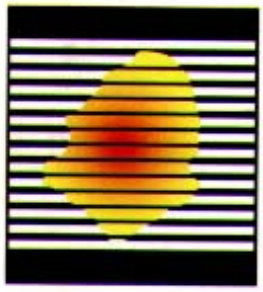

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SIMULTANEOUS REMOVAL OF SiF_4 AND NO_x USING A CORONA DISCHARGE

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ABSTRACT

The combustion exhaust containing NO_x, flourosilicate SiF_4, heavy-metals and other toxic compounds were treated with small scale equipment (10 Nm^3/hour) on by-pass of the glass oven. The equipment consists of two corona discharge blocks (each contain 12 coaxial corona discharge tubes), with gas flow rate 4.5 m/s. The gas flow is directed firstly downwards and then upwards (in U shape). The ultrasonic aerosolator was used for spray of $Ca(OH)_2$ water solution for neutralisation on the inlet of discharge system. The size of droplets was 0.5-10 μm and applied amount between 0,5-2 l/hour of liquid. The discharge parameters were U=7,8 kV, discharge current I=13,5 mA, power consumption 7,86 Wh/Nm^3.

The removal efficiencies were 71% for NO_x, 74% for SiF_4 converted to HF, 68% for all Cl containing compounds converted to HCl, 99,2% for Pb, 95,5% for As. The negative polarity of discharge appeared more effective. The qualitative analyses of products were performed using IR analysis (gaseous products) and isokinetic sampling (solid particles) by authorised measuring group. Analysis of solid and liquid products from the system was realised additionally using IR spectrometry. The solid fluorosilicates $CaSiF_6$, silane SiH_4, CaF_2, NO_2F and NOF were found as products from IR absorption spectra.

INTRODUCTION

In the last decade, our life-sustaining environment has changed more rapidly than it did during any comparable period of history. Acid rain, global warming, the ozone layer depletion are the most important problems today. The environment is polluted by chemicals emitted directly from identifiable sources or by chemicals formed indirectly through photochemical reactions in the air. All these chemicals have more or less toxic effects, endangering human health, therefore their removal or at least maintenance within a certain level is necessary. In the recent years, there is a growing interest for gas cleaning techniques of non-thermal plasma.

Exhausts from a glass furnace usually (depends on a type of a glass) consist of particles cca 1μm containing many metals (Pb, As, Cd, Co, Cu, Ni, Cr, Zn, Mn, Se, Sb, Ba, B) mainly in their native oxide form. The most dangerous are compounds of Sb, As, Se, Pb and carcinogen Cd and Cr as well. For entrapping of these particles from glass furnace emissions mainly filters and electrostatic precipitators (EP) are used. However only some EP suitable for a high temperature conditions can be used.

In glass production the concentration of nitrogen oxides NO_x (mainly NO) in furnace exhaust is very high up to 30 000 ppm..

In the case of opalescent glass production, the exhaust gases include fluorosilicate SiF_4. These compounds affect synergistically simultaneously with NO_x. According to literature SiF_4 removal can be done by absorption in alcalic solutions with the efficiency lower than 40%.

This article deals with an information on testing results of the corona discharge equipment in by-pass waste gasses ducting of the glass furnace in Ornela a.s. Desná (Jizerské hory). The equipment in its effect has tried to associate simultaneous removal of particle's emissions (with a great efficiency on Pb and As), NO_x and flouro-compounds as well.

EXPERIMENTAL SET-UP

The discharge system was designed for 10 Nm^3/hour and presented schematically in Fig.1. The main part of the system consisted of two series-coupled corona discharge blocks. Inside each of two blocks, there were 12 coaxial discharge tubes with 50cm length and 20mm in diameter. As a material for these coaxial discharge tubes, we decided to use brass for the outer electrode, while central electrodes (6mm in diameter) were made of copper with an external thread. The gas flowed through the blocks firstly downwards and then upwards (in U shape) with a flow rate ~ 4.5 m/s.

The system was equipped with ultrasonic aerosolator on the inlet of the discharge system to spray $Ca(OH)_2$ water solution for neutralization of HF origined by the discharge from SiF_4. The aerosolator was able to spray 2 dm^3/ hour, where 90% of droplets have size is 0.5-10μm.

The HV power supply was direct-current voltage source with 500W power output, voltage range 0,5-20kV and maximal current 30 mA. The complete equipment was also supplemented with a discharge parameters measuring system, ventilators for cooling of electrodes, flap valves, rotameters and air conditioning inlet and waste piping.

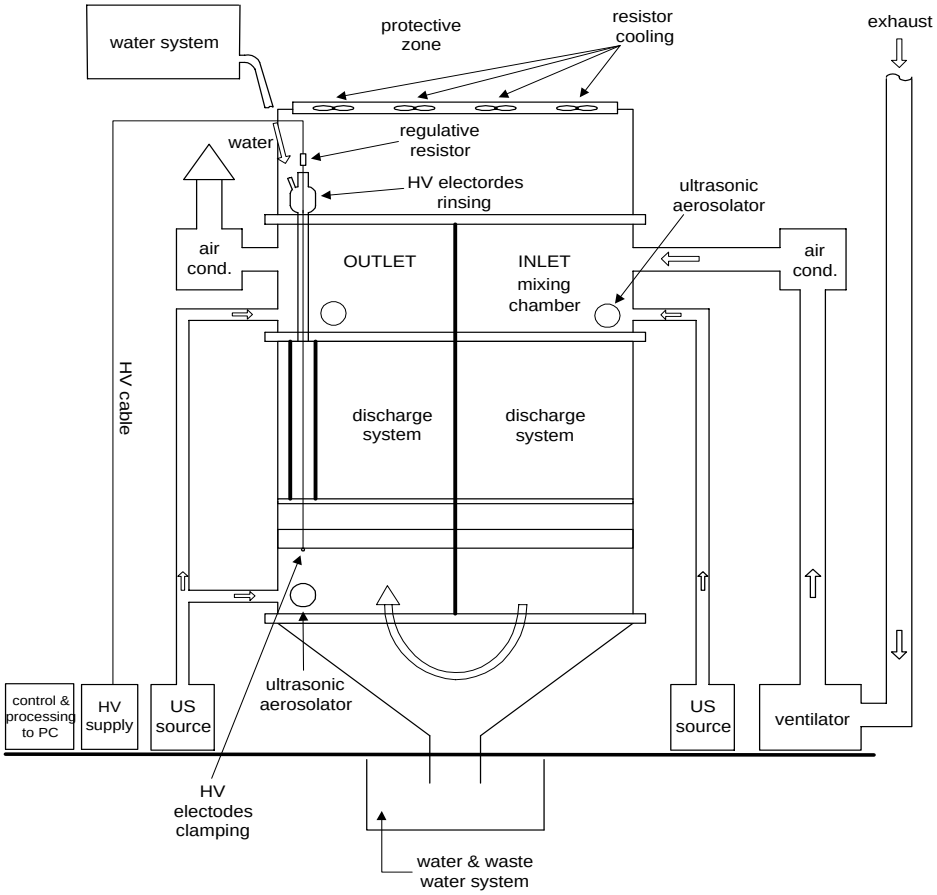


Fig.1 The corona discharge test-scale equipment

EXPERIMENT - METHODS & RESULTS

During the tests on glass oven exhaust bypass the corona equipment worked for several days and was tested for both polarities of the discharge. The main goal of our experiments was to suppress the concentration of desired toxic compounds coming from glass production processes and to maximise the removal efficiency of the equipment. The following compounds were analysed particularly by official measuring group and particularly in our laboratories: NO_x, CO, SiF_4 ovecounted as HF, inorganic compounds of chlorine as HCl, total solid contaminating compounds; metals as As, Pb. The measurements and calculations of following parameters O_2, CO_2, water vapour, gas flow volume and rate, temperature, pressurealso were made.

Samples withdrawal, measuring points and flowmeters were placed ahead of ultrasound aerosolator (inlet measurements), respectively behind all the equipment (outlet measurements) The samples were taken from the inlet and outlet simultaneoulsy and within the same time moment. The results are presented in the tables 1, 2 and 3.

	Initial concentration before a discharge action [mg/m3] negative - positive pol.	Relative concentration decrease [%] after the negative corona discharge	Relative concentration decrease [%] aftre the positive corona discharge
NOx	2107,4 - 1964,8	64,4	71,2
HF	9,16 - 1,28	74,1	58,6
HCl	11,87 - 16,94	67,2	64,2
solid states	133,14 - 81,28	87,6	86,6
Pb	52,84 - 16,57	88,0	79,6
As	3,75 - 1,00	89,5	82,3
CO	1,64 - 1,49	85,1	74,8
CO_2	3,8 - 3,9	58,7	65,6

Table 1 Combustion products average removal efficiencies

polarity	before discharge	after discharge
+	14,2	19,0
-	14,3	18,8

Table 2 Oxygen concentration ahead and behind the discharge equipment

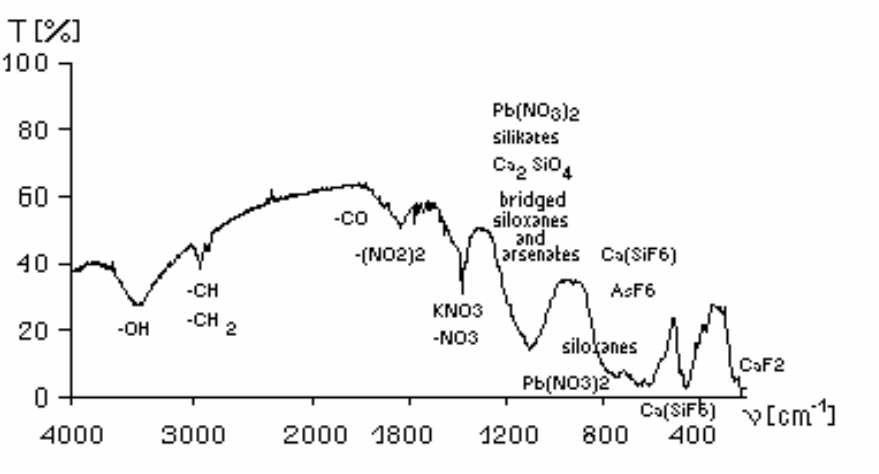
polarity	before discharge	after discharge
+	69,1	26,2
-	78,9	24,4

Table 3 Water concentration ahead and behind the discharge equipment

The exhaust gas entered the first sector of the system together with the sprayed $Ca(OH)_2$ water solution with the flow almost 500 (470+33) dm^3/min. The major part (approx. 90%) of the solution of $Ca(OH)_2$ and water reacts with different components of combustion gasses in discharge chamber. The rest of the solution condense on the outer electrode and splash particles and reaction products down to water & waste system.

Solid products analysis

The solid dust products concentrated in the bottom part of the discharge system. The products mainly consisted of metal native oxides and other compounds from glass oven that had changed their chemical and structural composition under the discharge influence. We have analysed two samples of the dust. The one that comes from the discharge equipment and the other from the heat recuperator installed in exhaust piping before corona discharge equipment. Both



samples were analysed with the use of KBr pellet making technology of IR absorption spectrometry and are on Figs. 3, 4.

Fig. 3
Infrared absorption spectrum of solid product collected in the bottom part of corona discharge equipment after discharge action.

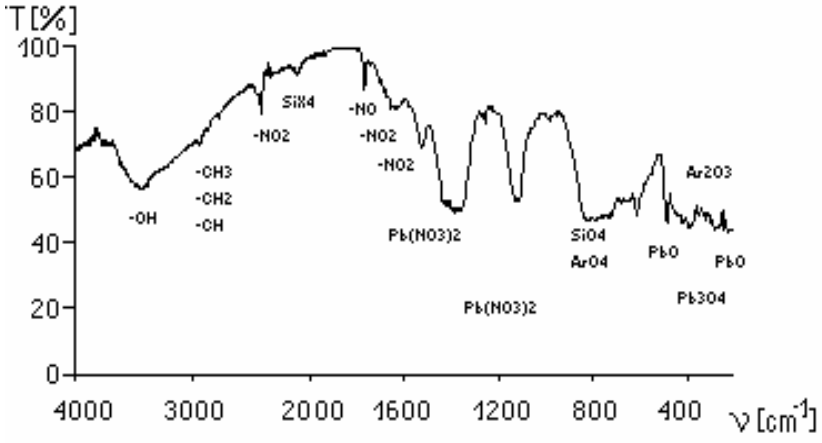


Fig. 4
Infrared absorption spectrum from solid deposits on the heat recuperator installed on exhaust pipe from glass oven situated before the discharge equipment.

Based on the spectra we ascertained and claim that :

- Pb and As oxides almost disappeared from the spectra. The Pb oxides changed to $Pb(NO_3)_2$ and As oxides were mainly converted to bridged arsenates form and partially also to arsen fluorid.
- gaseous fluorocarbonate SiF_4 reacted with $Ca(OH)_2$ water solution associating $Ca[SiF_6]$, CaF_2 and Ca_2SiO_4.
- nitrogen transformation to higher oxidation levels in the compounds including nitrogen and oxygen have occurred (nitrosyl complexes were transformed to nitro a nitrito complexes and nitro complexes oxidated to nitrates)

Liquid product analysis

According to the fact that exhaust contains water and $Ca(OH)_2$ water solution is added by ultrasonic aerosolation, the exhaust interactions with water and $Ca(OH)_2$ played an important role. The analyses of the liquid product samples that collected in the bottom part of the equipment was made with another method of IR absorption spectrometry (figures 5,6).

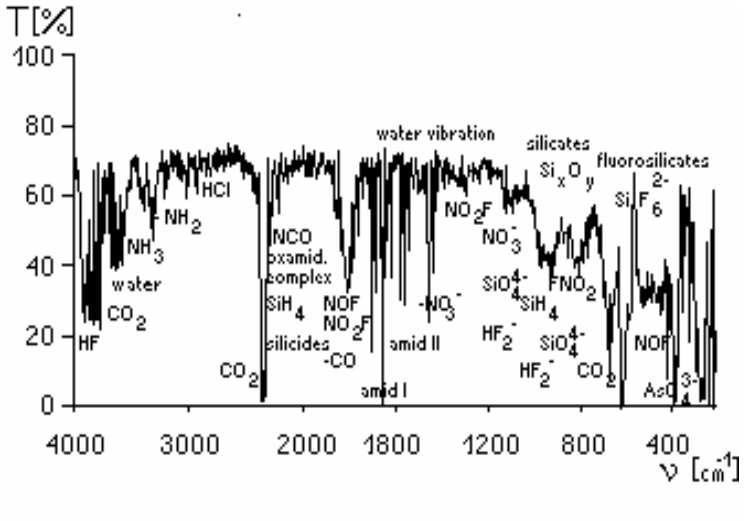
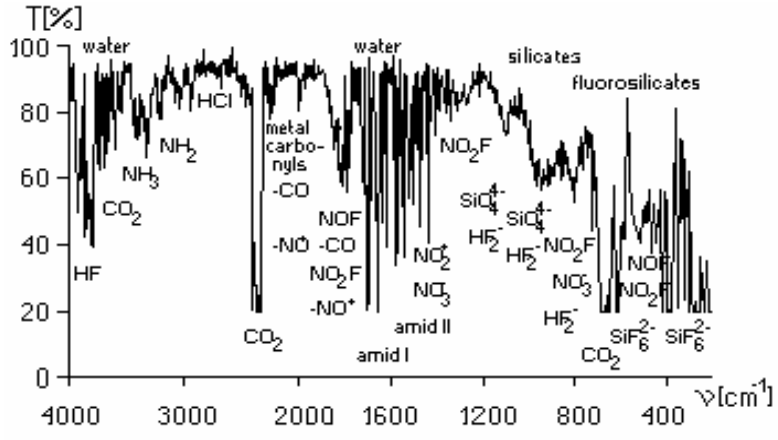


Fig.5 Liquid product after action of positive corona discharge.

Based on the achieved spectra we ascertained and claim that :

- plasmochemical reactions SiF_4 with $Ca(OH)_2$ lead to $Ca[SiF_6]$ and CaF_2 association. If SiF_4 decay the free F and SiF_3 radical were created.
- water was strongly ionised and dissociated in the system and thus atomary H and OH radical were created.
- atomary hydrogen presence in combination with fluor leads to HF and $[HF_2]^-$ association, where $[HF_2]^-$ ion initiated CaF_2 association.
- atomary nitrogen and hydrogen presence in combination with fluor lead to free radicals NH, NH_2, NF, NF_2 and ammonia association.
- free flour atom attracted NO_x, while water soluble NOF and NO_2F were associated. NO interacted even intensive with NF and NF_2 radicals associating NONF, $NONF_2$.
- the liquid sample collected at the bottom of the equipment was limpid and had a neutral pH.

CONCLUSIONS



The system was tested continuously within several days and it worked without any problem and deviations. Assumed removal efficiency of the equipment for the extremely low input concentration was proved unambiguously. According to our measurements and calculations the removal efficiency was following : 71.2% for NOx, 74.1% for HF, 67.8% for HCl, 87.6% for solid matters, 88,8% for Pb, 89.5% for As, 85.1% for CO and 65.6% for CO. Similar combination of compounds was refereed in [1].

REFERENCES

[1] I.N.Toumanov: Combined plasma-sorption process for producing monosilane from fluorine raw material, Proceedings from 12th International Symposium on Plasma Chemistry, Vol.2, pp. 619-624, University of Minesota, 1995