APPLICATION OF LOW TEMPERATURE PLASMAS PRODUCED BY PULSE CORONA DISCHARGES TO FLUE GAS CLEANING PROCESSES

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Abstract: Pulse corona discharges may be a convenient source of active electrons for oxidation of gaseous pollutants. As such they have been successfully applied both in laboratory and pilot plant experiments to the removal of SO_2 and NO_x from the flue gases. This paper summarises the present status of such applications and knowledge of physical and chemical processes involved. It also reports on recent investigations of corona discharge properties and suggests criteria in designing pulse voltage generators and reactors. At last the optimisation of energization and the correlation between the structure of corona streamers and the chemical activity is discussed.

1. Introduction

Up to date, a great number of experimental investigations have been carried out on the cleaning of flue gas by pulse corona and on the chemical kinetics of NO_x and SO_2 in presence of ammonia. There are also papers which review the basic phenomena and discuss the possible industrial applications [1, 2]. In this paper only some aspects especially important for the industrial applications will be considered and discussed.

Pilot and laboratory tests have indicated significant technical and economical advantages of the flue gas cleaning processes based on pulse corona discharges compared to the traditional ones [3]. However when considering the industrial applications still a number of problems must be solved as, for instance the protection from electromagnetic interference, the utilisation of produced ammonia sulphates and nitrates and the possible ammonia slip. All the tests have indicated that in any case the required electrical energy will represent the largest operating cost and that the design of cost efficient pulse voltage generators is greatest challenge for further study.

The energy consumption depends both on the reactivity of the induced reactions and on the energy conversion efficiency from the main to the corona streamers. Current researches are thus focused on these two points: increasing the chemical reactivity by enhancing various heterogeneous reactions and the mass growing processes; optimising the streamers characteristics in order to produce more active electrons per unit of injected energy [4, 5].

This paper summarises the present status of such applications and the knowledge of physical and chemical processes, it reports the results of recent investigations on the properties of corona streamers and on the design of efficient pulse voltage generators.

2. Present status of $DeNO_x/DeSO_2$ by pulse corona

Many experimental results indicate that by using pulse corona and ammonia injection, gaseous NO_x and SO_2 in the flue gas can be simultaneously transformed into solid particles of ammonia sulphate and nitrate. The process depends on several operating conditions such as temperature, humidity, electrical energy injected into the gas per unit volume. Generally positive corona is used because it allows the injection of larger quantities of energy with the same peak voltage and consequently a greater removal rate of the pollutant gases [6]. The formation of ammonia sulphate seems to be dominated by thermal reactions.

Comparing the corona process with the E-beam process, the most important differences are:

- a different energy distribution of the produced electrons. In case of E-beam the electrons are injected at energies between 0.3 and 1 MeV; in case of pulse corona the mean energy of the produced electrons is in the range of 10 to 15 eV.

- a different space distribution. In case of E-beam the electrons are uniformly injected into the gas; in case of pulse corona the electrons are produced within the thin filaments of the streamers. This implies a very non uniform production of radicals and of chemical reactions. Because many elementary processes show a larger cross section around 10 eV [7], the initial G-value for primary radical production is supposed to be larger in pulse corona streamers. However, the effect of reverse reactions under the high dose rate occurring inside the streamers channel is supposed to penalise the G-value in corona streamers processes [8].

After the initial radical production by electronic reactions the chemical oxidation and mass growth processes are supposed to be similar. Although on a very different time scale, the whole process is also supposed to be similar to that leading to the acid rain formation.

Although reliable theoretical models are available for some of the basic physical processes [9, 10], the complexity of the global process is such that, up to date, it is impossible to predict reasonable results and even to state the effect of variations of the operating conditions or design parameters. In particular the experimental required energy is much smaller than the predicted, suggesting that some energy transformations have not been taken into account [11, 12]. Moreover the possibilities to trigger chain reactions and to enhance the removal efficiency by means of multiphase chemical reactions have been suggested but not yet proven in actual gases. At last the characterisation of the by-products and their utilisation still need additional investigations

3. Current status of chemical kinetics of $DeSO_2$ and $DeNO_x$

Based on plasma and radiation chemistry, several comprehensive chemical kinetics have been proposed especially for the E-beam process in last few years [13, 14].

It has been generally recognised that OH radicals play the most important role, that the main reactions which produce OH radicals are the positive ion-molecule reactions and that because of its lower pressure, sulphuric acid undergoes nucleation and particle formation.

For explaining the relative decrease in energy requirement when relative humidity or NH_3 injection are increased, heterogeneous phase reactions have been supposed. There is evidence that the oxidation processes may last much longer time than the treatment time in the reactor; the filter which collects the ammonia sulphate and nitrate downstream the irradiation reactors contributes to the removal rate by 75% when fabric and 40% when ESP. The presence of fly ash in the reactor also contributes to increase the removal rate of SO_2 [12]. All these factors are supposed to increase the removal rate because they enhance the heterogeneous reactions.

Thus the overall removal rates depend on several operating conditions, especially relative humidity and temperature because not only because of different kinetic constants but also because of different reaction mechanisms [16].

4. Design of pulse voltage generator

Several electric circuits have been used for producing voltage pulses [17]. The most common circuit is based on the discharge of a capacitor on a low inductive circuit through a spark gap acting as a switching device. The voltage pulse is often superimposed on a DC bias voltage. Figure 1 illustrates the basic scheme of these circuits.

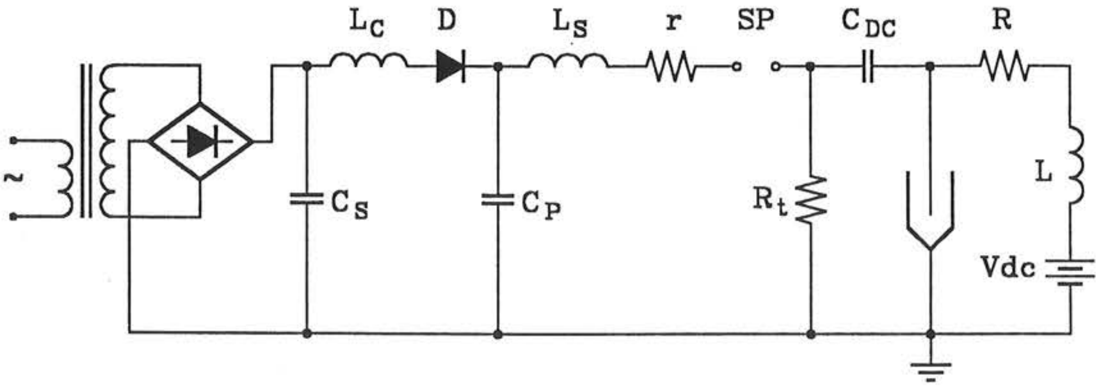

Figure 1: Basic scheme of pulse voltage generator

In order to reduce the total costs for flue gas cleaning by pulse corona, when setting up the reactor and pulse voltage generator the following four points should be adopted to evaluate the design:

1 the energy conversion efficiency;
2 the maximum power output and the life time of the devices;
3 the energy injection per pulse and per unit volume;
4 the induced chemical reactivity per unit energy.

These four points do not only depend on the pulse voltage generator but also on the matching between generator and electrodic structure of the reactor, properties of corona streamers and induced chemical mechanism.

Recently the relevant characteristics of pulse corona discharge, such as voltage/current function, volume density of streamers, propagation speed of streamers and energy distribution of the produced electrons have been extensively investigated through the measurement of electrical and optical quantities [18].

It has been found that the main parameters which influence the properties of streamers are the rise rate and the peak value of the voltage pulse and the composition of the gas.

The influence of the capacitor type pulse voltage generator on the pulse corona streamer and its optimisation in view of the best energization for inducing chemical reactions was also recently discussed in terms of electrical and optical measurements [5, 19]. It was found that the energy conversion processes from the main power supply to the reactor depend on the reactor size, emitting wire, DC level, stored energy in the circuit and pulse voltage shape. A very simplified method to achieve a complete matching between the generator and the reactor was proposed by means of adding proper a DC bias voltage. The required DC bias voltage can be estimated considering the electric field in the streamer channel E_a and the gap distance between electrodes d.

It has been experimentally observed that once the applied voltage becomes high enough that streamers cross the gap and reach the cathode, the total residual voltage between electrodes is almost constant. Under complete matching, the residual pulse voltage on the emitting wire should be reduced to zero and corona current should last from several tens to few thousands nanoseconds. It has been also experimentally observed that the pulse voltage oscillograms are quite independent on the tail resistor R_t, but it depends on the streamer intensity [4, 5].

Neglecting the losses due to the conversion of energy from the main to the storing capacitor which can be minimised by using oscillating circuits and semiconductors [20] and supposing that pulse duration is much shorter than the time constant determined by the tail resistor and the pulse forming capacitor, the circuit losses are mainly due to the spark gap and to the voltage drop produced on the DC coupling capacitor. The loss due to the spark gap can be evaluated as that occurring on an equivalent resistor of value less than few ohms; the loss due to the voltage drop on capacitor C_{DC} can be estimated according to the following relations:

$$Q = C_p \cdot (V_1 - V_2)$$

$$Q = C_{DC} \cdot (V_2 - V_p)$$

$$V_r = V_{DC} + V_p$$

where V_1 and V_2 indicate the voltage on C_p before and after the pulse voltage respectively; V_{DC} is the DC bias voltage; V_r represents the total residual voltage between electrodes; V_p is the residual pulse voltage after streamer quenching; Q indicates the total charge outflow from the pulse forming capacitor.

It comes from the previous set of equations that:

$$V_2 = \frac{C_p \cdot V_1 + C_{DC} \cdot (V_r - V_{DC})}{C_p + C_{DC}}$$

and, when $V_{DC}=V_r$, the efficiency becomes:

$$\eta = 1 - \frac{1}{2 + {C_{DC}}/{C_p}}$$

It can be seen that, according to the experience, with increasing DC bias voltage the corresponding residual pulse voltage decreases, which means that the efficiency in injecting energy is increases. The efficiency of the energy transfer depends only on the ratio C_{DC}/C_p. If this ratio exceed 20 the efficiency exceeds 95%. This simplified estimation agrees very well with the experimental results.

The rise rate of the voltage pulse is often considered one of the most important parameter. The experimental observation, however, suggests that the key parameters which influence the corona streamers are the corona inception voltage and the stored energy in the circuit. The inception voltage V_c is determined by the rise rate [dV/dt] of the voltage pulse. Figure 2 indicates the effects of the rise rate of the pulse on the corona inception voltage.

It has been also supposed that the peak corona current is directly proportional to the number of streamers and to the charge per streamer. Figure 3 illustrates the effects of corona inception voltage on the peak corona current I_p. It can be concluded that the streamer density and the intensity of each single streamer can be increased by increasing the inception voltage.

The increase of the duration of the voltage pulse, i.e. the time to half value, increases the development of the secondary streamers and of the thermal energy injected. At extreme situation it may also lead to the development of an arc.

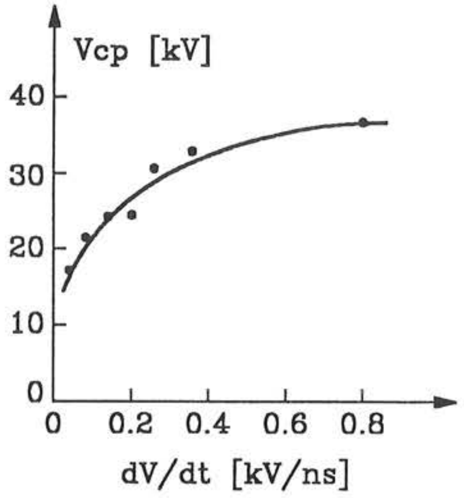

Figure 2: Effect of rise rate of voltage pulse on corona inception voltage; wire-cylinder electrode structure, cylinder radius = 100 mm, wire = 5mmx5mm, V_{DC} = 29 kV, V_1 = 50 kV, room temperature

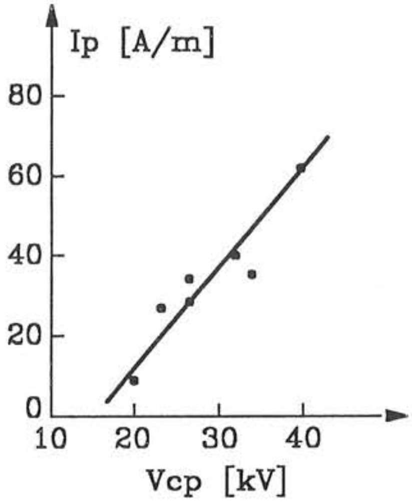

Figure 3: Effect of inception voltage on peak corona current under the same conditions of figure 2.

As the cost of the pulse voltage generator is mainly determined by the rise rate of the voltage pulse, the following data are recommended in order to produce pulse corona discharge after voltage pulse reaches its peak value without exaggerating the pulse rise time requirement.

Applied pulse voltage (kV)	50	100	150
Suggested rise rate (kV/ns)	1.0 ÷ 1.5	3.0	6.0

5. Design of electrode arrangement of reactor

The required volume of reactor depends on the amount of pollutant gas, on the energy injection intensity per unit reactor volume and on the chemical reactivity per unit injected energy.

Considering a simple geometry such as coaxial cylinders, the electrode arrangement is defined by two main parameters: the radius of the emitting wire and the radius of the reactor. It has been observed that the function of peak corona current versus applied voltage changes, as indicated in Figure 4, when different emitting wire are used with the same power supply circuit. It was also observed that with a constant rise rate of the voltage pulse, the corona inception voltage is almost constant as indicated in Figure 5. This means that the density of the primary streamers only depends on the total applied voltage on the emitting wire.

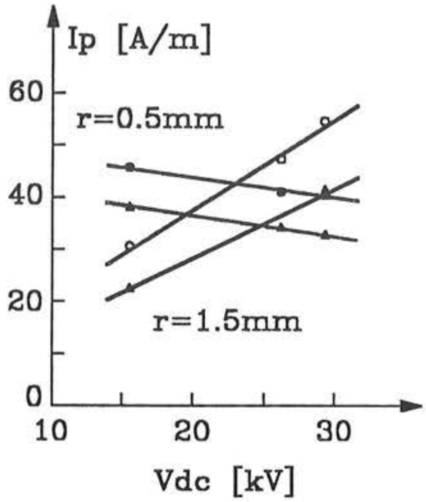

Figure 4: Effect of the emitting wire on corona peak current with different DC base voltages. R = 100 mm, L_S = 0, V_1 = 40 kV, V_1 = 50 kV

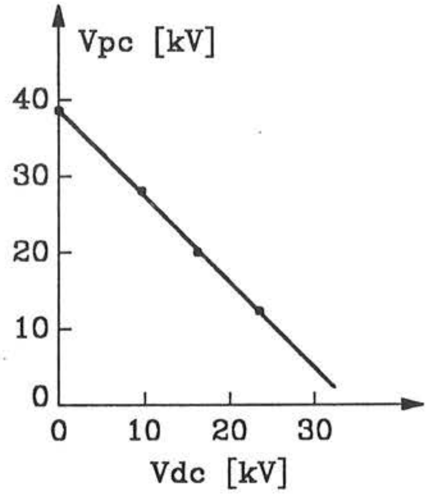

Figure 5: Effect of DC bias voltage on pulse voltage inception. R = 100 mm, r = 0.5 mm, L_S=32 μH, V_1=50 kV

It comes that the criteria for the design of the electrode arrangements are the following:

- DC bias voltage should satisfy the matching requirement;
- the emitting wire should be such as not to allow corona with the DC voltage level.

If we suppose that the DC corona onset voltage is determined by the critical field E_C on the emitting wire, a very simplified model for designing the electrodes of the reactor can be derived. In case of wire-cylinder reactor it results:

$$V_{DC} = E_a \cdot (R - r)$$

$$V_{DC} = V_c$$

$$E_c = \frac{V_c}{r \cdot \ln\left(R/r\right)}$$

where Vc is the DC corona onset. When supposing that the field E_a in the streamers channel and the critical field E_c are about 6 kV/cm and 30 kV/cm respectively, the ratio R/r is about 14 the diameter of the cylinder is given by the characteristic of Figure 6 in function of the DC bias voltage level.

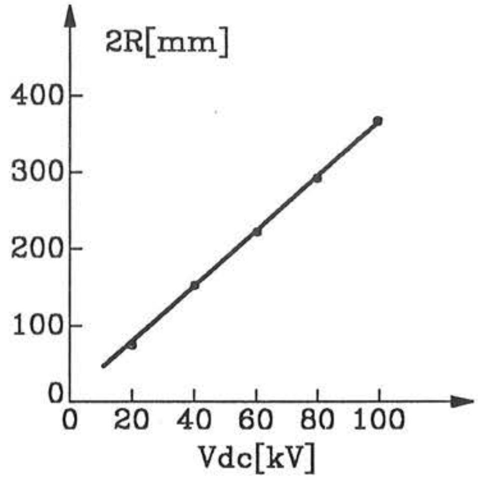

Figure 6: Radius of cylinder as function of the DC bias voltage

When designing the electrode arrangement and DC bias voltage for pulse corona treatment of flue gases, the same criteria can be applied. However the electric field in the streamer channel may be higher and thus also the DC bias level should be increased.

For industrial applications, the radius of a single reactor tube should be as large as possible in order to reduce the cost of material and increase the duration of the primary streamers. However, due to the matching requirement, the radius is limited by the available DC bias voltage level as indicated in Figure 6.

As far as the length of each reactor tube is concerned, it has been found that the streamer are uniformly distributed along the emitting wire at least within 4 meters [4]. The required length can be determined by the energy injection per unit length of the emitting wire, which is determined by the pulse voltage shape and the pulse repetition rate.

6. Streamer properties and optimisation of energization

Generally speaking, for inducing chemical oxidation by pulse corona streamer, the produced active electrons per unit injected energy represents the key factor in the process. Regarding streamer head propagation and channel evaluation, pulse corona streamer can be divided into two periods; the first corresponds to the propagation of the head and the second corresponds to the flow of current after head stop. The corresponding time-resolved and space-resolved electric field distribution is different, and this lead to different electron energy distribution.

The electron energy in function of the applied electric field is empirically given by the following equation [21]:

$$T_e = a + b \cdot \frac{E}{n} + c \cdot \left(\frac{E}{n}\right)^2$$

where a, b and c represent empirical coefficients. It appears evident that active electrons ($T_e > 5eV$) are only produced during streamer head propagation; the electric field along the streamers channel being much lower [22]. Consequently the energy injected into the corona discharge can also be divided into two parts; the first part may be called active energy injection for streamer head propagation and the second one passive energy injection after streamer head stops.

It is obvious that the pulse voltage shape dominates the two parts of energy. In order to optimise pulse voltage generator to promote chemical reactions, two types of energization were proposed according to the two kinds of energy injection, which may correspond to the same total energy injection but different active and passive components [4]. In terms of spectroscopic measurements it was found that, the active energy injection per unit of total injected energy is increases with increasing the rise rate of the voltage pulse [5].

There are very few results which correlate the chemical reactivity with the different structure of pulse corona discharge. Recently published results [23] seems to support the theoretical statement that the previously called active energy lead to a greater chemical activity and to a higher removal rate of gaseous pollutants. Although the removal rate of SO_2 may strongly depend on thermal reactivity, Figures 7 and 8 seems to indicate an influence of pulse voltage shape on the removal of SO_2 under the same total energy dissipation.. Also in this case a stronger chemical reactivity seems to be associated to a faster rise rate.

According to the limited number of test results it seems very probable that increasing the active energy injection the chemical activity may be increased.

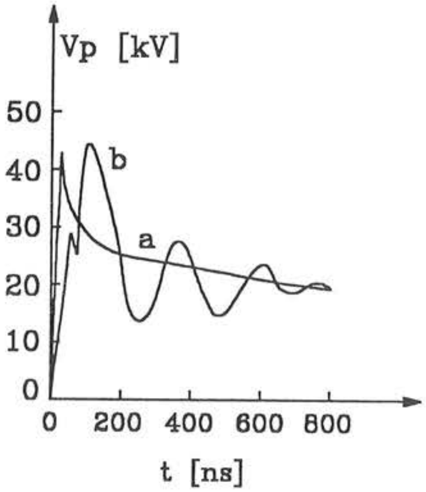

Figure 7: Two typical voltage oscillograms. R=50 mm, wire: 4mm x 4mm, V_{DC}=15 kV, flow rate: 0.35 Nm^3/h, treatment time = 10 s

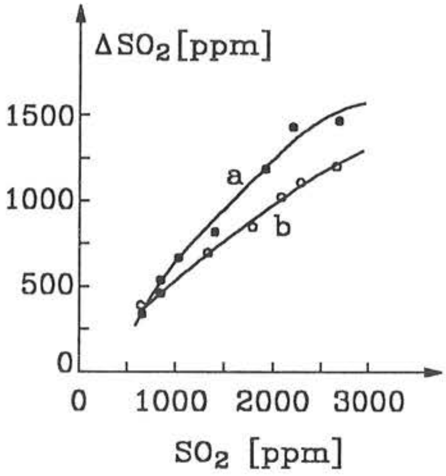

Figure 8: Removed SO_2 versus different initial concentration with the two voltage pulses of fig. 7

7. Concluding remarks

Based on electrical and chemical measurements, following conclusions can be made on the energization of pulse corona streamer for flue gas cleaning.

1 One of the main obstacles for application of this technique is the energy consumption. The current main researches to reduce the global energy consumption is to enhance various heterogeneous reactions and to optimise streamer structure.

2 According to a very simplified method to achieve a complete matching between pulse voltage generator and electrode arrangement of the reactor, the criteria to design pulse voltage generator and reactor are proposed.

3 The total energy injected into the reactor by the corona discharge is subdivided into active and passive parts, the first being responsible for chemical activity. Consequently an optimisation of energization can be obtained by reducing the passive energy injection.

8. Acknowledgements

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