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Gliding arc. Applications to engineering and environment control

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Abstract : New way of plasma generation by formation of gliding electrical discharges (called GlidArc) has been developed. At least two diverging electrodes other are placed in a fast gas flow and in the flow direction. The discharges are organized between the electrodes and across the flow. The displacement of the discharge roots on electrodes prevents their erosion. The electrical energy is directly and totally transferred to the gas. All gas or vapor, also dusty and/or misty, can be directly processed at any inlet temperature and 0.1 - 5 atm pressures. Big plasma volume at relatively low energy density is out of the thermodynamic equilibrium. Some applications of the GlidArc were tested in laboratory and industrial scale reactors :

- flame overheating (electro-burner),
- air depollution from volatile hazardous compounds,
- complete or partial valorization of concentrated H_2S or $H_2S + CO_2$ mixtures,
- flue gas SO_2 reduction to elementary sulfur,
- natural gas conversion to the syngas ($H_2 + CO$).

Inexpensive gliding electric discharges can considerably reduce the nuisances of classical gas processes. Such discharges bring to these processes an easily controllable energy so that high energy consuming thermal processes at high temperatures can be substituted by this cold and catalytic plasma process at lower energy expense.

INTRODUCTION

Electrical energy is commonly considered as a clean one and therefore specially well adapted to eliminate the toxic and evil-smelling vapours and gases without creating any green-house effect due to an uncontrolled emission of CO_2 from classical fuel combustion. Interest for electrical-created plasma-assisted chemical methods of hazardous gas and vapors cleaning consists in very high specific throughput of the discharge volume. This value is by 4 orders of magnitude higher than other electric methods : electrochemical or thermo-electro-chemical. Key answer for plasma-chemical methods is however an optimization of their energetic characteristics.

Generally, conventional electric arcs or plasma torches generating a so-called "thermal plasma" seem not to be well adapted to plasma chemistry of gas which can not easily interact with a confined zone of very high energy. Under atmospheric or higher pressures, thermalization and high temperatures of several kK are observed. In such conditions, the process of gas processing is first of all its complete thermal dissociation followed by recombination in cooler parts of the flow. An over-heating followed by rapid cooling (in order to quench the high temperature chemical equilibria) can give interesting laboratory results and hundreds of papers have already been published. The only survival among the industrial arc gas processing, so widely present in the first decades of this century, remains the production of acetylene from light hydrocarbons (Hüls, Germany) thanks to some specific local conditions.

Another way of plasma-chemical gas processing is the non-thermal one when silent, glow, corona, short pulse, micro-wave or radio-frequency (RF) electrical discharges are directly produced in processed gas, mostly under low pressure. Very interesting laboratory results were obtained under quite a low specific energy consumption due to the presence of very active species (radicals, excited molecules). Generally, the glow discharge in low pressure gas seems to be a simple and inexpensive way to achieve a non-thermal plasma where the electric field ionisation processes predominate over the thermal ones and give relatively high energy electrons as well as excited ions, atoms and molecules which carry out selective chemical transitions. The power of glow discharges is however limited by the glow to arc transition when gas, initially below 1 kK, becomes hot (> 6 kK), and while the electron temperature, initially high enough

(> 12 kK) to promote direct molecular transitions, becomes close to the gas temperature. The discharge voltage suddenly decreases during such a transition, making it necessary to increase the current in order to have more power. But the current increase thermalizes the medium ! Moreover, it seems necessary to operate at low pressures in order to obtain the advantage of the selective high and non-thermal energy delivered from the glow discharge - but an operation at atmospheric pressure is desirable for industrial viability ... Up to now the unique well known industrial application is the ozonizer. A recent study of Harry and Yahya (1) shows how to obtain a higher power loading without the glow to arc transition at about 250 mb (so within the capability of a single Rootes blower) in the fast gas flow with an axial discharge. Interesting semi-industrial results were obtained in Italy via pulsed corona discharges produced in an electrostatic precipitator in order to remove NOx and SOx from flue gas (2). Advantages of the supersonic Very High Frequency (VHF) plasmatrons were underlined in several papers from Rusanov group (Russian Research Center Kurchatov Institute, Moscow) published since 1981... A new way of an industrial size plasma generation by formation of gliding electrical discharges at near-to-atmospheric pressures is being developed in Orléans, France (3).

GLIDING ELECTRICAL DISCHARGES

Presentation

As schematically shown on Fig. 1 at least two electrodes diverging with respect to each other are placed in a relatively fast gas flow (> 10 m/s) and in the flow direction. Gliding discharges are produced between the electrodes and across the flow. They start at the spot where the distance between the electrodes is the shortest, and spread by gliding progressively along the electrodes in the direction of flow until they disappear after a certain path. This path is defined by the geometry of the electrodes, by the conditions of flow and by the characteristics of the power supply. The electrical discharges immediately reform at the initial spot.

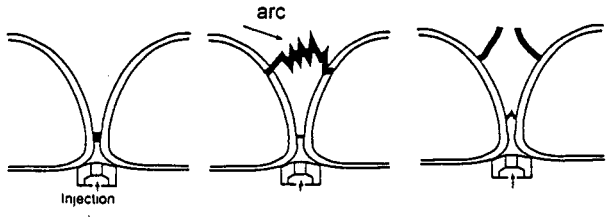


Fig. 1. Start, life, and disappearance of the gliding discharges.

The displacement of the discharge roots on uncooled electrodes prevents their chemical corrosion or thermal erosion by usual high current arc establishment. The electrical energy (either DC or AC current may be used) is directly and totally transferred to the processed gas. The average voltage ranges from 0.5 to 10 kV for currents from 0.1 to 50 A (per discharge). The instantaneous voltage, current and dissipated electric power observed via digital oscilloscope (see Fig. 2) show almost random feature of the history of each gliding breakdown powered by a direct current arc supply (two parallel generators : one is a high voltage generator used to ignite the discharge and the second is a power generator 800 V, 60 A). In series with the power generator there is a variable resistor 25 Ω and also, in order to delay the breaking off of the arc, a selfinductance 25 mH (4).

This transient characteristics under atmospheric pressure is similar to the glow discharges characteristics. It is difficult to define what "the glow discharge" is and what "the low current arc" is when the electric energy is put across the fast and turbulent gas flow and when the discharge (or arc) roots move rapidly along the electrodes. So we use both terms : discharge or arc and call such a device as GlidArc. Figure 3 shows some 10 240 measured points of the voltage, current and dissipated electric power observed via digital oscilloscope during 200 ms when one couple of diverging electrodes is put in 85 mm inner diameter tube with 120 Nm³/h flow of air under atmospheric pressure. The same points corresponding to the current and correlated voltage are presented on Fig. 3 showing almost random feature of the history of each gliding breakdown.

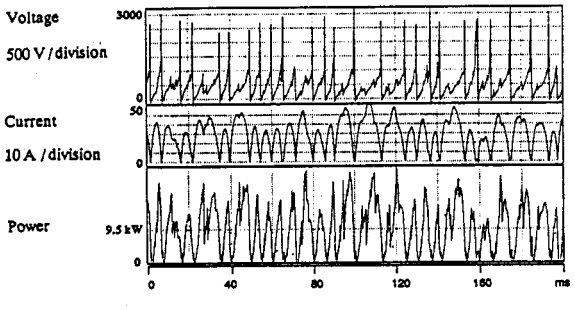


Fig. 2. Voltage, current and power curves in 120 m^3/h air flow rate (mean values : 450 V, 20 A, and 9.5 kW).

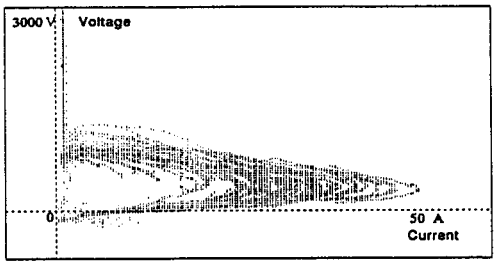
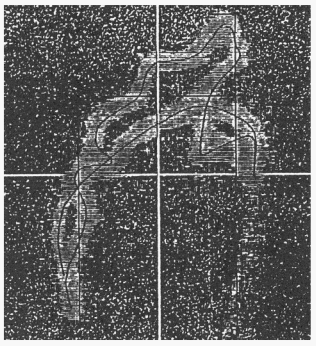


Fig. 3. Voltage as a function of current (the same conditions as in Fig. 2).

Physical model (5)

The discharge starts at the shortest distance between the electrodes and within a time of dozen μs there is formation of a low resistance plasma; the voltage falls to dozens V. The small plasma volume is then dragged by the gas flow at a speed of about 10 m/s, and both the length and voltage of the arc column increase together with the distance between the electrodes. The plasma is close to the thermodynamic equilibrium because the electrical power delivered by the generator is sufficient to compensate energy losses by thermal conduction.

Later the heat losses continue to increase, but since the electrical power cannot increase any further, it is no longer possible to sustain the arc in equilibrium. The gas temperature will fall rapidly to about 2000 - 3000 K, at the same time as the electron temperature remains at about 1 eV. These conditions are similar to those prevailing in moderate pressure high frequency discharges; the plasma conductivity is maintained by step-wise ionisation processes, and the arc can continue its evolution with much smaller heat losses of 0.15 - 0.20 kW/cm. During the nonequilibrium period the dissipated power remains practically constant : 75 - 80 % of the total energy input to the arc is dissipated during this period.



A striking phenomenon occurring during the transition between the two periods is the sudden increase in arc length (in the ratio of 3 - 4) illustrated on Fig. 4, which shows two pictures of the arc, taken with a high speed camera and separated in time by 0.5 ms (6).

Fig.4. Sudden increase in arc length.

APPLICATIONS

Reactors based on GlidArc principle can directly process atmospheric, lower or higher pressure gas or vapour (cold or hot) of almost every kind (Ar, N2, O2, H2, CO2, CO, H2S, SO2, N2O, CH4, other hydrocarbons, freons, steam, air, and some of their mixtures, etc.) at negligible pressure drop.

The electrical energy is directly used to produce a non-equilibrium" and very reactive medium allowing efficient gas processing so that up to 45 % of this energy may be directly absorbed in an endothermal reaction. Therefore the main innovative aspect of the GlidArc processes is certainly the way the chemical reactions are activated via powerful electrical discharges under near-to-atmospheric pressures.

The GlidArc reactors can be implanted in many different processes that give them some advantages over conventional ones. Several applications, mostly to engineering and environment control, were already tested in laboratory and industrial scale reactors proposed for large ranges of gas flow and dissipated electric power :

- air depollution from industrial volatile hazardous compounds like solvent vapors (xylene, toluene, heptane, tetra-chloro-ethylene, methyl-ethyl-ketone), ammonia, free or linked phenols, formaldehyde, organic nitrates, diluted mercaptans and/or H2S, diluted methane, etc.
- flue gas depollution from soot, Poly-Aromatic-Hydrocarbons, SOx and NOx
- complete or partial valorization of concentrated H2S or H2S + CO2 mixtures (SulfArc process)
- conversion of the natural gas to the syngas (H2 + CO)
- methane transformation to acetylene and hydrogen
- valorizing destruction of N2O
- reforming of heavy petroleum residues
- decomposition and valorization of concentrated freons
- CO2 dissociation
- overheating of steam, oxygen, and other gases or flames
- ignition of propellants
- UV generation
- decontamination of soil or industrial sands
- activation of organic fibers
- and other.

Some of these applications are communicated in details (7-10) to the 11th International Symposium on Plasma Chemistry, Loughborough, 1993. These ones (and some others) are briefly described below :

Electro-burner (11)

We have already checked on CH4/air or H2/air lean mixtures that Glidarc can easily substitute a classical burner when

- the gas mixture to be burnt has an insufficient content of combustible gases (which requires for an extra energy supply),
- an addition of classical fuel (asking for an extra air with the nitrogen ballast) dilutes the fumes too much , increases greatly their volume and requires a much bigger flue-gas treatment installation,
- the gas pulsation renders difficult the operation of the classical burner (which requires an extra security).

The GlidArc structure can also be added to chemical burners in order to :

- achieve higher temperature flame
- have a free choice of both temperature and red-ox conditions.

Air depollution from some volatile organic compounds (12)

Exhaust air from chemical processing, plastic manufacturing and processing, mechanical engineering, electronic, glass, paper, printing, paint manufacturing, metal degreasing and other industries can contain some amounts of volatile, mostly organic compounds. These compounds, mostly the vapors of organic compounds (VOC) such as aromatic hydrocarbons (toluene, xylene, ethyl benzene), esters (ethyl acetate, butyl acetate) or alcohols (butyl and propyl ones), are considered as pollutants. To avoid the risk of exceeding a threshold or explosion limits, the concentration of solvent vapors in the circulating air is kept low (for the same reason the exhausted air cannot be recirculated without at least a partial depollution).

Several processes are proposed to lower the VOC emission. Except the condensation, all other processes should be less or more completed by a final combustion of concentrated vapours or an incineration of diluted ones. Two kind of incinerators are employed. The catalytic incinerator can be easily poisoned, and the commonly used thermal incinerator is very expensive : one has to heat the exhaust air up to about 850°C to mineralize all organic compounds. A fuel addition is necessary and even with a heat recovery added, the costs of both the process and heat recovery installation are high. For example, about 0.16 kWh of thermal energy is necessary to depollute 1 Nm³ of the exhaust air from several hundreds ppm down to 50 ppm in the case of xylene.

Xylene was used as a test molecule to show the feasibility of the low temperature plasma assisted VOC incineration using GlidArc reactors. Tests (12) were performed in a semi-industrial pilot at 120 Nm³/h polluted air flow rate and close to the conditions of the air exhausted from an automobile paint tunnel. This pilot shown schematically on Fig. 5. contains two electrodes put in a 85 mm inner diameter ceramic tube. The gliding arcs are DC powered at the same time from an ignition supply (up to 1 kW and 5 kV) and from a main power supply (up to 15 kW and 900 V) generators. The pure air was partially saturated with o-xylene by controlled liquid xylene injection to the entering air. Some results of air depollution are presented on Fig. 6.

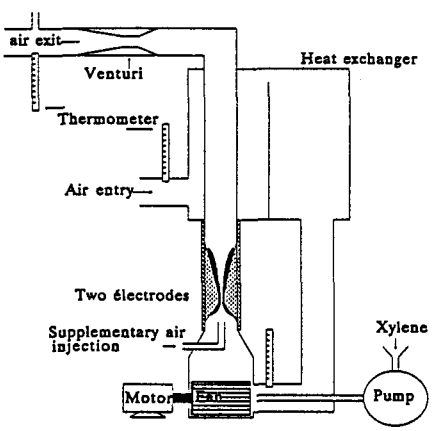


Fig. 5. Semi-industrial GlidArc reactor

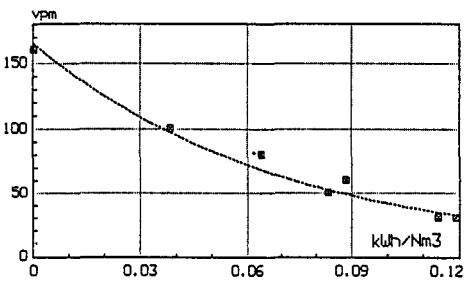


Fig. 6. Energetic cost of plasma assisted incineration of cold air polluted by 160 ppm of o-xylene.

At the atmospheric pressure one needs less than 0.1 kWh of electrical energy to depollute 1 Nm³ of cold air from 160 ppm to below 50 ppm. Better depollution is possible : one can easily obtain 30 ppm level at 0.12 kWh/Nm³ expense in the same apparatus. A preheating of the entry air by a waste thermal energy is a positive factor and further lowering of the process specific energy consumption is expected.

A low increase of the processed air temperature (less than 200°C) as well as a low level of the combustion products at the exit of the apparatus can have a practical application for a better integration of the incineration step in a whole industrial process. The organic solvent vapor incineration is therefore becoming much easier and inexpensive. A pilot plant is being developed in France to clean out thousands of cubic meters per hour of polluted air at high electric power supplied by a multi-output generator from Plasma System Ltd., UK

Several newer feasibility tests on air depollution from other organic vapours performed in a laboratory scale reactor at up to 16 Nm³/h and 2 kW were also communicated (13, 14) :

1. *Heptane* vapours (2200 ppm) in air were completely mineralized, mostly to the CO2 in six-electrodes GlidArc reactor at 1.8 Nm³/h air flow at 0.94 kW total electrical power.

2. The initial concentration of 1800 ppm of *toluene* vapours in air was reduced to 140 ppm in the same reactor at 2.0 Nm³/h and 0.84 kW.

3. Some 66 % of the *methyl-ethyl-ketone* initially at 2000 ppm in air was incinerated mostly to the CO2 in the same reactor at 3.2 Nm³/h flow rate and 0.89 kW.

4. 100 % of the *tetra-chloro-ethylene* initially at 500 ppm in air at 1.9 Nm³/h flow rate was transformed to the CO2 and HCl in the same reactor at 0.90 kW and some additional water injection (240 g/h).

The inlet polluted air was always slightly wet (about 15 % of relative humidity), and it had an ambient temperature. No other energy sources were applied, no heat recovery was taken into account. The entry and exit concentrations were from mass balances and specific Dräger tubes, (classical gas chromatography was also employed), the air flow-rate - from mass flow meters, and consumed electric power - from precise watt-meter.

Incineration of some sulphur compounds (15)

Hydrogen sulfide is present in the fluids issuing from under the ground, such as geothermal fluids, natural gases, gases stored in natural reservoirs or fluids used for assisted oil recovery. The H2S is also present in the industrial gases such as those issuing from oil desulfurization, coking plants, rubber pyrolysis, metallurgy, paper-making or viscose industry, the gases issuing from the desulfurization of biogases, the tail gases issuing from the processes of depollution already installed, etc.

The stink of very toxic H2S can be detected in air at 0.2 ppm while the threshold limit without adverse effects is 10 ppm. Methyl mercaptan CH3SH contained in biogases is even more toxic than H2S, possesses more repulsive odor and its threshold limit is 0.5 ppm. The product of H2S or mercaptans incineration is SO2, also toxic (threshold limit 5 ppm) but it can only be detected by smell in concentrations of 3 ppm. It would be therefore suitable to transform very diluted hydrogen sulfide or mercaptans to SO2 in order to avoid at least an olfactory fatigue. However the lower H2S (or CH3SH) flammability limit at 20°C and 1 atm in air is about 4 % so one needs to add a fuel in order to burn these compounds when diluted in air or other carrier gas.

Some runs with a laboratory scale GlidArc reactor (six electrodes, 3-phases AC, 2 kW at 10 kV AC open circuit voltage) show that it is very easy to completely incinerate the hydrogen sulfide or methyl mercaptan in air or in CO2 at H2S or CH3SH concentrations much lower than the limit of inflammation, followed (or not) by a process in which SO2 is destroyed or valorized. The proposed process can also be used for total valorization of H2S contained in concentrated gas mixtures (see later on) :

1. 7 Nm³/h of air contained 0.7 % H2S has been completely depolluted at energy cost of 0.14 kWh per 1 Nm³ of treated air (without any preheating).

2. 3.8 Nm³/h of CO2 contained 1.85 % H2S gas was mixed with 1.9 Nm³/h of air and processed at 0.63 kW. The complete H2S transformation to SO2 was observed at 0.17 kWh per 1 Nm³ of this "acid gas".

3. 16.2 Nm³/h of air was completely depolluted from the methyl mercaptan at 0.12 % initial concentration and the total power of the 6-electrodes GlidArc reactor of 1.0 kW. The energy cost is then about 0.06 kWh per 1 Nm³ of processed air.

All quantitative analysis were performed using calibrated Dräger tubes for H2S, CH3SH or (H2S + SO2). The classical gas chromatography was also employed. The gas flow rates were measured by calibrated mass flow meters. The electrical power absorbed in the reactor was measured by classical watt-meter.

The inexpensive gliding electric discharges are capable to reduce considerably the nuisances of existing processes of industrial depollution from the VOC's or such sulfur-contained compounds as H2S or mercaptans.The use of such discharges can bring to these processes an easily controllable energy. High energy consuming and troublesome thermal incineration at high temperatures can be substituted by this particularly cold and catalytic plasma assisted process at lower specific energy expense.

H2S partial valorization (7)

Large quantities of hydrogen sulfide are commonly present in industrial gases and in non-condensable gases issuing from geological fluids (natural gas production and geothermal energy exploitation). These waste gases occur as a moisture saturated mixture of mainly two acid gases : CO2 and H2S. A typical mixture of acid gases in natural gas exploitation is CO2 80% and H2S 20%. Increasingly, stringent air-emissions regulations (especially H2S) are prompting plants processors to try new technologies with the goal to determine the most economical and effective way. Various processes (thermal or chemical) can be used to treat these gases but, in this case, they cannot operate correctly or their operating cost reach an unacceptable level.

A standard Claus process of partial H2S valorization (only sulfur recovery) is based on thermal gas processing :

$$H_2S + 1/2\ O_2 = SO_2 + H_2O \text{ (thermal stage)} \quad (1)$$

$$SO_2 + 2\ H_2S = 3\ S + 2\ H_2O \text{ (both thermal and catalytic stages)} \quad (2)$$

so that

$$H_2S + 1/2\ O_2 = S + H_2O. \quad (3)$$

The classical Claus cannot be sustained if CO2 concentration exceeds 60 % or if H2S concentration is less than 7 %. But the GlidArc reactor can easily be used as an oxidation stage to produce necessary SO2. Such application is one of two versions of our proposed SulfArc process. Assuming that SulfArc is only acting as an electrical burner instead of a gas burner, the needed air remains only the one reagent corresponding to the H2S processing. Because there are no combustion byproducts (CO2, N2, H2O), this can reduce the total volume of the treated gas by 40 % to 80 % without any CO2 increase in flue-gas.

In such a modified Claus process, SulfArc can also act before each catalytic stage where a shift reaction takes place between the SO2 and the remaining H2S to form elemental sulfur and steam according to the reaction (2) followed by a sulfur vapor condensation. This allows the possibility of an drastic improvement of all gaseous processes.

On the basis of our previous laboratory results (16) a real size pilot plant is actually installed near Zmigrod (Poland) to treat 60 m³/h of gases (75 % CO2, 20 % H2S, 5% hydrocarbons) issuing from natural gas MEA desulfurization. This experimentation has three main goals :

- to confirm the results at a significant scale,
- to study the ability of SulfArc to improve Claus processes,
- to study the possibilities and costs of gas valorization.

Industrialization of the SulfArc process is linked with the results of the pilot experiments, more particularly :

- influence of water vapor and oxygen (from air) concentrations,
- influence of pressure and inlet temperature,
- influence of electrical parameters,
- capability of multi-stage SulfArc reactors.

The SulfArc process would present numerous advantages over the known processes :

- destroying all H2S present in gas, without employing a chemical additive and with a low consumption of electrical energy
- very elastic as it may be used with any flow rate and/or temperature without limit of pressure of the gas or steam and without limitation concerning the initial gas or steam composition; in particular, a high CO2/H2S ratio in the gas is not detrimental, in contrast to other processes
- requiring no particular preliminary treatment in charges containing methane as the methane reforming process (a partial plasma assisted oxidation by CO2) does not compete with hydrogen sulfide abatement process
- no catalyst so no risk of such catalyst being "poisoned" by any component found in the fluid to be treated
- easy to be carried out at different points of a desulfurization installation; allowing rapid elimination of poison gas in one step; adapted to any size, easy to start, regulate and stop rapidly
- pressure drop is low, and the reactor is very compact
- no chemical reagent
- able to handle large volumes of gas and wide ranges of power.

The SulfArc can be tailored to fit several particular applications in refineries, geothermy, natural gas fields, metallurgy, paper mills, biogas generators, etc. :

- treating a poison and corrosive gas stack when the presence of oxygen in the gas can be tolerated (for example a Claus tail gas),
- treating a relatively small gas stream, either on a continuous or intermittent basis, with a tolerated presence of oxygen,
- as a mobile apparatus for oil, gas and/or geothermal fields under prospecting, etc.

High-H_2S gas total valorization

When the H_2S concentration in the off-gas is quite high the total valorization of the both components, sulfur and hydrogen, is possible. In such a case one can obtain pure sulfur and hydrogen (or CO as hydrogen equivalent).

The hydrogen is very weakly bound in the H_2S molecule and this fact is the main drawback in the widespread Claus process in which the hydrogen becomes transformed into water and therefore cannot be reused for oil desulfurization or as modern fuel. The economic advantages of hydrogen (and sulfur) recovery from H_2S were recognized in the seventies and some thermal processes have been proposed; 0.25 kWh/Nm³ H_2 is the lowest theoretical limit for such a dissociation. However, a thermal dissociation of H_2S is less than 15 % at 1200 K under atmospheric pressure.

A way of the H_2S total valorization goes through a direct use of plasma processes at near-to-atmospheric pressures. Arc, radio-frequency, microwave and capacity-type discharges through H_2S were already described but most of them could not have an industrial application because of costs, product separation problems, electrode erosion, low pressure use, and limitations in industrial size and/or efficiency of proposed electric power supplies.

A close-to-thermal plasma-chemical process of complete H_2S valorization in $H_2S + CO_2$ gas mixtures :

$$H_2S + CO_2 = H_2O + CO + S \qquad (4)$$

has also been checked in a "controlled-arc reactor" under atmospheric pressure at 6 kW power (16). In this case it can be considered that the carbon monoxide is hydrogen equivalent since the "shift reaction" can easily transform CO into H_2. Total destruction (and valorization) of hydrogen sulfide was observed at the Specific Energy Requirement (SER) of 7 kWh/Nm³ H_2S without any heat exchange or preheating (but using Argon for plasma torch).

Advantages of the Non-Thermal plasma processes were underlined in several papers from the Kurtchatov Institute published since 1981. For example an experiment (17) in a supersonic Very High Frequency mild vacuum plasmatron showed up to 45 % dissociation degree of H_2S at the SER of 0.84 kWh/Nm³ H_2. Actually the group works on up to 1 MW microwave discharges (MCW) for a close-to-industrial scale decomposition at the SER of about 1 kWh/Nm³ H_2 (17).

When the H_2S/CO_2 = 69/31 gas mixture was processed in Orléans at atmospheric pressure in a 3-electrode bench scale GlidArc reactor at the Specific Energy Input (SEI) of 0.36 kWh/Nm³ H_2 a 39 % H_2S transformation has been obtained in one pass at a very high electric-to-chemical energy transfer of 32 % (heat recovery was not taken into account). The energetic efficiency is defined here as a part of the total electric energy input to the reactive system and used to drive the endothermal reaction characterized by its standard enthalpy of 0.25 kWh/Nm³ H_2 or 0.76 kWh/Nm³ CO. This means that the production of 1 Nm³ of H_2 + CO mixture in a laboratory scale SulfArc process would cost only ~ 2.6 kWh of electrical energy (15).

New experiments (8) in the RSC Kurtchatov Institute was performed using the GlidArc reactor to decompose pure H_2S as well as some mixtures $H_2S + CO_2$ at lower pressures in order to compare the results to those obtained in other plasma reactors in view of the hydrogen production. The experimental reactor was totally built in Moscow and several experiments were performed for different gas composition, pressures, flow-rates, dissipated power, electrode materials and electrode gap.

1. Up to 45 % dissociation rate of pure H_2S was observed for this one-pass reactor without any re-circulation nor gas preheating. The best SER result obtained was 4 kWh/Nm³ H_2 for the largest possible electrode gap of 3 mm and a for relatively low SEI of 1 kWh/Nm³ H_2S. Much lower energy costs should be obtained with a complementary ignition system allowing a much larger electrode gap.

2. Two gas mixtures at the molar proportions H_2S/CO_2 = 60/40 and 25/75 were also checked. The results indicate a minimal SER = 5.5 kWh per 1 Nm³ of produced H_2 + CO product at a rather interesting (from an industrial point of view) high pressure range of 0.5 - 0.7 atm. The energy cost of H_2S complete valorization in the poorer H_2S/CO_2 gas mixture is twice as high as compared to the richer one.

The main difference between in Orléans and Moscow experiments is the way of the discharge current limitation : inductance coils were used in Orléans, while capacitors are applied in Moscow. It was already observed in Orléans (5) that the gliding discharge has a "soft" (glow) feature as concerns the way of the electric energy injection to the gas when coils are employed. A "sharp" (spark) discharge is observed when capacitors are used because of a higher instantaneous current injected to the processed gas. Coils seem to be well adapted to process a $H_2S + CO_2$ mixtures whereas capacitors are better for pure H_2S decomposition. (Energy cost of pure H_2S decomposition was about 8 kWh/Nm³ H_2 with the coil limitation (15)). Is the well known very fast recombination of hydrogen with sulfur vapor attenuated when a spark discharge is present whereas a glow-discharge feature helps to process $H_2S + CO_2$ mixture ?

A relatively high energy cost of H_2S decomposition in the GlidArc could be reduced by electrode structure and both electrotechnical and plasma parameters optimization. Maybe one could not get here an efficiency better than the efficiency obtained in the MCW-discharge because of a non-steady-state organization of the GlidArc with a strong thermal non-equilibrium. However, to compare the GlidArc with the MCW-discharge, one has to take into account a very simple and inexpensive plasma-chemical GlidArc-based reactor. The use of the GlidArc reactor is therefore shown as an interesting perspective for H_2S-rich waste gas total valorization at a low energy cost, especially to process high-CO_2 gas mixtures which are not acceptable for classical processes.

Cold-plasma reduction of flue-gas SOx to elemental sulfur (10)

Removal of SOx from Flue Gases (FG) and its eventual conversion into saleable products is one of the most important tasks in the environmental engineering. Many as yet inadequately economic processes have been developed for FG Desulphurisation (FGD), usually involving SO_2 oxidation to waste-gypsum at an electrical energy consumption of ~ 1 MWh per ton SO_2 (~ 1.4 % of effective loss in power station efficiency), in addition to considerable reagent purchase costs and transportation costs of reagents and products.

The sulfur concentration in the FG varies from 0.05 to 1 % (it contains about 90 % of the sulfur as SO_2, the rest as SO_3). One group of about 30 basic FGD is based on the FG sorption-desorption step which gives a concentrated SOx for a next step processing. For example a Hoechst-Uhde installation in Frankfurt a/M for the FGD (~ 95 % SO_2 is removed) and then SO_2 transformation to H_2SO_4 is based on adsorption and desorption (oxidizing atmosphere, 400°C) process of SOx + NOx from the stack on an "Aktivkoks". The concentrated gas is then purified from NOx and transformed to H_2SO_4. This installation can produce 1600 t/year of S-equivalent H_2SO_4.

A reduction of SO_2 to elemental sulfur via following summary exothermal reactions :

$$SO_2 + 2\,CO = S + 2\,CO_2 \qquad (5)$$

$$SO_2 + 2\,H_2 = S + 2\,H_2O \qquad (6)$$

$$2\,SO_2 + CH_4 = 2\,S + CO_2 + H_2O \qquad (7)$$

would be however more interesting, but it needs to be carried out at the temperatures of 700°C to 1600°C, or in presence of catalysts (which are easily poisoned).

It is therefore interesting to propose a plasma-chemical reactor to reduce SO_2 to sulfur without using any solid or liquid catalyst but only via catalytic species continuously produced in plasmas, in the homogeneous phase with respect to the gas input. On the other side it was important to prove (done in the Warsaw's Industrial Chemistry Research Institute) that one can desorbe the SO_2 from an activated coke using a reducing gas instead of the air or steam commonly employed, so that a mixture of SO_2 with a reductant gas can be directly processed in GlidArc.

Several GlidArc experiments were performed at about 1 atm for different gas composition, pressure, flow-rate, and dissipated power, for the same electrode material (stainless steel) and electrode gap. Laboratory scale reactor for SO_2 processing was built as a one-step, steel, water jacked, 5.4 liter cylinder in which 6 knife-shaped steel electrodes are put around the gas enter nozzle of 3 mm diameter. The electrode gap is starting at 3 mm (ignition) to become about 100 mm at the electrode top (arc disappearance). The reactor was connected to a small 3-phase 50 Hz power supply composed of 6 neon-sign 10 kV transformers (a self-inductance current control).

The electric power injected to the reactor was carefully measured via both digital and watt-meter and classical kWh counter. The input gas flows of pure SO_2 and a reducing gas were measured via separated mass flow-meters and then mixed together before entering the reactor. The total flow-rate of the gas mixture was at the range of 2 Nm^3/h. The SEI could be precisely determined for each experiment. Solid sulfur was collected on the cold reactor walls. The Orsat apparatus, specific Dräger tubes, and gas chromatography analysis were used to check both the input and output gas compositions.

1. *Hydrogen as reducing gas* : Gas mixture of 37 vol. % SO_2 + 63 vol. % H_2 at initial temperature of 20°C and the total flow-rate of 2.3 Nm^3/h was processed at 1.6 kW electric power dissipated in the reactor. As result the main reaction (6) was observed while a secondary reaction :

$$S + H_2 = H_2S \qquad (8)$$

contributed in very limited way giving only 0.5 vol. % of H_2S in the outlet gas. The output gas analysis (SO_2, H_2, and H_2S) and mass balance indicate that as much as 67 % of the initial SO_2 was reduced to the elemental sulfur (solid elemental sulfur and water were collected on the reactor walls).

2. *Methane as reducing gas* : Gas mixture of 57 vol. % SO_2 + 43 vol. % CH_4 at initial temperature of 20°C and the total flow-rate of 1.8 Nm^3/h was processed at 0.5 kW electric power dissipated in the reactor. As result the main reaction (7) and the secondary one :

$$SO_2 + 2\,CH_4 = S + 2\,CO + 4\,H_2 \qquad (9)$$

elementary sulfur was precipitated on the reactor walls. The side reaction (8) contributed in a very limited way giving only 0.2 vol. % of H2S in the outlet gas. The output gas analysis (SO2, CH4, H2, CO2, CO, and H2S) and mass balance indicate that as much as 64 % of the initial SO2 was reduced to the elemental sulfur.

No chemical corrosion nor erosion of GlidArc electrodes were observed during quite long runs of the reactor when processing SO2-rich gases. All that means that in spite of the results of our preliminary study one can imagine a new FGD process in which :

old : whole FG from a thermal power station traverses a sorbent (for example an activated coke) so that all SOx are absorbed there;

new : SOx is desorbed using a reducing gas (like methane) so that SOx concentration can attaint an important value of about 25 % ;

new : this gas mixture is transformed to liquid or solid saleable sulfur in a GlidArc-type plasma reactor (complete transformation is not necessary as the non-reacted gas mixture can be reburnt in the boiler).

The inexpensive and very simple gliding electric discharges are found to be capable to considerably reduce the nuisances of existing processes of industrial depollution from SOx. High energy consuming and troublesome thermal or catalytic reduction of SOx can be substituted by this particularly cold and catalytic plasma assisted process at lower specific energy expense : less than 0.25 kWh per 1 Nm^3 of the concentrated SOx from desorption process, so less than 0.3 MWh/ton SO2, so only about 0.5 % of the electric energy produced by a typical power station.

The proposed process makes it possible to destroy all SOx present in gas, without employing a chemical additive and with a low consumption of electrical energy. Its conditions of use are very elastic as it may be used with any flow rate and/or temperature without limit of pressure of the gas and without limitation concerning the initial gas composition. In particular, NOx and/or HCl presence in the gas is not detrimental, in contrast to other processes of the sulfuric acid production from the FG. The process requires no particular preliminary treatment in charges containing carbon monoxide, CO, methane, other unburnt hydrocarbons or VOC's. Furthermore, as the process does not employ a catalyst, there is no risk of a such catalyst to be "poisoned" by any component found in the FG to be treated. The process may be adapted to any size, it may be started, regulated and stopped rapidly and easily. The pressure drop is low, and the reactor is very compact.

The proposed process can be tailored to fit several particular applications in industries like : thermal or electric power plants fed by ensulfurated coal, bitumen, tar, oil or gas; also mobile boilers (like ships), petroleum refinery for waste Claus tail-gas depollution, coal gas production, metallurgical plants like autogenous non-Fe sulfidic ore concentrate smelting process.

Oxidation of CH4 by CO2

Transformation of CH4 + CO2 mixtures into synthesis gas (syngas) :

$$CH_4 + CO_2 = 2\,CO + 2\,H_2 \qquad (10)$$

is currently of great interest both for transformation of natural gas and the safeguard of the environment since it may lead to the destructing valorization of both CH4 ("associated" gas from remote petroleum fields) and CO2 (thermal power stations) which are responsible for the greenhouse effect.

Conventional electric arcs allow to use for it important SEI's. For example SEI > 15 kWh/kg CH4 (9, 18) leads to a complete dissociation of methane; concentrations of H2 and CO obtained are very close to those calculated for a thermodynamic equilibrium at 2000 K (temperature of exhaust gases). The chemical efficiency (ratio of the energy required to drive this endothermal chemical reaction at 298 K to the used electrical energy) is about 28%, but the main driving plasma-forming gas remains Argon (unless pure H2 or CO2 are accepted by high-current arc electrodes).

Use of a cold plasma at atmospheric pressure with a tri-phase GlidArc was already proposed (4, 19). Newer results (9) for different injected mixtures in which x = CO2/CH4 varied between 0.5 and 2 are presented in Table 1 for a constant electric power of 2.5 kW. One can compare there the concentrations of main components of exhaust gases : measured and deducted from relations of thermodynamic equilibrium at exhaust gas temperature.

Table 1. Measured and calculated concentrations of CO2, CH4 , CO, H2, and H2O in exhaust gases.

CO2/CH4	CH4		CO2		CO		H2		H2O		T (K)
mole/mole	exp.	th.	exp.	th.	exp.	th.	exp.	th.	exp.	th.	th.
					(in % vol.)						
0.50	44	47	19	17	9	12	12	14	0.2	2.7	810
1.00	40	41	38	38	9	12	11	11	1.0	2.9	750
1.50	33	32	46	46	9	12	9	6	2.8	3.2	750
2.00	26	26	52	52	10	13	7	6	3.6	3.5	750

We see a rather satisfying agreement between these values for CH4, CO2, CO, H2, and H2O. The formation of a certain quantity of acetylene is observed, which was not expected at these temperatures in the framework of thermodynamic equilibrium. The specific energies involved are lower than used in arc experiments and methane dissociation is not complete. However the GlidArc allows to get the syngas at low temperature (750 K) with much higher (up to 40%) chemical efficiency, without using a catalyzer.

CONCLUSION

The electrical energy is directly used to produce a non-equilibrium and very reactive medium allowing efficient gas processing so that up to 45 % of this energy may be directly absorbed in an endothermal reaction. Therefore the main innovative aspect of the GlidArc processes is certainly the way the chemical reactions are activated via powerful electrical discharges under near-to-atmospheric pressures.

The inexpensive gliding electric discharges are capable to reduce considerably the nuisances of existing processes of industrial depollution from the VOC's, such sulfur-contained compounds as H2S or mercaptans, and SOx. The use of such discharges can bring to these processes an easily controllable energy. High energy consuming and/or troublesome classical processes can be substituted by this particularly cold and catalytic plasma assisted process at lower specific energy expense.

The use of the GlidArc reactor for concentrated gas endothermal processing is shown as an interesting perspective for H2S-rich waste gas total valorization at a low energy cost, especially to process high-CO2 gas mixtures which are not acceptable for classical processes. Interesting low-energy non-catalytic way of syngas production from both waste natural gas and CO2 (or directly from a biogas) is shown, too.

Actually developed GlidArc reactors can be DC or AC powered up to an industrial size, have two or more electrodes (3-phases, 6-phases, n-phases, parallel, serial or mixed mounting) and show no significant electrode corrosion for the fluids already tested : different gases or vapors with or without liquid or even solid admixtures.

REFERENCES

1. J.E. Harry and A.A.Yahya, *Plasma for Ind. and Environment Techn. Conf.*, Oxford, England, Paper 7.3, 1990.
2. L. Civitano, G. Dinelli, I. Galimberti, M. Rea and R. Turri, *IX Int. Conf. on Gas Discharges and their Applications,* Venice, Italy, p.603 (1988).
3. H. Lesueur, A. Czernichowski and J. Chapelle, *French patent* 2 639 172.
4. H. Lesueur, A. Czernichowski and J. Chapelle, *J. de Phys. (Suppl.)*, **18,** 49 (1990).
5. A. Fridman, J. Chapelle, A. Czernichowski, H. Lesueur, J.M. Cormier and J. Stevefelt , *Proc. ISPC11,* Loughborough, UK, 1993.
6. J.M. Cormier, F. Richard, J. Chapelle and M. Dudemaine, *2nd Int. Conf. on Electrical Contacts, Arcs, Apparatus and their Applications,* Xi'an, China, 1993.
7. H. Lesueur, A. Czernichowski and M. Granops, Gliding arc reactor for H2S partial valorization, *Proc. ISPC11,* Loughborough, UK, 1993.
8. S.V. Saniuk, S.S. Kingsep, V.D. Rusanov and A. Czernichowski, Complete valorization of H2S or H2S + CO2 waste gases in a gliding arc reactor, *Proc. ISPC11,* Loughborough, UK, 1993.
9. K. Meguernes, J. Chapelle and A. Czernichowski, Syngas (H2 + CO) production using electrically assisted methane partial oxidation by CO2, *Proc. ISPC11,* Loughborough, UK, 1993.
10. A. Czernichowski, J. Polaczek and T. Czech, Cold-plasma reduction of flue-gas SOx to elemental sulfur, *Proc. ISPC11,* Loughborough, UK, 1993.
11. H. Lesueur, A. Czernichowski, J. Chapelle, *J. de Phys. (Suppl.)*, **18,** 57 (1990).
12. A. Czernichowski, H. Lesueur and G. Fillon, G., *Workshop on Plasma Destr. of Wastes,* Odeillo-Font Romeu, France (1990).
13. A. Czernichowski and H. Lesueur, *10th Int. Symp. on Plasma Chem.*, Bochum, Germany, p. 3.2.1 (1991).
14. A. Czernichowski and T. Czech, *IIIrd International Symposium on High Pressure, Low Temperature Plasma Chemistry (HAKONE III),* Strasbourg, France, 1991.
15. A. Czernichowski, H.Lesueur, T.Czech and J. Chapelle, *10th Int. Symp. on Plasma Chem.*,Bochum, Germany, p. 3.2.22 (1991).
16. A. Czernichowski, P. Jörgensen, H. Lesueur, J. Chapelle and K. Meguernes, *J. de Phys. (Suppl.)*, **18,** 65 (1990).
17. R.I. Azizov, A.K. Vakar, V.K. Givotov, E.G. Krasheninnikov, M.F. Krotov, S.Ju. Malkov, G.I. Novikov, B.V. Potapkin, V.D. Rusanov and A.A. Fridman, *J. Techn. Phys.* **55,** 79 (1985).
18. P. Jörgensen, J. Chapelle, A. Czernichowski and K. Meguernes, *ISPC8*, Tokyo, p. 695 (1987).
19. A. Czernichowski, H. Lesueur and J. Chapelle, *Proc. 9th World Hydrogen Energy Conf.*, Paris, p. 43 (1992).