have been found.

This system was also used to decompose a R23 waste gas stream, typically occuring ina chemical industry process as second application. It was found, that with a specific energy of 0.8 – 1.0 kW/kg R23 the decomposition rate was more than 99.99%.

6. References

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