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STATE OF THE ART OF PLASMA CHEMICAL SYNTHESIS OF HOMOGENOUS AND HETEROGENOUS PRODUCTS

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Abstract - Since 1960 many studies have been devoted to physical and chemical transformations in plasmas. In this paper we do not propose to make an exhaustive overview but to underline the main development points of plasma chemistry.
First after a brief historical review, we present the plasma chemical reactors and describe the different types of plasma generators.
We discuss then of the two main parameters to be taken into account in plasma chemical reactor : mixing of the reactants and quenching. We examine models taking into account kinetics, diffusion and mixing of reactants and also the catalysis problems.
Secondly we recall the energetic situation and the advantages of plasma chemical reactors. We review the actual industrial plasma processes, essentially surface treatment and spraying, spheroïdization, ultrafine powders production, remelting, ozone production and we try to guess what will be the future tendencies in the industrial development of plasma processes either for high quantity production and for high commercial added value products.
In the third part we deal with the diagnostic techniques. For the plasma, attention is given to the assumptions involved in each techniques specially with regard to the local thermodynamic equilibrium. We describe a few techniques of measurement of the temperature and population of excited species by emission and absorption, enhancing the advantages of laser light scattering. For the condenses particles injected in a plasma jet we present the most recent techniques to measure in flight their velocity (LDA), their temperature (statistical pyrometry), their diameter and their flux.
In the last part, through four examples : nitric oxide synthesis, acetylene production, plasma spraying and extractive metallurgy we try to show, what progress the development of the measuring techniques and of the modelisation has brought and what is still to be made.

INTRODUCTION

Since 1960 many studies have been devoted to physical and chemical transformations in plasmas. Unfortunately at the beginning, the unsuitability of the theoretical concepts used for the understanding of the phenomena, associated with a rather poor perception of the economical considerations led, in the late sixties, to a lack of a coherent research programs in United States. However, in the seventies with the improvment of our understanding of the fundamental phenomena in the plasma, and with the situation arising from oil crisis, interest in plasma chemistry has been renewed. The progresses that have been done in measurement techniques and data acquisition (cross sections and kinetics constants even for excited states, diffusion coefficients, thermodynamic and transport properties of different mixtures, velocity and temperature measurement of particles in a plasma jet) and for the modelisation, allowed an important reduction of the energetic costs of reactions. This reduction coincided with a tremendous increase of the cost of oil and a better evaluation of the economical cost of some well selected plasma chemical or physical processes have allowed some new industrial development. Concurrently the industrial search for new processes using electrical energy has developed research in the field of plasma chemistry.

I - WHAT IS PLASMA CHEMISTRY

I-1. Historical

If one except nitric oxide synthesis by Zeus with lightnings, the first laboratory plasma experiment was performed by Henry and Dalton in 1797 with a capacitive discharge in methane where they get acetylene. The studies in discharges at the end of the nineteen century led in 1905 to the industrial nitric oxide synthesis by Birkeland and Eyde (1). Unfortunately the efficiency was poor and the process was abandoned for the classical Haber process

with ammonia. The studies developed then up to the end of the second world war were essentially (2) concerned with hydrocarbons, H_2, N_2, O_2 and O_3. With the development of the HF torches in 1948 (3) and of the DC arc torch (4) the number of studies in plasma chemistry increased considerably. In the seventies with the improvment of the measurement techniques the role of the kinetic, electronic, vibrational, rotational excitations, the role of the non equilibrium state and of the metastable states become better understood thus allowing a better correlation between the discharge conditions and the products obtained.

I-2. The plasma chemical reactor

Generally (5) the experimental considerations in plasma chemistry may be divided into three parts. Fig. 1 corresponding as first approximation to the three stages of the reaction

- plasma generation
- reactions with the plasma gas
- quenching and recuperation of the formed products

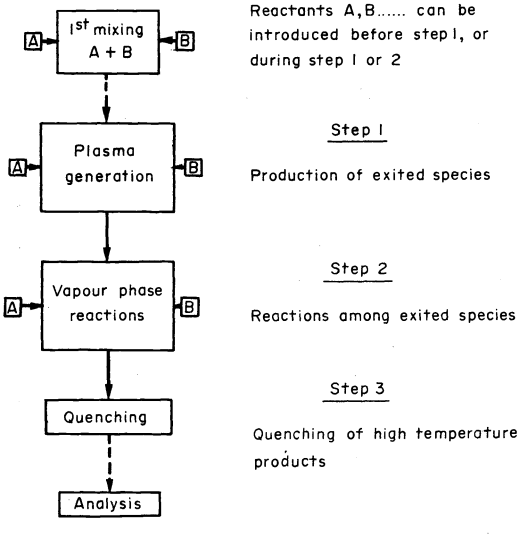


Fig. 1 - A plasma chemistry reaction

Unfortunately, the plasma characteristics are not independant of the choice of the source and its choice is of considerable importance for the others stages and the reactor must be conceived around the plasma source. So we will successively study the plasma generation, the problems of introducing the reactants in the reaction area and the quenching.

I-2-1. Plasma generation

The physical properties of the plasmas used in plasma chemistry (high and low pressure arcs, glow discharges, HF discharges ... (5)) are very different. Usually the state of the plasma is characterized by the electron energy (kT_e) and electron density (n_e). Generally, when the pressure is lowered, the ratio T_e/T_h of the electron temperature to the heavy particles temperature, increases from about one at one atmosphere to about 100 for pressures below 1 Torr. It is the same when one considers the intensity of the discharge current : more than 50 A for a ratio of about one and less than 1 A for a ratio lower than 50.

One has to remind that, at pressures near the atmosphere and high power levels, it is possible to treat an important mass flow rate of products while at low pressure, the power and mass flow rate are usually low.

When T_e/T_h is near unity the gas temperature is high (a few thousand K) and these plasmas are well suited for reactions that needs high enthalpy tranfer (fusion, spheroïdization, spraying, vaporisation) or for the synthesis of inorganic materials (ceramics, NO, C_2H_2...). Often however the temperature and density gradients are high along the radius of the plasma and it is difficult to get the same treatment for the products injected. One also has to remind that as soon as a cold reactant is injected in the plasma the equilibrium situation is completly perturbated.

The plasmas with high T_e/T_h have usually the heavy particles temperature rather low (often near ambiant) and they are well suited for the treatment of low quantities of material very sensitive to the temperature effects (organic compounds for example).

From an economical point of view it is known that HF and microwaves (MW) plasma generators cost in investment as much as 3 to 10 times (depending on the frequency) more than DC or AC arcs per kilowatt of power level. Moreover the thermal energy transfer efficiency is roughly betwenn 1/2 to 1/3 for HF or MW plasmas compared to arcs. Obviously cost is not

the only criteria since as one has to consider also the nature of the reactants to be treated, specially when dealing with agressive gases such as oxygen and chlorine.

Finally we have summarized in table 1 the main characteristics of plasma used in plasma chemistry

Type of plasma	Maximum power (kW)	Frequency range (kHz)	Pressure range (Torr)	Arc current intensity (A)	T_e/T_h	T_h (K)	Thermal efficiency %	Nature of the products treated	Quantity of the products treated g/s
Glow discharges (6)	10	0	10-100	10^{-2}-1	5-100	<1000		non agressive gas	10^{-3}
Corona discharge (7)(8)	5	< 500	760	$<10^{-1}$	5-100	300		any gas	< 1
Micro-waves (MW) (9)(11)	5	310^5-210^6	10-760		2-100	<3000	20	any gas	$< 10^{-1}$
HF (12)(14)	1000	10^3-2.10^4	10-760		1-50	<10000	< 50	any gas or solid particles	< 50
Arcs (15)(59)	10000	D.C.or0.1	100-760	> 50	1-5	2000 20000	< 90	non agressive gas solid particles	< 100

Table 1 : Main characteristics of plasma sources

I-2-2. Mixing of the reactants

As we have indicated on Fig. 1, the mixing of the reactants can be done before or after the plasma generation.

a) - Mixing before plasma generation. In this case there is no problem for mixing the gaseous reactants but one has to be sure, as soon as the plasma is in contact with electrodes, if any, that there is nc reaction with them for example with agressive gases like oxygen, chlorine... With solid reactants when the problem with the electrodes is solved the heat transfer to the particles is much more efficient (12) specially if the material to be treated is uses as anode (60) as in the Mc Rae plasma furnace (52). One has also to think about the reaction to be performed and its selectivity. For example (61) if one injects oxygen and nitrogen into a plasma before the plasma generation the NO synthesis might be decreased because, in certain conditions,the main processes are :

$$N + O_2 = NO + O$$
$$O + N_2 = NO + N$$

and it is preferable to dissociate only N_2 to get N and then to inject cold O_2 after plasma generation.

b) - Mixing after plasma generation. In this case there are no problems with electrodes but the injection of a cold reactant in a plasma is often difficult, specially if it is a hot heavy particles plasma with a high viscosity and this injection modifies strongly the plasma excitations and temperatures. One has to study the heat and mass transfer and the excitation transfer that often becomes the main reaction process

I-2-3. Quenching

Quenching in plasma chemistry plays two important roles

. to withdraw excess energy from the excited new species which are formed,
. to prevent the inverses reactions that destroy the new products.

This is obtained by :

- excess energy removal, that is to say the reduction of the kinetic temperature that governs the creation-destruction equilibriums
- the more or less specific destruction of the electronic and vibrational excited species (walls, collisions, recombinaisons) that can induce new reactions, some time undesirable.

As well in hot as in cold plasma, in most cases of plasma chemistry, quenching is the most important phenomena determining whether a new product is obtained or not.

In a hot heavy particle plasma, the quenching rate is of first importance and must be greater than 10^5 K/s to be efficient. The moment of the quenching and the law of quenching ($dT/dt = f(t)$) are also of primary importance (62).

I-3. Modeling

I-3-1. In gaseous phase

Modeling of homogenous reactions is particularly sensitive to the basic assumptions envolved, specially in the quenching stage, to take into account the rapid variation of temperature of the excited species. The parameter to be considered is the Damköhler parameter (63) D_I, ratio of the chemical reaction time t_c to the mechanical residence time t_m. The equilibrium is obtained for $D_I << 1$, for example in a D.C. plasma jet it implies reaction times shorter than 10^{-7} s. The equilibrium calculations are now well known (64-67) although they do not describe what happens during the cooling phase, that is to say, the quenching. In all the cases one has to take into account the kinetic calculations (68) for which the two problems that remains to be solved are the lack of the data specially of excited states (69-71) and the "stiffness" of the numerical integration methods (72).

I-3-2. With solid particles injected in the plasma

To perform the calculation of the transport properties of the plasma (78-82) the first hypothesis is that the plasma is in ETL but one of the main problem is the lack of datas for interaction potentials in complex mixtures. Then the heat and mass transfer between plasma and particles is determined though equations (63-88) using empirical correlations. But there is still a lot of work to be done to take into account all the phenomena (for example the cooling of the plasma by the particles (89)) and to determine the mean values of the transport properties to be used between the plasma and the particles especially during the evaporation stage. The chemical changes are, in most cases, governed by diffusion (86) corresponding to long times (>0.1 s) and thus necessitating plasma furnaces with long residence times for particles (36-59).

II - INDUSTRIAL APPLICATIONS OF PLASMA CHEMISTRY

II-1. Energetic situation

The apparent fast decrease of the world reserve of oil and natural gas and the tremendous increase of their prices lead to a complete reevaluation of their use as energy sources. Taking into account the energy reserves (cf table 2 (90), the use of electricity produced either from nuclear plants or coal plants seens to be the most reliable for the end of this century. For example in France, nuclear power plants are expected to supply about 45 % of the electrical energy demand in 1985, giving rise to a supposed decrease of the relative cost the electric energy compared to other sources of energy.

			Energy (in billion t.e.c.)			
		available ressources	obtainable ressources	1973	Demand	2000
Fossil Energy	Coal	10 000	600	2,7		4
	Oil	> 150	> 150	4,2		6
	Natural gas	>	> 75	1,1		2
	Shale		1 000			1
(uranium, thorium, plutonium)	Geothermal	10^{11}	300(year)	0.001		0.3
	Nuclear	> 65 000(year)	>20 000(year)	0.08		15.3
Renewable	Solar	150 000(year)	1 500(year)			0.5
	Wind	3.10^8(year)	10(year)			
	Ocean		80(year)			
	Tidal	4(year)	0.1(year)	0.0006		0.001
	Hydro	10(year)	0.3(year)	0.2		0.4
			TOTAL	8.3		29.5

Table 2 : Energy sources

Further the world ressources of energy and carbon raw materials have been developped, up to now, through oil and natural gas and heavy chemistry and energy have had a parallel development (91) in this conditions a distinction between the raw material for the energy use and for the chemical use becomes necessary. For example in the USA (92) an increase of the oil consumption for the chemical uses and a decrease for the energy uses in now forseen Fig. 2.

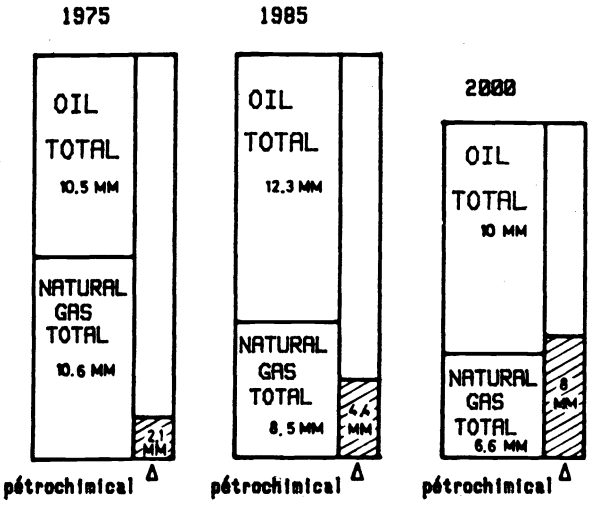


Fig. 2 - Present and projected need of hydrocarbons for petrochemical and as a source of energy in U.S.A. Reprinted from (92)

This new situation of various types of energy sources and of the raw materials implies naturally that many chemical processes at high temperature use electrical heating or reactions under plasma conditions.

We have to emphasize that the plasma chemical processes have the following important advantages :

- they can be operated and stopped very quickly,
- they have a high energy density and the reactions are very fast compared to the classical reactors allowing the use of small units with a rather low investement cost,
- they are usually not polluting.

II-2. Industrial plasma processes

The plasma chemical processes used now in industry are getting wider acceptance, but due to the oil price before 1973 they essentially concern the treatment of products in rather small quantities with a high or medium commercial added value.

II-2-1. Surface treatment

Surface treatments either by thin film deposition with low pressure plasma or by plasma spraying to give some specific properties to the surfaces are the most widley used plasma chemical processes.

- integrated circuits technology :

. the plasma activated chemical vapour deposition (93,94) allows the passivation of the integrated circuits by the means of Si_3N_4 protection layer deposited at temperatures lower than 400°C as used by Texas instruments, or the deposition of dilectric films (Si, Si_3N_4, $Si_xO_yN_z$...) (95,97). Reactors are now on sale (LETI in France, Applied Materials in USA).

. plasma etching (98-101) with selective etching of different materials (Si, SiO_2, Si_3N_4, Al) by a reactive plasma (CF_4 for example) seems a best way than the classical humid processes ant it is now used in industry (L.F.E., T.P.C., Texas, I.B.M. ...)

- surface treatment by cathodic pulverisation or ion plating is now on commercial operation for the preparation of electrically conductive or semi-conductive layers, wear resistance layers, dielectric layers... (102-106), for the surface hardness and wear resistance of machine tools (107-108) or for anti-corrosive layers (109).
- plasma polymeric surface treatment can be used, to modify the adhesion and wettability properties of surfaces. This technique now used in industry (R.P. France) allows the suppression of the solvents, it is also used in printing for the linkage of polyethylene (110-111).
- plasma spraying is used on commercial scale since 1960. The plasma jets are well suited to melt a powder feed and project the droplets at high velocity against a material to be coated. This coating : nickel aluminide, cermets, carbides, oxides, borides, silicides, refractory metals are used for their wear, oxidation or corrosion resistance, as thermal or electrical barrier, as controlled coefficient of friction surfaces (112-115).

II-2-2. Particles treatment

- spheroïdization in used commercially for zirconia (IONAC Tafa (116), for magnetite (117) or ferrosilicon used for photocopy (118) (Xerox Co)
- ultrafine powders with a very high specific surface is obtained from vapo-condensation in plasma : titanium pigments in a 400 kW HF torch (12) or in a 500 kW DC arc (119), silica powders are also produced by different plasma processes (120).

II-2-3. Other treatments

- the remelting plasma furnaces for noble metals (Ni, Mo, Ta, Ti..., ...) are used in Europ

USA, Japan and USSR at a scale of 200-600 kW (121-129-12). They allow the production of very pure metals with an energy consumption of a few kWh/kg. Some plasma furnaces are used in USSR to produce nitrogen super saturated steels (up to 1.8 % (12)).
- the corona discharge is used for the industrial ozone production (130).

II-3. Future tendencies in the industrial development plasma chemical processes

Up till now, the industrial use of plasma chemistry has been developped essentially for products with an important added commercial value or when the plasma route was the only way to get the product. However due to the increasing price of oil it is reasonnable to think that in the next decade plasma processes will be developped to produce high quantity of rather low added commercial value products. We will give below a list of some plasma processes that, to our opinion, present some industrial interest in a next future.

II-3-1. Plasma chemistry for high quantity production

- acetylene production : if the low cost of oil with the development of ethylene production led, in the late sixties, to the abandon of the production of acetylene with the big 10 MW plasma furnaces of Huels, Hoechst, Dupont de Nemours (131-133) the increasing cost of oil now may probably lead to the development of the production, with plasma furnaces, of acetylene (AVCO processes (44-134)) or maybe ethylene from coal.
- nitric oxide production : actually the nitric acid is produced through ammoniac, itself obtained with methane which price is increasing each day. With its actual price a plasma process should cost less than 7 kWh/kg to day, but if the methane price keeps increasing with the same rate, the plasma process can be competitive at 16 kWh/kg in 1985 in France. The numerous laboratory studies on NO synthesis in plasma (135-140,61) shows that the energy consumption is regularly decreasing and for example in Thermodynamic laboratory at the University of Limoges we have now less than 20 kWh/kg of NO and a nitrogen conversion greater than 10 %.
- extractive metallurgy : of course the plasma furnaces are not designed to replace the blast furnaces but from now on they might be competitive to the classical production processes of ferro-alloys or noble metals. Started and stopped very quickly they produce high purity metals and extensive work is now devoted to them. The recent studies are devoted to the chromium or vadanium ferroalloys (141-148) with furnaces scaled up to 1 MW (148) or to the molybedenite desulphurization (149-150). The results of Bethlehem (52-151) on a 1 MW furnace and the results of Foster Wheeler (152-153) to get iron seems to be very encouraging on an economical point of view for casting (154-148).
- complex materials treatment : fusion of various ceramics in rotating furnaces (either vertical or horizontal drum (155-159) may also gain some industrial interest. Studies are developed for the industrial spheroïdisation of clays (89) and the plasma treatment of apatitics phosphates is intensively studied in USSR (160).
- production of dispersed materials : spheroïdization of small metal particles will be interesting for sintering and give a new market for plasma treatment. The nitrides, carbides, oxides... obtained by plasma processes have usually interesting internal structures and the materials obtained by sintering them, with additives or not, are heat resistant and stable to thermal shock and so may be used to improve the working temperature of motors or turbines and then their efficiency.
- low grade ore treatments : with the decrease of the high grade ore reserves or with the international conjoncture incertainities for the stores, the studies started a decade ago may find a renewed interest for example for tin, lead or manganese (161-167).

II-3-2. Plasma chemistry of high commercial added value products

- electronic circuits : this plasma techniques yet widely used in industry will be developed
- pure silicium production : the production of silicium high purity for solar cells is now tested in arc plasma but also in low pressure plasmas for the deposition of thin films
- plasma chemical stereochemistry : the selective excitation of nitrogen or oxygen metastable molecules allows specific organic reaction as developed in France by Air Liquide with ($O_2 {}^1\Delta_g$) (168-169). For example numerous studies are developed for the production of hydrazine by formation of the NH_2 radical in plasma (170-172).

II-4. Conclusion

The interest of industry in plasma chemical processing semms to be increasing due to progresses made in understanding the phenomena involved and the substantial improvment in process efficiency. Their has also been a shift towards an increased industrial utilization of electrical energy as a result of the oil crisis. However new plasma processes will be acceptable on industrial level only if the conversion rate is increased and the specific energy consumption decreased. Since we have now rather good models for homogenous phase reactions as well as for particles treatment, the main problem is essentially a lack of experimental data, such as kinetics coefficients for reaction with excited species, velocity, diameter and temperature evolution of the particles in plasmas. It is therefore very important to be aware of the last techniques developed for this measurements specially the laser techniques which are very promising. These will be considered in the next section.

III - PLASMA DIAGNOSTICS

III-1. Diagnostics of the gas phase in a plasma reactor

In this section a review will be made of the different diagnostic techniques currently used for the determination of the temperature and composition profiles in a plasma reactor.

Attention in given to the assumptions involved in each technique especially with regard to the Local Thermodynamic Equilibrium (LTE) hypothesis which is necessary with all of the classical spectroscopic techniques (173-176).

The other question which also arises in all optical measurements on plasmas is the treatment of the radiative transfer through the plasma. Since optical observations are always made along a line passing through an inhomogeneous, and sometimes absorbing medium, the measured quantity represents the integral of that property along the optical path. The local profiles can only be obtained in this case by such techniques as the Abel inversion (177-180) or other more sophisticated methods in the case of optically thick plasmas (181) or non axisymetric plasmas (182-185).

Over the last few years, as a result of the rapid development of laser technology, new plasma diagnostic techniques have been developed which do not require the LTE hypothesis. Laser scattering techniques such as the Thomson and Rayleigh scattering, Raman scattering, and resonance fluorescence are typical examples.

These have the added advantage of having a good spacial and temporal resolution. The former being due to the fact that the measuring volume is the point of intersection of the excitation beam and the optical path of detector as shown in Fig. 3. The temporal resolution can be obtained using a pulsed laser as the light source. Pluses shorter than one microsecond can be obtained without difficulty.

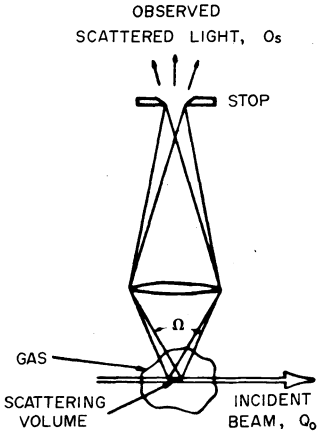


Fig. 3 - Geometric configuration fo light scattering diagnostics

III-1-1. Conventional spectroscopic methods

Under L.T.E. conditions, line volumic emission coefficient is a function of the concentration of the transition upper level. The emission coefficient value measurement - if the transition probability of the investigated is known - combined with the law of mass action (Saha-Eggert equation and Guldberg-Waage equation) allows the determination of the temperature. Different methods based on the ratio of two lines emission coefficient are extensively covered by Drawin (175).

With plasmas of pure gases such as Ar, He, N_2 or air (187-190), measurements of the continuum emission represent the simplest method for determining the plasma temperature. In gases which form negative ions, the intensity of the affinity continuum resulting from the attachment of the electron may be also used for diagnostic purposes. This method is specially useful for the investigation of halides such as SF_6.

A powerful diagnostic tool for the determination of the electronic concentration, which does not require the L.T.E. hypothesis, involves the measurement of the atomic line broadening. This is true especialy when Stark broadening is predominant and the Van der Waals, resonance and Doppler broadenings can be neglected (176-191). However since the Stark broadening is particularly important for hydrogen, a convenient diagnostic method consists of adding H_2 to the plasma gas whenever possible as long as the original plasma is not distrubed (192).

Nevertheless these methods may be used only at high temperature and electronic concentration (at p = 1 atm..., T > 6 500 K and $N_e > 10^{15}$ cm^{-3}). These conditions are only fulfilled in an high intensity arc or in the core of plasma jet. At the contrary, in the plume of a plasma torch with N_2 as plasma gas for example, the gas temperature is about 3 to 6 000 K and the plasma is quite out of L.T.E.. But the relaxation times of rotation-rotation exchanges are so short that the molecule rotational temperature is always equal to the neutral

translational temperature. A few measurement methods of the rotational temperature of melecule N_2^+, N_2, C_2, CN ... may be found in (176, 193, 194).

III-1-2. Methods based on refractivity

Since the refractive index of the different constituents of the plasma are additive, the overall plasma index can be calculated as follows :

$$(n-1)_{plasma} = (n-1)_{molecules} + (n-1)_{atoms} + (n-1)_{electrons} + (n-1)_{ions} \quad (1)$$

The contribution of molecules and atoms represented by the first two terms on the right hand side of equation (1) is adequately described out of the ultra-violet region by the equation :

$$n-1 = A + B/\lambda^2 \quad (2)$$

the constant A and B have been measured for most gases. The contribution of excited states to the refractive index is usually small since the ground state population far exceeds that of excited states in moderatly hot gases.

The contribution of charged particles represented by the last two terms on the rigth hand side of equation (1) is given by :

$$n^2 = 1 - \omega_p^2/\omega^2 \quad (3)$$

where ω_p is the plasma frequency. Under typical plasma conditions, ω_p may be taken as the plasma frequency of electrons :

$$\omega_p = (4 \pi N_e e^2/m_e)^{1/2} \quad (4)$$

The electronic contribution to the refractive index is more sensitive to the wavelength than that of the neutrals. By performing diagnostic measurements at different wavelengths, it is possible to separate the contributions of the electrons from that of the neutrals.

It is noticed from equation (3) that the refractive index of the plasma is higher the longer is the wave length of the incident beam.

H_e-N_e laser was widely used at high electronic concentration ($N_e \sim 10^{17}$ cm^{-3}) because it can oscillate at wave lengths 0,63 µm, 1,15µm and 3,3 µm (195-205). Nevertheless at lower electronic concentrations ($n_e \lesssim 10^{17}$ cm^{-3}) a CO_2 laser which oscillates at 10,6 µm is needed (207-209). For electronic concentrations lower than 10^{14} cm^{-3}, plasma frequency lies in the millimeter wave length range and the most suitable laser for refractive index measurements is HCN-laser which operate on the wave length λ = 337 µm (210-221) ; recent papers mention a H_2O laser which oscillate at 119 µm (212-213). For low pressure discharges microwave interferometry is very convenient (214-216).

An extensive development of refractive index measurement with numerical examples is given by Schreiber (203).

There are numerous different experimental setups, which have been developed for the determination of the electronic concentration, based on the measurement of the refractive index (195-223). The simplest method
- the ray bending technique - is schemed on figure 4 for a cylindrical plasma column.

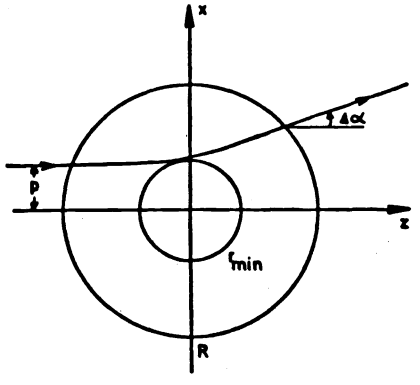


Fig. 4 - Geometry refractivity measurements : ray bending technique for a cylindrical plasma

In this case it is assumed that the electron density N_e has its maximum value in the center of the discharge and decreases monotonously towards the boundary. The plasma column acts, therefore as a cylindrical diverging lens. The measurements of $\alpha(p)$ distribution, via Abel inversion, leads to $N_e(r)$ distribution. Assuming an analytical profile $N_e(r)$ the calculations may be significantly simplified.

The holographic inferometry method - reported by Bauder (186) - while being more sophisticated offers several important avantages. This method can be used in the double pulse or real-time holographic inter-ferometry mode. In both cases, the reference beam of a classical interferometer (such as a Mach-Zehnder interferometer) is replaced by a first exposure of the holographic plate in the absence of the plasma. A second hologram is then taken on the same plate, but this time in the presence of the plasma. Since an identical optical path was used for the generation of the first hologram as well as for the surimposed hologram taken through the plasma, disturbing effects of low quality optical components and reaction chamber windows cancel. Fig. 5 illustrates a typical set-up for such holographic interferometry technique using either a pulsed laser source for double pulse holography or a continuous wave (CW) laser for real time observation of the plasma trhough the processed first hologram.

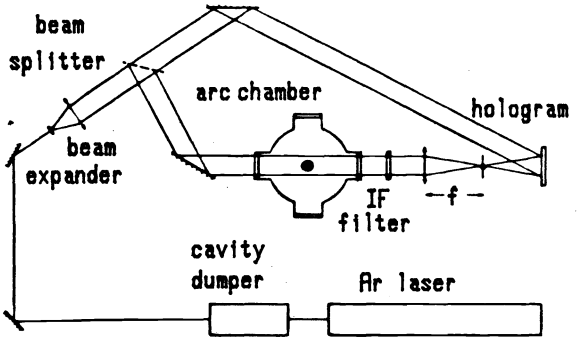


Fig. 5 - Holographic interferometry (schematic). Reprinted from Bauder (186)

In the first case, the wave fields which existed at different times for the two exposures are reconstructed simultaneously. It is thus possible to study the interference pattern resulting from this reconstruction of the two original wave fields. In the case of real-time holographic inter-ferometry, the inter-ference pattern to be investigated is generated by reconstructing the wave field of the first exposure and superimposing it on the wave field as it exists in the presence of the plasma. Numerous successful applications of this method have been reported in litterature (219-223). An interesting application of holographic interferometry to non-symetrical cold gas flow fields is described by Matulka (224).

These methods are very convenient to get a spatial picture of the electronic concentration of a non stationnary plasma even near the electrodes.

III-1-3. Thomson and Rayleigh scattering of laser light

Electromagnetic radiation is scattered by particles. Owing to the large difference between the masses of electrons and nuclei the principal contribution to the scattered light is always made by the free or bound electrons (175-225).

First we shall consider the free electrons. The intensity of the scattered light is proportional to the Thomson scattering cross section, σ_{T_e}, for an individual electron : $\sigma_T = 8\pi (e^2/m_e c^2)^2/3 \simeq 6.65\ 10^{25}\ cm^2$. Moreover not all scattered light is received by the detector, since observations are performed only in selected directions as shown on Fig. 3. In fact in order to improve the spatial resolution, as determined by the point of intersection of the incident beam and the receiver field of view, one is forced to use small angle apertures to observe the scattered light. The ratio of the scattered light actually observed to the intensity of the laser beam is typically of the order of 10^{-10} and 10^{-14}. Accordingly only radiation delivered by giant laser pulses (pulsed Ruby or Yag lasers) provides sufficient incident intensity for a measurable number of photons to be scattered by a laboratory scale plasma.

Further details of the theory of Thomson light scattering is given by Kunze (225).

In the special case of equal electrons and ion temperatures ($T_e = T_i = T$) and using lasers with a wavelength, λ_o, much shorter than the Debye length, λ_D, ($\lambda_D >> \lambda_o \leftrightarrow$ normal Thomson scattering), the frequency distribution of the light intensity is a Gaussian one, centred at frequency υ_o of the incident radiation. The width at half intensity is proportional to the temperature T at the point of observation. On the other hand when $\lambda_D >> \lambda_o$ and $T_e \neq T_i$, the frequency distribution of the scattered light is composed of three peaks, a central one

at υ_o with a width at half-intensity which is proportional to T_i and two narrow satellites, shifted by $\pm \Delta\upsilon$ whose value depends on T_e Fig. 6. The central peak has a gaussian profile and corresponds to the ion component of the scattered spectrum ; the satellites have a Lorentzian profile and represent the electron component of the scattering spectrum.

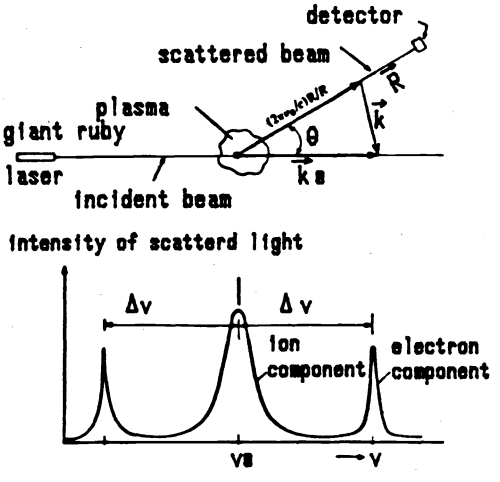


Fig. 6 - Spectral distribution of light scattered by a plasma ($\alpha >> 1, T_e = T_i$) Reprinted from (174)

Electrons in bound states also contribute to the scattering spectrum. The total cross section for coherent scattering of single particles of kind Z in the quantum state i is given by

$$\sigma_i^2 = \sigma_T \, (N_i - \Sigma_j (E_j - E_i)^2 f_{ij} / ((E_j - E_i)^2 - (h\upsilon_o)^2))$$

where N_i is the number of bound electrons in the quantum state i, $E_j - E_i$ the energy difference between i and j, and f_{ij} the absorption oscillator strength. When the wavelength of the laser light is much larger than the wavelength of the resonance transitions, one have usual Rayleigh scattering. In this case the scattering cross-section per atom is determined by the total polarizability of the atom and is proportional to the fourth power of the frequency of the incident light. Nevertheless Rayleigh cross sections, which are of the order 10^{-28} cm^2, are substantially smaller than the Thomson cross sections (about 10^3 to 10^4 times).

The experimental difficulties in such measurements should not be underestimated. In order to obtain an umperturbed scattering spectrum the stray-light intensity must be suppressed to a level of no more than a tenth of the intensity of the scattered light. This is particularly a very hard problem that conventional light traps does not solve fully (225). It should be noted that Rayleigh scattering is generally used for calibrating detection devices used in Thomson scattering experiments.

It should be underlined that these methods do not imply any equilibrium hypothesis and that the results have a good special and temporal resolution.

Thomson scattering has been used under a wide range of plasma conditions (226-232) For example Depts (229) has used it for the simultaneous recording of the local N_e and T_e profiles at many positions in a medium sized toroidal plasma. In this case, a Q-switched ruby laser oscillator/amplifier system producing a power of 200 MW within 15 ns is employed for the 90° scattering experiment. Observation of the Thomson-scattering light was made using a commercial optical multichannel analyzer consisting of a vidicon camera tube (ISIT) with scanning electronics, analog-to-digital conversion and data storage. The selection of spectral and spatial elements and the data handling system is shown in Fig 7a. The laser beam (B) passes through the discharge tube (T), containing the plasma. A 150 mm long section of the laser beam is imaged by lens L_1 through the window V_1 onto a fibre-optic image guide, F. The latter consists of a linear array of 300 fibres and receives an image of 25x0.065 mm^2 The exit face of the long bundle forms the entrance slit of a spectrometer containing a collimator lens L_2 transmission grating G and prism P to obtain a non-deviating system. The condensor lens L_3 focusses the spectral image on the ISIT detector tube. The image is scanned in successive tracks of 500 channels each (2D mode) ; the signal per channel is integrated and digitized. To reduce the amount of primary data, an accumulation register has been added to the system to allow the storage of a number of spectra with a reduced spectral resolution.

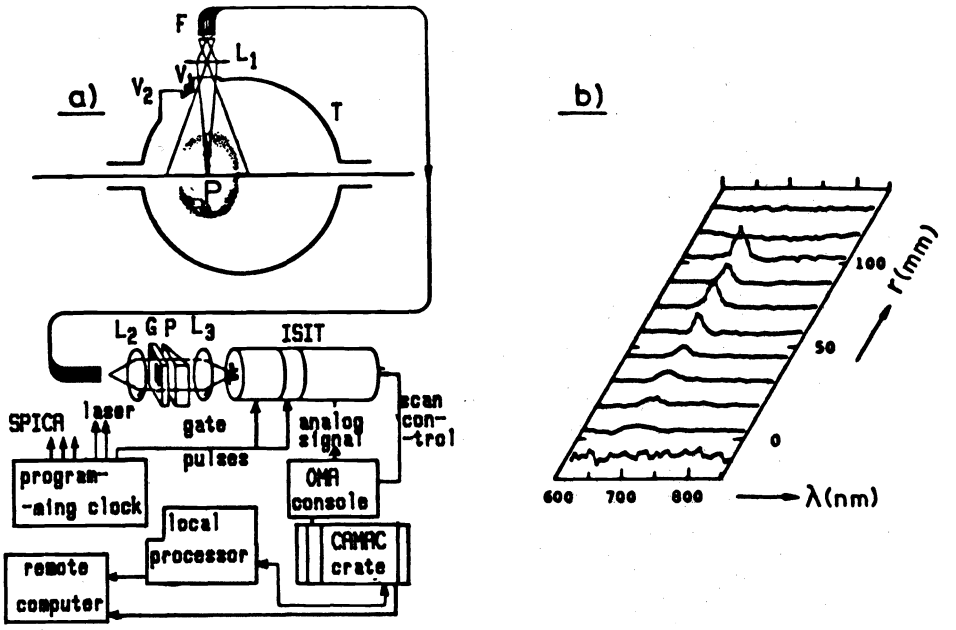


Fig. 7 - Thomson scattering : a) the SPICA detection system
b) example of spectra taken from different radii
Reprinted from (229)

Fif. 7b shows a typical example of observed spectra. The values of the temperature and the density for an individual track are finally determined by fitting a gaussian curve to the measured points. The detection limit is on the order of $N_e = 5 \times 10^{20}$ m^{-3} ; this density produces a signal of about 250 counts per track, collected typically from a scattering volume element which has the length fo 14 mm, and a diameter determined by the beam width of 1 mm.

The work of Vriens (233-234) is a good example of the use of non resonant Rayleigh scattering in low-current Ar, Ne and Xe arcs. The light source, in this case a pulsed non-Q-spoiled ruby laser, has an energy level of 0.5 J within 0.34 msec. The scattered light intensity was large enough to be discriminated from the background light of the discharge, without affecting the plasma field.

Pyanitskii et al. (235-236) pointed out the possibilities of using Rayleigh scattering of CW gas laser radiation for diagnostic purposes applied to plasmas generated by conventional D.C. plasma torch ($T_e \sim 12\ 000$ K, $N_e \sim 10^{17}$ cm^{-3}). Fig. 8 shows a the schematic diagram of the experimental setup.

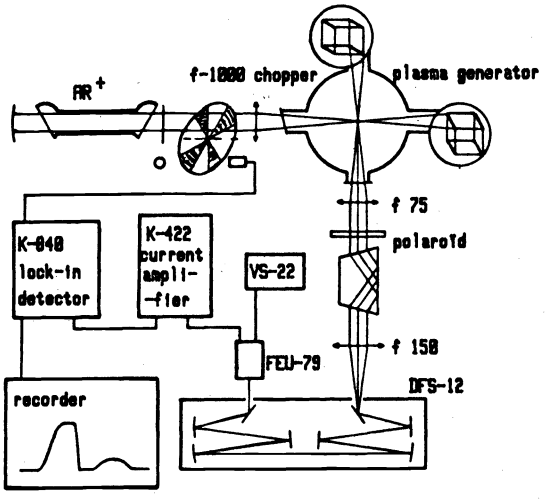


Fig. 8 - Schematic diagram of the experimental apparatus using Rayleigh scattering in a D.C. plasma jet. Reprinted from (235)

The laser beam (Argon ion laser : 1.6 watt, at λ = 514.5 mm) was modulated at a frequency of 1 kHz, at which the noise of the plasma under study was minimal. It was focused on the plasma burning in A_r or N_2 at atmospheric pressure with a current of 30 - 45 A. Radiation scattered at an angle θ = 90° by a volume located on the arc axis was collected by a lens with aperture ratio 1 : 2.8 and was directed into a double monochromator. The spectrum was measured with a photomultiplier and a lock in amplifier connected to a recorder. The intensities of the scattered emission were measured in the range 5096-5145 Å by continuous scanning at a rate of 10^{-2} Å/s, and also by stepwise coverage of this range with an $\sim$ 500 s duration of recording on one wavelength. In both cases the time constant of the lock in amplifier was τ = 100 s. The width $\delta\lambda_a$ of the instrumental slit function was 1.5 or 4.5. Å. The wide slit function was used when it was necessary to increase the signal-to-noise ratio. The measured spectra of the scattered emission were compared with the theoretically calculated spectra

III-1-4. Raman scattering

Diagnostics of hot flows by Raman scattering have spread over the last five years, essentialy under turbulent flame conditions (238). In contrast to Rayleigh scattering, Raman scattering in reserved to molecular spectroscopy only. It is an inelastic scattering technique in which the scattered signal consists of radiation that has suffered a frequency shift characteristic of the stationary energy states of the irradiated molecule. Raman spectroscopy represents a particularly powerful tool because it enables even a trace constituent to be both identified and quantified relative to the major constituants of a mixture. In this section we will give a brief review of two aspects of this promising technique : vibrational Raman scattering (VRS) and coherent anti-Stokes Raman scattering (CARS).

a) Vibrational Raman scattering. The quantitative characteristics of Raman scattering (239-241) can be explained in terms of the energy levels of a molecule, such as those shown in Fig. 9.

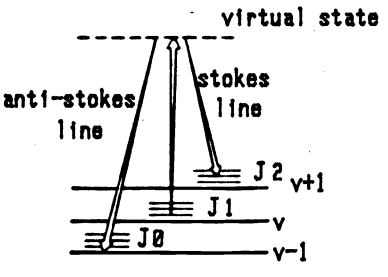


Fig.9

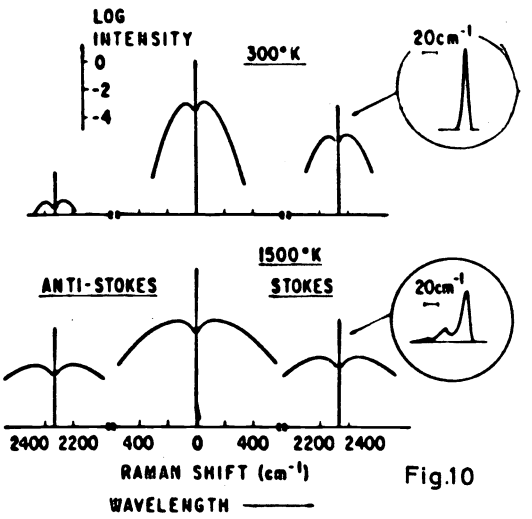


Fig.10

Fig. 9 - Schematic representation of Raman vibrational Stokes and anti Stokes scattering

Fig. 10 - Raman and Rayleigh scattering from N_2 at 300 K and 1 500 K for an exciting laser line in the mid visible. Reprinted from (239)

If a molecule gains energy during a scattering event, it goes to a higher energy level. Conservation of energy requires that the scattered light shifts to a longer wavelength λ, which is called Stokes Raman scattering. On the other hand, if the molecule loses energy, the corresponding scattered light is shifted to a shorter wavelength. This process, which can occur only with excited molecules, is called Anti-Stokes Raman scattering. Of course the number of possible lines is tightly limited by selection rules (242).

$\Delta v = 0, \pm 1$ $\quad\quad$ $\Delta J = 0, \pm 2$ for diatomic molecules

The strong central peak characteristic of vibrational Raman scattering is called Q -branch ($\Delta J = 0$) ; it is surrounded by weaker vibrational bands called the O and S branches ($\Delta J = -2$ and $\Delta J = 2$ respectively). Typical Raman and Rayleigh scattering spectra from N_2 at 300 K and 1 500 K are shown in Fig 10 for an exciting laser line in the mid visible (239) The central unshifted peak correspond to Rayleigh scattering which is flanked by vibrational Raman scattering peaks. The vibrational Q-branches on the Stokes and anti Stokes sides are shown at the characteristic Raman shifts which is equal to 2331 cm^{-1} for N_2. It should be noted that the relative intensities in Fig. 10 are drawn on a logarithmic scale and that the

frequency axis has two breaks. Fig. 11 represents the computed spectra of Stokes Q-branch of N_2 at different temperatures.

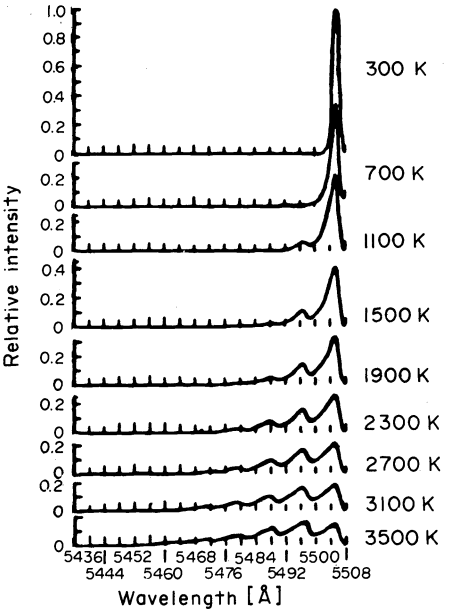


Fig. 11

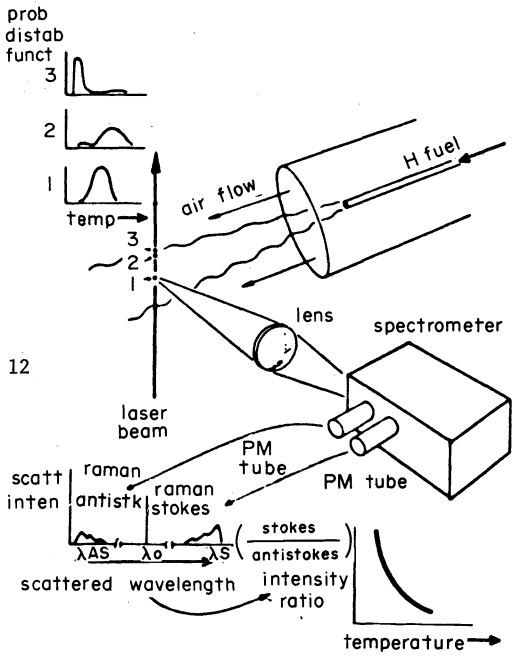


Fig. 12

Fig. 11 - Computed spectra of the Stokes Q branch for N_2 at different temperatures (laser line : argon 488 mm). At 300 K only vibrational band 0-1 occurs whereas at 1900 K 1-2 and 2-3 bands appear. Reprinted from (238)

Fig. 12 - Schematic of turbulent combustor geometry and optical data acquisition system for vibrational Raman scattering temperature measurements using Stokes/anti-Stokes intensity ratios. Also shown are the expected Raman contours by each of the photomultiplier detectors, the temperature calibration curve, and several expected pdf's of temperature at different flame radial positions. Reprinted from (239)

Density measurements can be obtained from vibrational Raman scattering observations by comparing the intensity of the observed line with that of a known reference such as ambiant air. Temperature measurements can be obtained as function of the ratio of two bands, such a Stokes and anti Stokes pair, the ratio of the fundamental band to a hot one, or from a band countour fit (243).

According to the Placzek theory, the Raman differential cross section can be calculated by a theoretical treatment of the polarizability of molecules exposed to the radiation field (244-245). Since these are extremely small : ($d\sigma/d\Omega \sim 4\ 10^{-31}$ cm^2 sr^{-1} for the $0 \rightarrow 1$ vibrational Q branch transition in N_2 gas when excited at 514.5 mm (240)),the scattered signal is quite low ; thus limiting the applicability of this technique.

Temperature measurements for turbulent flames by vibrational Raman scattering have been extensively made by Lapp (243) who obtained a high temporal resolution by use of short time duration pulsed laser. His experimental set up, composed of Stokes/anti-Stokes diagnostics, applied to a turbulent diffusion flame is shown in Fig. 12. The laser source used was a modified Phase-R flashlamp-pumped dye laser which can produce submicrosecond pulses in the mid-visible with energies of 1 J within a spectral width of $\sim$ 0.15 mm. All laser shots were monitored for laser spectral position and lineshape with a TV camera coupled to a small grating monochromator, and for laser pulse energy. Also shown in Fig. 12 is a schematic of the relationship between SAS intensity ratios and temperature, and expected forms of the probability distribution functions (pdf's) of histograms of temperature at various flame positions.

A slight different technique was used by Pealat (246) and Bai-ly (247). Their method was based upon the use of a high power (free-running ruby) laser which can provide a time history of composition and temperature fluctuations over the duration of its relatively long laser pulse (typically 0.1 to 1 msec). About 1.5 J of light energy at the ruby wavelength (694.3 mm) is required to provide a statistically signifiant measurement of major constituent densities and temperatures from a test zone of 1 mm length in flame gases at 1 500°K. These workers used a laser providing 100 kW of circulating power within the laser cavity averaged over 0.7 msec. Thus, they obtained roughly fifty distinct measurements in that short period.

Within the limits of short pulse duration, this time history can be used to provide pdf's, correlation functions over short times, and the mid to high frequency portion of the frequency spectrum of turbulence fluctuations. However, it is not easy to obtain simultaneous measurements at several spatial points (spatial multiplexing) with this technique (239).

Further details on applications of vibrational Raman scattering can be found in (248-251).

b) Coherent Anti-Stokes Raman Scattering (CARS). As pointed out earlier the major disadvantage of spontaneous vibrational Raman scattering is the extremely low level of the scattered signal. Moreover in the presence of dust or soot particles in the hot flow, they are heated up by the high power laser pulse and generate a strong blackbody radiation which can mask the Raman scattering signal if the partial pressure of the specie under study in less than 10^{-2} atm (252).

CARS is a quite new method extensively developped by Taran et al (252-255) at ONERA. This technique, very sophisticated and therefore rather expensive, has a sensity of the order of 10^{-3} mole fraction and well as greatly reduces interference from stray light and particulate matter.

CARS signal is observed when two colinear light beams of frequencies ω_1 and ω_2 ($\omega_1 > \omega_2$) traverse a medium with a Raman active vibrational mode of frequence ω_v such that $\omega_v \sim \omega_1 - \omega_2$. A new wave is generated at a frequency of $\omega_3 = 2\,\omega_1 - \omega_2$ in the forward direction fig. 13. This wave is colinear with the incident beams. It results from the inelastic scattering of the wave at ω_1 off the molecular vibrations which are being coherently driven by the waves at ω_1 and ω_2.

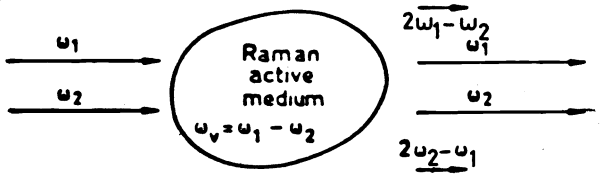


Fig. 13 - CARS and CSRS

The experimental arrangment conceived by Taran (255) is shown in figure 14. It consists essentially of a passive Q-switching ruby laser (1 MW within 8 ns) and of a dye laser. The dye beam is spatially matched to the ruby beam by means of a telescope and superposed on it by a dichroic mirror. The incident beams split by an aluminium coated wedged mirror : 80 % is focused on to the measuring volume (flame, plasma) while the reminiding 20 % is focused on to the reference cell.

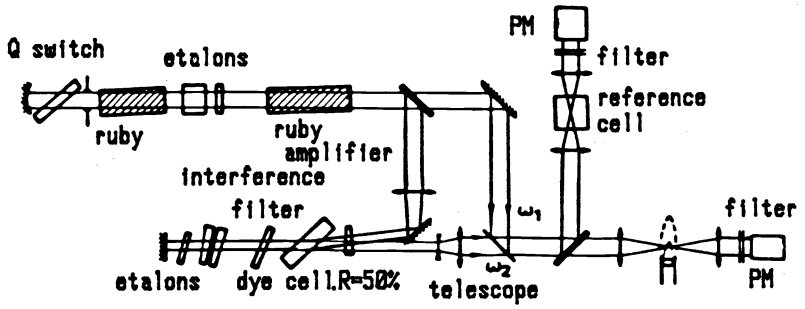


Fig. 14 - CARS experimental arrangment. Reprinted from (253).

When performing a measurement, the dye laser is tuned and scanned while the currents land P_{ref} of the photopultipliers are integrated in RC circuits and read on scope. The square root of the ratio (P/P_{ref}) is then averaged and plotted on semi-log paper. This presentation gives signals of the susceptibility of the medium under study proportional to the concentration of the probed species ; the log display has the advantage of permitting direct comparison of line shapes and giving a measure of the rotational temperature.

CARS has the following disadvantages :

-its detection limit is between 0.1 and 1 % due to the presence of the non resonant background,
- it is sensitive to lasers instabilities,
- it is subject to saturation at the higher power levels.

On the other hand, it has the advantages of being :

- insensitive to fluorescence interference
- extremely luminous (10^5 to 10^{10} more intense than normal Raman scattering).

For these reasons, CARS may be prefered to normal Raman scattering for the following measurements :

- study of reactive media (chemical synthesis in plasma...),
- analysis of media containing particulate matter (sooting flames, plasma spraying...),
- investigation of flows near solid obstacles (as close as 10 µm of the surface).

III-1-5. Resonance fluorescence

Atomic resonance fluorescence, extensively developped at the University of Florida by Winefordmer and Omenetto (256-257) is widely used for qualitative and quantitative measurements of the concentration of trace elements in flames. Presently this technique extended to molecules is finding increasing applications in plasmas either for diagnostics purpose or for the study of elementary processes.

In this section we will briefly review the analytical approach proposed by Daily (158-261) to solve the diagnostic problems in reacting turbulent flows. Like in the others laser light scattering diagnostic methods, the measuring volume is irradiated by a high power laser beam. However, in this case, the laser frequency must be exactly tuned to that of an appropriate transition frequency of the probed molecule.

If the exciting light is of intensity I_ν at the frequency of an absorption line of the molecules considered, the moleculees are excited to the higher energy level according to the following simplified two levels model :

$$N_1 + h\nu \xrightarrow{B_{12}I_\nu} N_2 \qquad (5)$$

where N_1 and N_2 are the lower and upper state concentrations respectively, B_{12} is the Einstein coefficient for absorption and $B_{12}\ I_\nu$ is the probability of excitation. The upper level is then depopulated according to equation (6)

$$N_2 \xrightarrow{A_{21}} N_1 + h\nu \qquad (6)$$

where A_{21} is the Einstein coefficient for spontaneous emission.

In using the fluorescence phenomena for diagnostic purposes, a high power dye laser beam is focused in the measuring volume and the radiation, received by the detector is measured. Because the higher excited energy levels are so sparsely populated, virtually all the reemitted radiation is due to the molecules that were originally in the lower energy level. Thus the lower level concentration can be related to the intensity of the emission signal using the corresponding rate equations. Either CW or pulsed lasers may be used although pulsed sources generally lead to a high signal to noise ratio, as previously discussed.

Unfortunately, however, spontaneous emission is not the only process for desexcitation of an excited molecule. Collisional desexcitation, or quenching, as represented by equation (7), can also occur at rates generally much faster than that of radiative desexcitation

$$M_2 + M \xrightarrow{Q} N_i + M^* \qquad (7)$$

where M is the collision partner. The superscript * indicates that M may be internally excited after the collision and the subscript i represents an intermediate level between 1 and 2 levels. From the equations (5) to (7), we can obtain that,

$$dN_1/dt = -N_1B_{12}I_\nu(t)+\left|Q_{21}+A_{21}+B_{21}I_\nu(t)\right|N_2 \qquad (8)$$

and

$$dN_2/dt = -\left|Q-A_{21}+B_{21}I_\nu(t)\right|N_2+N_1\ B_{12}I_\nu(t) \qquad (9)$$

where Q is the total quenching coefficient for N_2, and Q_{21} is the specific probability that a molecule in the level 2 will be quenched to the level 1. The difference between Q and Q_{21} can be due to collisional transitions to different energy levels or to chemical reactions.

For the sake of simplicity, if we neglect the absorption breadening, the equation of radiative transfer may be written as follows

$$I(t) = h\ \nu_{12}\ N_2(t)\ \frac{A_{21}}{4\pi}\ L + I_o \qquad (10)$$

where I(t) is the total intensity, L is the length of the measuring volume and I_o the intensity due to the unirradiated plasma.

After the exciting radiation source has been shut off, I(t) decays exponentially

$$I(t)/I(t=o^+) = \exp\ (-(Q + A_{21})t) \qquad (11)$$

where $t = o^+$ represents the time immediately following the shutoff of the pulse. The time constant of the decay process ; which can be measured with Boxcar or Waveform Digitizer, gives the quenching coefficient (262).

With an exciting light pulse of sufficient intensity and duration, saturated excitation condition may be reached (263). In this case the integral of the decay curve as represented by equation (12) yields the required number density of the species in the lower energy level :

$$N_{10}=(1+g_1/g_2)((Q+A_{21})/A_{21})(4\pi/h\nu_{12})\int_{o^+}^{\infty} I(t)dt \qquad (12)$$

and g_1 and g_2 are statistical weights of the lower and upper levels respectively.

Dayly (263) has shown that this method, may be about 10^5 more sensitive than Raman Scattering.

Typical applications of resonance fluorescence have been reported by Stepouski (264) and Betchel (265) who used it to measure OH local concentration in turbulent flames.

Atomic resonance fluorescence may also be used for temperature measurement (256, 269-272), with a good precision between 600 and 3 000 K in the presence of appropriate elements such as In, Tl. Moreover a method, based upon laser saturated fluorescence described by She et al (274) allow the measurement of the velocity of individual atoms. In this experiment, shown in Fig. 15, the radiation beam generated by a tunable dye laser is split into two parallel beams separated by a distance, d. These are directed into the gas stream. The concentration of probed atoms must be such that no more than one resonant atom, on the average, are present within the viewing region. As one resonant atom moves across the parallel beams, it generates two light bursts separated by the atoms time of flight from one beam to the other, to as the bursts of fluorescence are analysed by a photon correlator, the gas velocity can be obtained according to v = d/to.

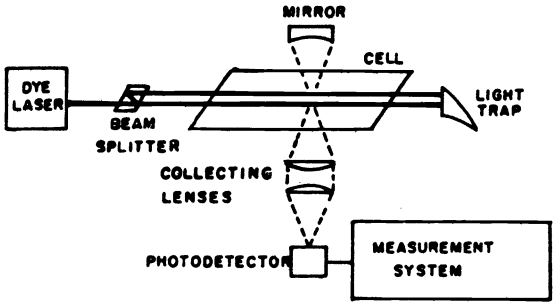


Fig. 15 - Experimental set up for measuring the velocities of individual atoms. Reprinted from (256).

Further details about resonance fluorescence applied to analytical spectroscopy may be found in (256) and (266-273).

III-1-6. Plasma gas velocity measurements

Most of the methods decribed suppose that the plasma is in local thermodynamic equilibrium.

The only method that does not disturb the plasma is the spectroscopic measurement of the Döppler of the lines (276). Unfortunately, this shift becomes sensible (more than a few hundreth of Angström) only for very high velocities (more than 2 000 m/s). Moreover it is usually necessary to take into account the radial gradients performing an Abel inversion and the other possible shifts due to the plasma (collisions, microfields...) (176).

A rather simple method consist in measuring the dynamic pressure of the gas with a probe. But, in that case, one has to know the plasma temperature and the probe disturbs the plasma flow (at least it must be precisely profiled) (277, 278). Also if the measurements give rather coherent results with monoatomic gases like argon or helium for temperature smaller than 10 000 K, the recombination of atoms on the probe wall modifies completely the equilibrium with diatomic gases as N_2 or H_2 and so the temperature and the results are not reliable.

Another technique consists of the observation of a small electric perturbation superimposed on the discharge either through the electrodes or with auxiliary electrodes (279-280). However to detect such a signal in a highly luminous plasma requires an important energy pulse to be supplied to the discharge (a few hundreth of Joules), which could perturbates the plasma and the measurements have to te extrapolated to the zero energy. Further the diffusion of the signal in the turbulent diatomic gases plasmas leads to the impossibility of using such methods under such conditions.

The fourth technique which is getting increasing acceptance is Laser Doppler Anemometry which uses very small particles injected in the plasma as tracer particles. The particle velocity, supposed to be the same as that of the gas is then measured by L.D.A. This method will be further discussed in the next section. Fluorescence laser technique can also be used in the absence of tracer particles as indicated previously (see and of § III-1-5).

III-2. Measurements on solid particles in a plasma

As we have already mentioned, the treatment of solid particles is, in most cases, done in thermal plasmas and one assumes LTE. The plasma being characterized by very important gradients of temperature and velocity, a ponctual measurement is necessary. The size of the particles being usually smaller than 100 µm, the number of particles passing at a given point of the plasma is very important (easily more than 1 000/s). Due to the plasma gradients and the particle size distribution, the particles velocities and temperatures will also be very different. It is then only possible to make a statistical treatment of the signals obtained. The quantities that have to be measured are, the velocity and the diameter of the particles (they can be evaporated very quickly), the luminous flux emitted by the particles themself. From this flux, knowing the diameter, the velocity and the emissivity of

the particles it then possible to deduce their surface temperature. Except for the luminous flux emitted by particles themself, the most reliable measurements are performed through laser ligth scattered by the particles. The power of the laser must be important for different reasons : the scattered light intensity varies with the laser beam power, the diameter of the particle and with the observation angle (281). For example for small particles (< 5µm), in a normal direction to the laser beam, the intensity of the scattered light, depending of the nature of the particle, might be 10^{-3} smaller than that for 50 µm particles. Further-more since the plasma radiation is important, specially in jet core, with the use of very narrow band filters (< 3 Å) to remove most of the radiation of the plasma, the scattered light intensity has to be important compared to the plasma signal, thus improving the signal/noise ratio of the measurement. That is why lasers with powers up to 5 W are often used for confortable measurements. On the other hand, the laser power should not be too high either to disturb the plasma.

III-2-1. Particles flux

The population of the particles in a plasma may be measured very simply, counting, during a given time, the pulses resulting of the light scatterd by the particles passing through a laser beam (for example an Ar^+ laser). With the powder flow rates used in plasma devices, either for spraying, spheroïdization, vaporization and chemical treatment, compared to the plasma flow rate, the particle density is very low. For example in plasma spraying with a particle flow rate of 2 kg/h and a gas flow rate of 80 Nl/mn with Cr_2O_3,40 µm particle, the density is 1200 cm^{-3} and the probability to have simultanously two particles in cylindrical laser beam of 100 µm diameter normal to the plasma jet axis is smaller than 0,01. Then using a laser of 100 µm diameter and detecting the scattered light at 90° with a diaphragm of 100 µm, a ponctual measurement can be achieved and for example Fig. 16 shows the distribution of alumina particles with a mean diameter of 18 µm injected in a nitrogen d.c. plasma jet.

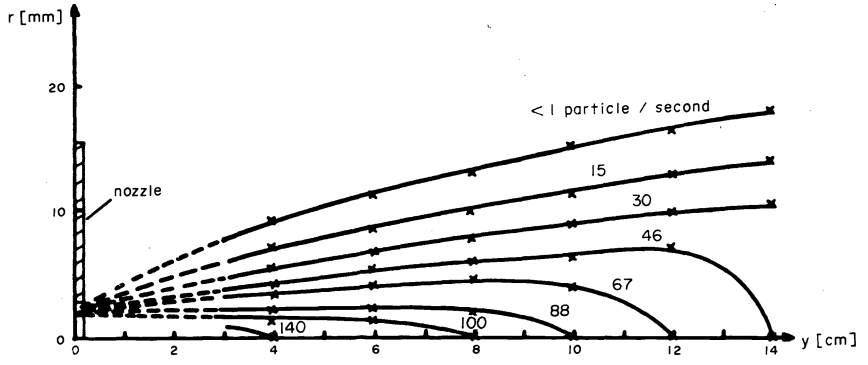


Fig. 16 - Alumina particles (ϕ 18.5 µm) isoflux curves in a DC plasma torch (290 A ; 100 V ; p = 72 %, N_2 : 37 Nl/mn ; H_2 : 11 Nl/mn

III-2-2. Particles velocity

a) Mechanical methods. The flow of particles is momemtarily stopped with a barrier, and then one observes the rate of the flow of particles downstream. With this technique a mean velocity is obtained in a plane orthogonal to the flow direction. With this technique it is possible to measure velocities between 50 and 200 m/s (282) but the plasma is strongly disturbed. It is also possible to improve a little bit this type of measurements when using two or more disks rotating at different speeds, a hole in each disk selecting the particles with a given velocity range.

b) Optical methods. The have been, up to day, the most often used. An image of the jet is photographically recorded either with rotating miror (283-284) or an ultra rapid camera (285). Velocities up to 750 m/s have been measured by this technique. Unfortunately, due to the high velocity gradients of the plasma and due to the size distribution of the particles, the velocity of the different particles observed on the same picture may vary from 1 to 20 and it is very difficult to determine a mean velocity from the over-lapping slopes of the trajectories.

One can also use optical detection of the particles connected to an electromic system for data treatment. This is for example the case of the "plasmascope" developped by Gold (286), which makes an analysis in space and time of the luminous perturbation of particles flowing in the plasma. Laser Doppler Anemometry is also an example of such methods.

c) Laser Doppler Anenometry. Since the first work of Yen et al (287) in liquids, numerous investigations have been made mostly in gases (286-188) and more recently in plasmas (289-293). The problems encountered in plasmas are the important background radiation of the plasma, the high velocity and temperature gradients. The latter necessitates a high spatial resolution and so a very narrow fringe spacing leading to a high frequency signal (the frequency is pro-

portional to the ratio of the particle velocity, in the direction normal to the fringes, to the fringe spacing in the interferential arrangement commonly used see Fig. 17. One has to mention also the problems of the electromagnetic saturation of the electronic devices (H.F. torches) or the electrical interference from large current arcs.

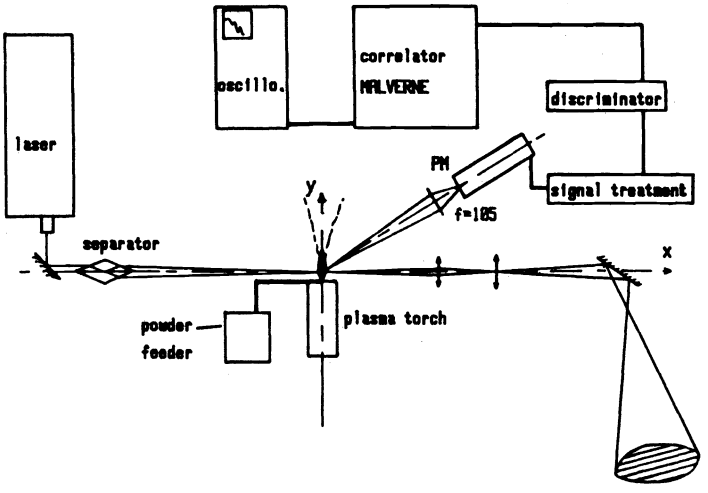


Fig. 17 - L.D.A. experimental set up. Reprinted from (275)

In the interferential arrangement commonly used, the laser beam is splitted into two beams of equal intensity Fig. 17 and a minimum number of fringes must be taken for a correct measurement (more than 6). But one has to find a compromise between a small measurement volume (ponctual measurement) and the fringe spacing that leads rapidly to very high frequencies with high velocity particles (with 150 µm fringe spacing and 300 m/s particles velocity : F = 60 MHz).

The signal may be analysed with three different techniques : frequency measurement, period measurement or photon correlator. The first system, in spite of some automatic devices (294-295), is not well suited for turbulents fluids, for particles with a wide velocity range or for low seeded gas. The counters that measure the time necessary for a particle to traval a certain distance (n fringes) is very well suited for plasmas (its velocity range is between 1 and 1000 m/s) specially if it is coupled with a microprocessor (295-296) performing a complete statistical data analysis giving the minimum and maximum velocities, the standard deviation as well as the probability distribution function. The photon correlator first used in plasmas by Vardelle (275) allows to extract signals with very low signal to noise ratio (almost one) making it possible to perform measurements even in the core of the plasma jet with very small particles (< 5 µm). Fig. 18 shows typical radial and axial velocity profiles for 18 µm diameter alumina particles injected in a d.c. argon-nitrogen-hydrogen plasma jet. The measured values dispersion is low on the torch axis (< 7%) but increases with the distance from the axis of the plasma (20% at r = 9 mn).

When the frequency of the LDA signal is too high for the electronic devices used, one can use the "method of focusing in two points". This method consists of splitting the laser beam into two beams that are then focused in two points separated by a small distance apart : 0,2 to 1 mn as represented on Fig. 19 (275). As the particle cross each of these two points, a small luminous pulse is emitted, and the time between two succesive pulses is used to calculate the particle velocity. However this technique needs a powerful laser and some precautions must be taken (275).

As we have already mentioned when the size of the particles is very small (< 5 µm), the equations of motion (297-298-83-85) show that the particles follows the fluid velocity and it can be used to measure the plasma velocity. However an important parameter to consider is the particles acceleration to reach the fluid velocity, acceleration which is a function of the plasma viscosity. For example at 8000 K with an hydrogen gas velocity of 1000 m/s and an argon gas velocity of 600 m/s the acceleration of a 20 µm diameter particle is 5 times greater in argon. At least one has to avoid the important effect of the kinetic energy of the particles on their trajectories (85-275) specially in arcs and to use for example the solution of Boulos (293) who seeded the plasma with alumina particles smaller than 5 µm diameter (elutriated from a fluidized bed) through the arc at a very small mass flow rate to avoid disturbing it.

III-2-3. Particles temperature

In principle, the intensity fo the radiant energy flux emitted from the surface of the particle is function of its temperature. When the particle velocity is relatively low (less than a few m/s) it is then possible to use the method proposed by Bonet (299) to measure

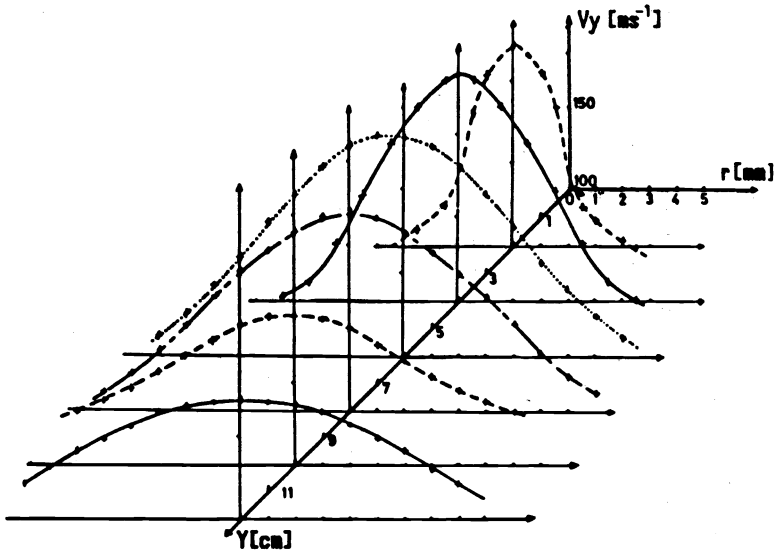


Fig. 18 - Radial alumina particle (ϕ 18.5 µm) velocity distribution along the jet axis of (D.C.) plasma torch (290 A ; 100 V p = 72 % ; N_2 : 11 Nl/mn) Reprinted form (275)

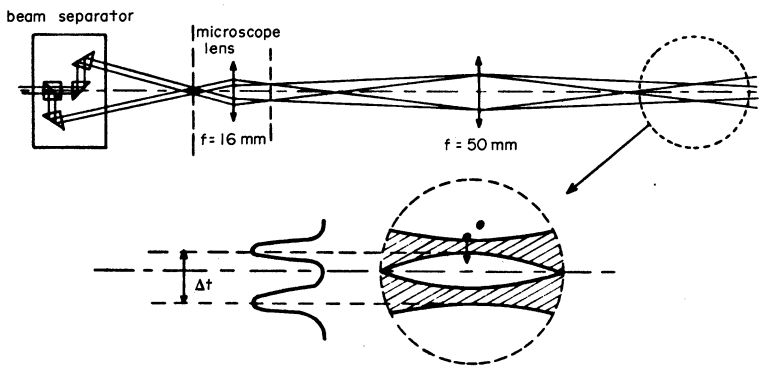


Fig. 19 - Particles velocity measurement : schematic of the method of focusing a laser team in two points. Reprinted from (275)

its temperature : a mochromatic photograph of the moving particles is recorded through a pyrometer which gives the reference radiation.

Lesinski (300) has developped a similar method by using a photomultiplier in place of the camera, the reference radiation being given by a hole travelling rapidly in front of a reference tungsten ribbon lamp. The particle surface temperature is obtained by measuring its surface emissivity.

The statistical treatment of the received signals first done by Lesinski, has been improved by Vardelle (275). The sampling volume Fig. 20 is imaged by two lenses on to a pine-hole put in front of an RCA 31034 C cooled phtomultiplier equipped with a band-pass filter (0,7 µm<λ<1,05 µm). The sampling volume is approximatively a cylinder of 150 µm diameter with its axis perpendicular to the plasma jet axis. The amplitude of current pulses generated by the particles crossing the sampling volume is a functio of particles size and shape, surface temperature, material emissivity and detection system arrangement. These signals are amplified, shaped and analysed by a multichannel analyser wich provides the histogram of pulses amplitude distribution Fig. 20. A previous calibration needed to know the pulse amplitude versus surface temperature, is performed by simulation of particles of known diameter, velocity and temperature Fig. 21 : the tungsten ribbon lamp and the pin-hole simulate the particle while the chopper simultates its velocity.

An histogram of pulses amplitude distribution is shown of Fig. 21 a. Taking into account the difference between the tungsten and alumina emissivities, the surface temperature histogram, plotted on Fig. 21 b, is obtained. Some plasma jet areas at different temperatures are included in the sampling volume, so the histogram is relatively dispersed. The most probable temperature is taken as the representative temperature T_s of the particles at the measured point.

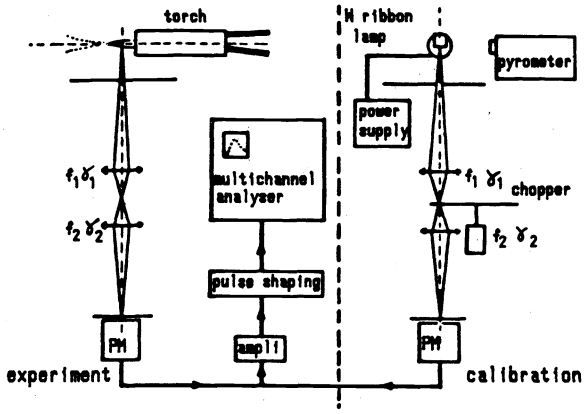


Fig. 20 - Experimental set up for surface temperature measurement. Reprinted from (275)

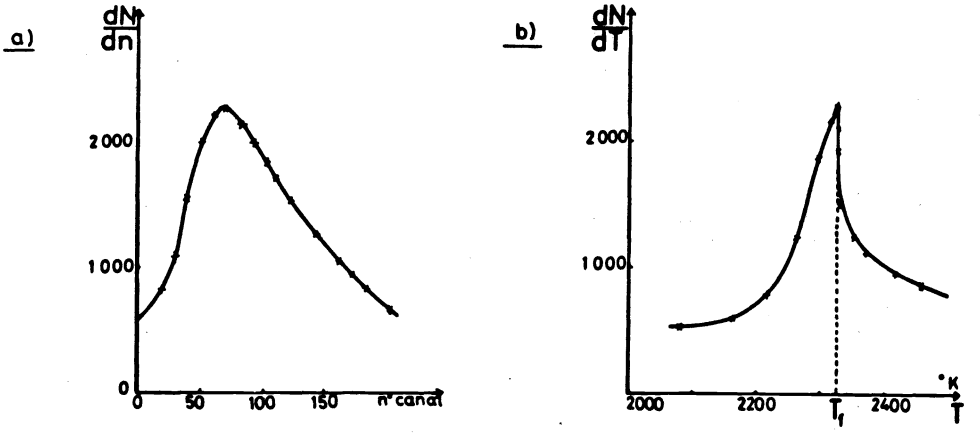


Fig. 21 - Alumina particles (ϕ 18.5 µm) surface temperature histogram. Reprinted from (275)

This dispersion is partially due to the fact that the signal obtained comes from the particles passing at any point of the plasma jet along the measurement cylinder, thus having encountered very different thermal conditions. A typical evolution of the particles temperature along the axis of a d.c. plasma jet is represented on Fig. 22.

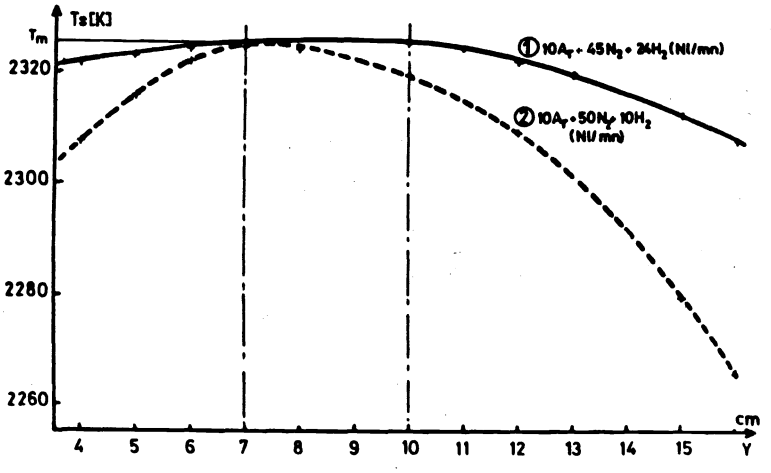


Fig. 22 - Alumina particles (ϕ 18.5 µm) surface temperature distribution along the jet axis of a DC plasma torch (290 A ; 100 V ; p = 72 % ; N_2 : 37 Nl/mn ; H_2 : 11 Nl/mn). Reprinted from (275)

To avoid this problem of dispersion a device is now studied at the Thermodynamic Laboratory of the University of Limoges, where the signals coming from the I.R.P.M. will be stored only when the particle will pass at a given point of the cylinder controlled by a P.M. imaging at 90° of the measurement cylinder.

III-2-4. Particle size measurements

The measurement of the particle size distribution in a two phase flow is of great importance for coal gazification, M.H.D. and plasma spraying and spheroïdization. The particle characteristics such as their mean diameter, size distribution, mass loading... may very widely in such systems where the size distribution range is usually between 0.5 and 150 µm.

The classical measurement technique (301) requiresthe extraction of a sample volume, thus perturbating the flow and giving the results with a rather long time after the sampling. That is why optical measurements giving continuous and rapid readout are much more preferable. Moreover, when using lasers, they are adaptable to high temperature systems in spite of their important background radiation.

The optical techniques are all derived of the Mie scattering theory (302) and they can be roughly classified into imaging and non imaging techniques.

Non imaging techniques have been recently reviewed by Holve and Self (303-304). These techniques can be subdivised into two classes : those which deals with a large number of particles simultanously and those which count and size individual particles one at a time. The former type includes the transmissometer which measures the attenuation of a light beam and yields a value for the integrated projected area of the particles in the beam (305). Others techniques have been described which measure the angular distribution of the light scattered from a large number of particles simultanously present in a small measurement volume. A new interferometric approach for the in situ particle counting sizing has been suggested by Farmer (306) using the shape of the signals of the scattered light of single particles passing through the fringes in the cross over volume of a dual beam laser anemometer (307). For M.H.D. diagnostic purpose, Holve et al (304) have set up a particle sizing counter which uses near forwardscatter light from a focused He-Ne laser beam, together with pulses-height analysis of the signals from individual particles. This instrument, which has the capability of truly in situ measurements with a working space of 50 cm between optical elements, allows to determine the size distribution in the 1-30 µm diameter range at concentrations up to 10^5 cm^{-3} in gas flows with temperatures up to 1600 K (304-305-308).

Imaging techniques include flash photography and holography (309). Holography is the only existing by which high resolution images of individual particles in a dynamic particle field array can be produced. It has been applied to the study of several type of conbustion by different investigators. One of the main problems to be solved is the loss of resolution due to the imaging through the turbid medium normally associated with combustion. Whereas a resolution of 1.5 µm would be appropriate to examine particles smaller than 50 µm, the presence of large temperature gradients surrounding a burning coal particle, requires a much higher interferometric sensitivity. Trolinger (310) has designed a holocamera shown in Fig. 23 to examine basic combustion phenomena in coal particles.

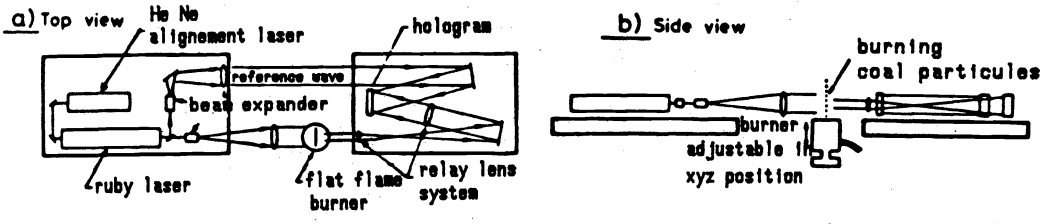


Fig. 23 - Holocamera for particle sizing : a) top view
b) side view

The required high resolution was achieved by magnifying, with high quality lenses, before recording by using near image plane holography to further relax hologram requirements and by precisely aligning the hologram during reconstruction. Thus a resolution, down to about 3 µm, has been attained at a working distance of 20 cm thus allowing observations of basic combustion events to be made with coal for the first time.

IV - EXAMPLES

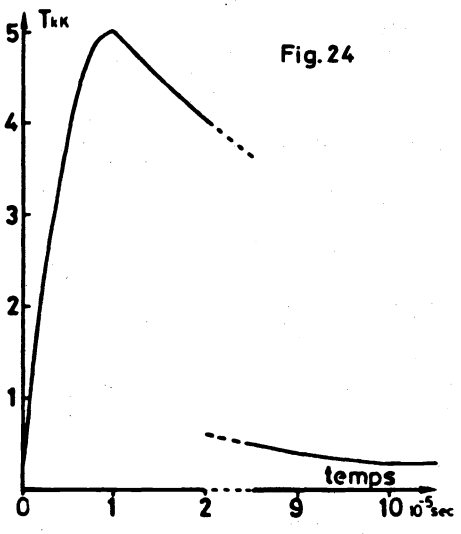
In this section we will try, through a few examples, to show what progresses in measurement techniques and modeling have been achieved and also what remains to be done.

IV-1. Nitric oxyde synthesis in d.c. plasma jets

Among the results presented at Limoges (135-141-61) we will discuss of the ones obtained with a D.C. plasma arc that seems to be best suited for an industrial application due to the investments cost and the attractive specific power consumption. In a 30 kW D.C. plasma generator (139) the plasma gas composed of a mixture of N_2 and O_2, is introduced into the

torch while cold oxygen in injected down-stream the arc at the nozzle level. This contributes to the quenching of the products which is completed by removing the gas through a water cooled probe. At the exit of the torch the specific enthalpy of the gas is between 2 and 8 kWh/kg and the velocity at the nozzle exit, measured without oxygen injection, is between 500 and 1 000 m/s. The specific energy consumption was less than 25 kWh/kg and the nitrogen conversion to NO was high as 11 % (molar).

The fact that the obtained conversion is larger than the equilibrium composition (6.5 % obtainable for an equimolar mixture) indicates that reaction kinetics could have an important influence on the overall conversion. Most of the models, starting from an equilibrium situation and taking into account the quenching only, leads to a nitrogen conversion smaller than 9 % (311-323). However when one considers the measured gas velocity, in our generator, assuming the plasma to be homogenous with a mean enthalpy temperature of 5 000 K, a simple calculation gives a residence time of the gas in the heating area smaller than 10^{-4}s. Using the relations given by Polak (318) the time necessary for NO to be in equilibrium in greater and it is then not possible to start the calculations from the equilibrium conditions. That is why in the model developped in Limoges (324) we have introduced a temperature evolution for heating and quenching on Fig. 24. The results obtained shows that the reaction $O_2 + N_2 = 2\ NO$, usually neglected in the others models, is responsible for the NO production at the beginning and that the NO production rate is maximum between 8 and 12 µs Fig. 25.



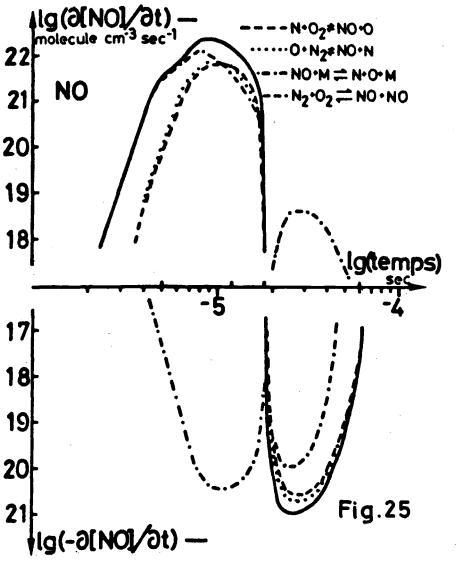


Fig. 24 - Evolution of the mean temperature of a nitrogen flow : (first heated in the arc region of a DC plasma torch and then cooled by cold oxygen injection in the nozzle of the torch), Reprinted from (139)

Fig. 25 - Evolution of the NO rate production as a function of time with a DC plasma torch. Reprinted from (139)

This simplified model allows to understand the experimental conversion rate obtained. Of course it might also be necessary to take into account the diffusion phenomena and the plasma temperature gradients specially with the possible reactions with excited species such as N (^{2}D), N_2 (A $^3\Sigma$) and ions O^+, N_2^+, NO^+, O^-. However to understand better the role (probably important) of the different species, measurements of the N_2(A), NO^*(C,A,B) and NO^V must be performed by laser fluorescence (with a pulsed ruby laser coupled with a dye laser) and the results coupled with the classical spectroscopic measurements (325) will allow us to develop our model.

From on industrial point of view, we will consider the process proposed by Vurzel and Polak (318) Fig. 26. The O_2-N_2 mixture admitted in (1) is compressed and admitted in an heat exchanger. Heated at a temperature T_1 the gas enters the d.c. plasma generator at point (3). Leaving the nozzle, the plasma at a temperature T_2 is rapidly cooled to T_3 with the recycled gases. The gas at T_3 is then used to preheat the plasma gas in (2) and then to heat water vapour. The important point elucidated by our kinetic calculations is that is not necessary to cool the gases under 2 000 K to achieve a good conversion rate.

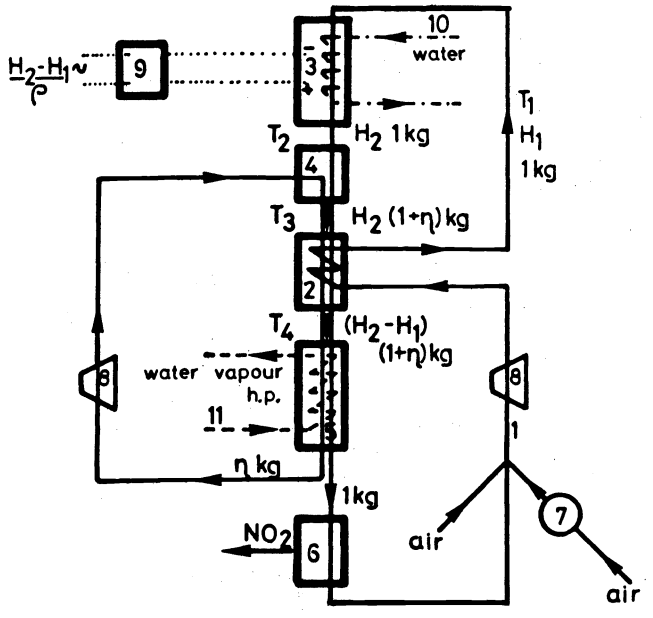


Fig. 26 - Nitric oxide production process
2 : high temperature heat exchanger
3 : plasma generator
4 : quenching device with recycled cold gas
5 : high pressure vapor generator
6 : NO_2 extraction device
7 : oxyton 8 : compressor, 9 : d.c. source
10 : cooling circuit of the plasma generator
11 : high pressure water vapour circuit
Drawn from a suggestion of Polak (328)

Then, with T_1 = 1 800 K, T_2 > 3 500 K, T_3 ∿ 2 000 K and 8 % of NO_2 obtained in the plasma, the specific energy consumption of the process is less than 7 kWh/kg of NO. Of course this calculation does not take into account the energy consumption of the compressors, of the cooling circuits and of the oxytone, but when comparing with classical process this must be less than 5 kWh/kg. At least in this conditions a 10 MW unit would produce about 1.3 t on of HNO_3 per hour. To be accepted in industry this specific energy consumption should be reduced by about 50 %. This could be done by reducing the energy consumption and increasing nitrogen conversion. The first experiments done have shown that a pressure increase (up to 10 atm) is favorable. Further Cavadias (326), in a HF N_2-O_2 plasma with a WO_3 deposit on the wall, has shown that, in its experimental conditions (10 T < p < 40 T), an heterogenous catalytic effect, ascribed to a nitrogen chimiesorption, allows to double the nitrogen conversion to NO.

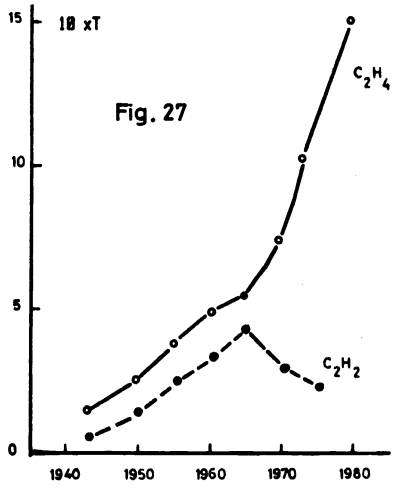
IV-2. Acetylene production in plasma

As already mentioned the acetylene production was one of the important application of plasma chemistry in the sixties. In the Huels (131), Hoechts (132) or Dupont de Nemours (133) 8 to 10 MW plasma furnaces either A.C. or D.C., hydrocarbons were injected in hydrogen plasmas, the quenching of the products being done by hydrocarbons and/or water. The specific energy consumption ranged between 6 and 10 kWh/kg of $C_2H_2$with concentration of C_2H_2 between 14 an 18 % by weight and concentration of C_2H_4 between 3 an 7 %. Unfortunately due to the low cost of oil at that time the process was abandoned at the end of the sixties and replaced by the production of ethylene by oil vapocraking. Ethylene then replaced acetylene for most of the chemical processes as shown on Fig. 27 representing the evolution of ethylene and acetylene production in the States.

However if in the U.S. the organic products are obtained at 97.5 % from ethylene and at 2.5 % from acetylene a few of then, corresponding to 18 % of the ethylene uses are more easily obtained from acetylene like C.V., vinyl acetate and acetaldehyde (328). In this conditions it is reasonnable to think that a plasma process using coal to produce acetylene could be of future interest.

Such a process has been studied by AVCO. Using a D.C. arc stabilized with hydrogen Fig. 28, coal particles are injected downstream the cathode, and before the anode, the mixing with the plasma gas being improved by a magnetic rotation of the arc.

The quenching is done by gas injection or coal powder. With such a device the specific energy consumption is 8.8 kWh/kg with a concentration of 15.5 % of C_2H_2. Taking into account some interesting products as HCN obtained by nitrogen injection to destroy



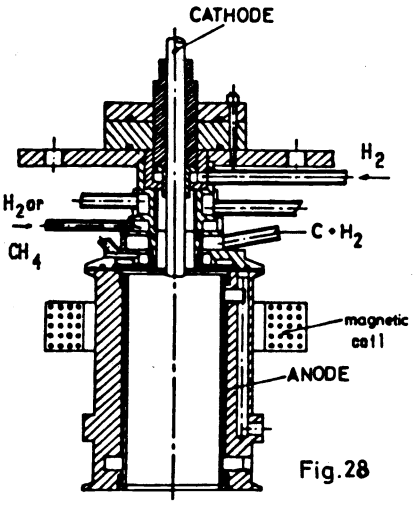


Fig. 27 - C_2H_2 and C_2H_4 evolution of the production in the U.S.E. Reprinted form (328)

Fig. 28 - AVCO plasma furnace

the coatings of free carbon, the cost of the process was evaluated by AVCO between 5.76 c/lb and 7.55 c/lb depending of the use of naphta for the quenching. Even if, in the actual oil situation, such a process seems to be industrially competitive some improvments could be done specially for the coal injection, the plasma gas and the catalysis.

For example the work of Rapakoulias and Amouroux (328) has shown, for the production of HCN and C_2H_2 in a HF plasma of N_2 and CH_4, the role of the vibrational and rotational excitations and of the different excited states as $N_2(A^3\Sigma)$ and $N_2(C^3\Pi)$. But maybe the most important point emphasized in this work is the heterogenous catalysis (chimiesorption of $N_2(A)$ states) showing that with a molybdenum grating in the reaction zone it is possible to increase the HCN formation by as much as 50 %. Of course all this results should be completed to take into account the role of the atoms and of the radicals formed (the laser fluorescence experiments could give very interesting results) and also to understand better the catalytic phenomena, but anyhow they are yet very promising and they could make the results even more industrially competitive.

IV-3. Plasma spraying

The formation of protective coatings by spraying a stream of molten metal or ceramic particles was first developed using combustion flames into which the spray material was fed as a powder, wire or rod. In the sixties, commercial plasma spraying equipment became available. These were composed of a d.c. plasma jet used to melt a powder and project the droplets at high velocity against the substrate to be coated. Now plasma spraying is widely used and generally better understood. It is not our intention here to describe all the materials that can be sprayed and the different problems encountered (see for example recently published reviews (112-113) but just emphasize some points. The properties required of plasma sprayed coatings may vary considerably depending upon the applications : low porosity for wear resistance and corrosion protection, porous deposit for thermal barrier... Anyhow the physical properties of a given material depend largely upon spraying conditions. The deposit consists of successive layers of material built up by the impact of molten droplets, projected at high velocity, which flatten against the substrate. From the theoretical treatment of this by Madejski (329-330) and assuming that the liquid droplet flattens before solidification occurs, we have for the ratio of the diameter of the flattened disc (D) to diameter of the initial drop (d) :

$$D/d = 1.29\left(\frac{\rho . v . d}{\mu}\right)^{0.2}$$

where ρ = liquid density, μ = liquid viscosity, v = droplet impact velocity. This formula underline the necessity to get molten droplets with high velocity to cover well the substrate. For example with molten alumina particles in the velocity range 100-400 m/s one gets D/d = 3-6 in reasonable agreement with the experimental results. For a given coating material, the porosity is related to the particle velocity and temperature. The role of velocity was demonstrated at Limoges (275) experiments in which γ particles with narrow size distribution (18 ± 4 µm) were sprayed using a N_2-H_2 D.C. plasma jet. A porosity of 23 % was observed at a 75 mm torch target distance but this was reduced to 11 % at 50 mm, distance which was found to correspond to the maximum particle velocity on the axis of the jet. The effect of the velocity is also shown by the radial variation of porosity in a deposit sprayed on to a fixed

target. The particle velocity is 150 m/s greater on the axis of the jet than at the periphery Fig. 29 and the porosity of the deposit was observed to range from 10 % on the axis of the jet to 22 % at 15 mm radius.

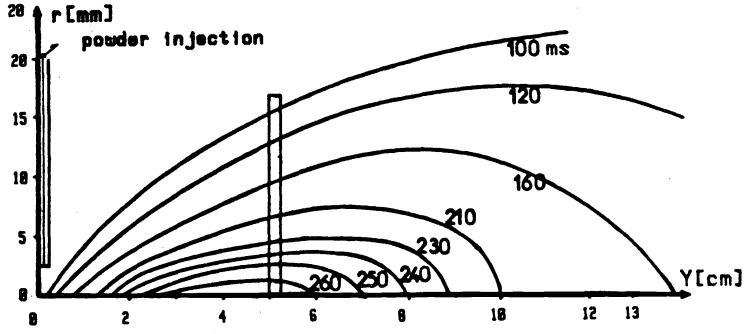


Fig. 29 - Alumina particles velocity field in a DC plasma jet (290 A ; 100 V ; ρ = 72 % ; N_2 = 37 Nl/mn ; H_2 : 11 Nl/mn). Reprinted from (275)

When one considers the important temperatures and velocity gradients in D.C. plasma jets and also the granulometry range of the powders it is clear that the velocities and temperatures of the particles will be very different. The important macroscopic parameters are very numerous, type of plasma gas, flow rate, arc current intensity and voltage, nozzle dimensions, particle injector position and inclination, carrier gas flow rate, target distance from the nozzle, position and gas flow rate of a compressed air barrier blast normally to the plasma jet to eliminate the particles that did not enter the plasma (331)... Then it is almost impossible to determine the optimal values of this parameters (even with statistical planned experiments). The only way to do it is to control this parameters with the statistical measurement of the velocities and temperatures of the particles. For example these measurements shows that for a given Al_2O_3 particle granulometry range, a given flow rate of the plasma gas (N_2-H_2 70 Nl/mn) and a given electrical power (30 kW) the injected particles should have velocities between 20 and 24 m/s. With smaller velocities the particles do not enter in the plasma jet and for greater they just cross it. Accordingly it was possible to determine the optimal macroscopic parameters required to obtain Cr_2O_3 sprayed deposits of less than 2 % porosity.

The temperature and the velocity particles measurements allows also a better control of the cooling rate of the particles (greater than 10^7 K/s) and thus of the cristalline structure of them (control of the γ or α phase of alumine particles)... At least, on a more theoretical point of view, this measurements will allow the experimental determination of mass and heat transfer coefficients between plasma and particles.

IV-4. Extractive metallurgy

A special attention has been given to the application of thermal plasmas to extractive metallurgy. In this case the interaction of the plasma gas, with its highly excited species, with the molten metal bath can completely modifies the equilibrium concentrations obtained with the classical furnaces. It is then possible, for example, to saturate steel with a high concentration of nitrogen and still have a rather uniform distribution of the nitride phase in the ingot which would be unattainable by others methods (12). It is also possible, by controlling the pressure in the alloying process, to avoid the losses of highly volatile components (Mm, Mg...) which take place in the classical processes (vacuum arcs, electron beam remelting...). The remelting of alloys in plasma furnaces such as those developed at the Baikov Institute of Metallurgy is Moscow (12), by the Ulvac in Japan (126), of the Linde type in USSR and GRD, by the Daido Steel in Japan (332) or by Electrotherm in Belgium (127), allows the refining of various metals, including heat resistant alloys, high temperature metals, ball bearing steels, high tensils special steels... (12-154). The use of reducing gases like hydrogen, ammonia, natural gas... allows melting with a deep deoxidation. In this type of remelting furnaces the specific energy consumption can vary between 0.6 to 6 kWh/kg. However an important cost item in this process is due to the gas used for the pilot plasma generator which is argon or helium. Fortunately the gas consumption seems to be independant of the charge and of the furnace power.

The reduction of oxides and ammonium salts of tungsten and molybdenum, of chlorides of tungsten, molybdenum, titanium, zirconium has been investigated in arc and HF plasma furnaces at the Baikov Institute of Moscow. Studies on the reduction of silicium chloride are performed in the U.S. (Westinghouse) or in France (ENSP, Limoges). With the gases the reactions rates are so high that the reaction is completed in less than a few milliseconds, however the important point for the selectivity of the products is the quenching rate. Fast quenching is responsible for the condensation of submicromic particles of pure metal which are characterized by enhanced chemical activity. Such fine powders are often used as catalysts,

pigments or as a bonding agent in powder metallurgy.

So far, plasma processes in extractive metallurgy have to play a great role in the effective utilization of polymetal ores and concentrates and in the processing of industrial wastes. Two types of treatment are possible corresponding to chemical reactions with the condensed phase or in the gaseous phase respectively. The first type is performed in furnaces fed with solid particles such as those of Bethlehem, Westinghouse, Foster Wheeler, Norande, Toronto, Limoges (154-148), where, up till now, iron ores, ferroalloys ores and molybdenite have been treated. The second type is performed through evaporation as those of tin slags at the N.P.L. (164). Although from an economical point of view (148-154) the Bethlehem (151) steel making plasma process seems to be industrially competitive, it is clear that much progresses remain to be done for a wider acceptance of plasma technology.

The two parameters that have to be reduced are the gas cost and the specific energy consumption (even if the relative cost of energy is supposed to decrease with the development of nuclear plants). For the gas, due to improvment of the torches or of the furnaces design (30-31-148), it is now possible, in most operations, to use hydrogen which is a much cheaper gas than argon or helium, except of course when their is a prohibitive dissolution of hydrogen is the metal. As for the specific energy consumption it is clear that it depends on the heat transfer in the furnace. Due to their high specific surface the heat transfer rates are much greater with particles than with solid bodies. Unfortunately the heating efficiency of particles is limited due to the fact that a large amount of energy is necessary to heat up the gas first, for example in an extinguishing plasma, the heating efficiency (compared to the power of the arc) is only of a few percents (112). When the particles are injected in the arc area the heat transfer rate may be increased due to the out of equilibrium boundary layer with the electrons. Relatively few studies has been concerned with the gas-particles out of equilibrium (333) heat transfer compared to that between a plasma and a wall (334-336). Moreower the transfer characteristics in the furnace is a function of the constriction of the plasma and depends on the electrode configuration, on the position of injection of the plasma gas and its flow rate (31). The way in which the particles are injected is also very important since it determine whether they can penetrate or not the hot zone of the plasma. For example this can be done using the magnetohydrodynamic pumping at the cathode tip as in fluid convective cathode furnaces (36-39). Another problem which deserves a special attention is the interaction between the plasma and the particles. For example with a very simplified model, Mathieu (89) has shown that in an extinguishing plasma used for the spheroïdisation of clay particles the fast evaporation of the small particles cools the plasma, thus reducing the heat transfer to the bigger particles and accordingly the overall energy efficiency of the process. The situation is more complicated in the presence of chemical reaction since it is not always the case that the reaction rate is controled by heat transfer. For example our calculations on the reduction of Fe_2O_3 particles in a hydrogen plasma has shown that the time required for the reaction products to diffuse from the particle (337) is about 0.2 s for a 100 µm, which is about five times the time required to heat the particle to the reaction temperature and to supply it with the necessary heat of reaction. In such a case it might be necessary to increase the particles residence time in the furnace by reducing the gas velocity, which might not necessarily be compatible with a stable plasma operation. That is why the falling film technique as developed by Mac Rae (151) represents a good solution of this problem, allowing residence times greater than 1 s. Fortunately the reduced specific surface of the falling film (compared to that of the particles) is compensated by the improved heat transfer rates due to the fact that the falling film is used as the anode (339-341) thus recovering up to 60 % of the arc energy losses. Further studies are needed to improve our understanding of the heat transfer to an electrode in the presence of chemical reactions.

From the above it is obvious that while plasma applications in metallurgy has made good progress a lot need to be done to understand better the fundamentals of the processes involved and to be able to improve the overall economic picture associated to this large scale plasma application.

CONCLUSION

If plasma chemistry is known since the beginning of the century, a lot of experiments has been made between 1955 and 1970. However important progresses have been achieved only in the seventies with the improvement of measurement techniques. This helped to identify, in homogenous reactions, the role of the excited states and of the kinetic, electronic, vibrational and rotational excitation and to show that the most important part of plasma chemistry is the quenching of the excited new species formed. For heterogenous reactions the improvment of the measurement techniques allows a better understanding of the heat and mass transfer phenomena between the plasma and the particles.

Among the diagnostic techniques used one has to emphazies the use of laser diagnostic, either to determine the rate coefficients of reactions with excited species specially the metastable ones that may allow specific stereochemistry or to study the particles velocity and size.

In the future as electricity becomes the most available and versatile source of energy, industrial uses of plasma chemical reactors will become increasingly attractive because :

- they can be operated and stopped very quickly
- their energy density is very high and the reactions are very fast compared to the classical reactors allowing the use of small units with a rather low investement cost
- they are usually not polluting

However, a lot of progresses has yet to be made to further understand what happens during plasma treatment from a microscopic point of view in order to improve the conversion rates and the specific energy consumptions. For example catalysis seems to be very promising but almost everything remains to be done.

The main areas of research in plasma chemistry seems now to be :

- research on reactions with excited states : stereochemistry with metastable states, eximers and flowing lasers...
- research on the destruction of polluting molecules (SO_2, NO_2, NO...), high atmosphere and space chemistry...
- production of molecules with high added values either in organic chemistry or for ceremics with specific cristalline structure...
- production of molecules with low added values improving the conversion rates and energy consumption, in particular, due to the oil crisis, researches are developped for NO production from air, C_2H_2 and C_2H_4 from coal...
- application of plasma technology to metallurgy allowing the local treatment of low grade ores and the production of high purity metals...
- production of submicronic powders or spheroidized particles for sintering...
- development of the plasma sprayed coatings for wear and corrosion protection, thermal and electrical barrier surfaces with low coefficients of friction...
- surface treatment in low pressure plasmas for electronic, optical and wear resistance applications...

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REFERENCES

1. Edstrom, J.S., Petrochem. Industr., 2, 399, (1904).
2. Shur, H., Bibliography of Plasma Chemistry, Part I, Literature up to 1950 - IUPAC Subcommitee Plasma Chemistry.
3. Eckert, H.U., High temperature science, 6, 99, (1974).
4. Gage, R.M., Arc Torches and process, U.S. Patent 2, 806, 124 (1957).
5. Venugopalan, M., Plasma chemistry. An Introduction. In : Reactions under plasma conditions. Ch XI. Vol. II (ed.) Venugopalan : Wiley Interscience N.Y. (1971).
6. Llewellyn-Jones, F., The glow discharge (Ed.) : Methuen London (1966).
7. Davidson, R.C., I.E.E.E. - I.A.S. Conference on applied electrostatics, Toronto (1978).
8. Thomas Kitze, P., Carley, J.F., R.G.C.P., 52, 463 (1975).
9. Hirsh, M., Décharges HF et microondes, Séminaire Chimie des Plasmas, Dourdan 20-24/02/78 (ed.) A.D.E.R.P. Orsay.
10. Fehsenfeld, F.C., Evenson, K.M., Broida, H.P., Rev. Sci. Instrum. 36, 294 (1955).
11. Hubert, J., Moisan, M., Ricard, A., Spectrochimica Acta, 33, 1, (1979).
12. Rykalin, N.N., Pure and Appl. Chem., 48, 179 (1976).
13. Mackinnon, I.M., Reuben, B.G., J. Electrochem. Soc., 122, 806 (1975).
14. Roman, W.C., Zabielski, M.F., Spectroscopic Gas Composition Measurement of UF_6 RF Plasmas. Presented at 30th Annual Gaseous Electronics Conference, Palo Alto, CA, oct. (1977).
15. Bose, T.K., Pfender, E., A.I.A.A. Journal, 7, 1643, (1969).
16. Shih, K.T., Pfender, E., A.I.A.A. Journal, 8, 211, (1970).
17. Cambray, P., Contribution à la mesure des flux de chaleur et de la vitesse d'écoulement du plasma dans un générateur à arc soufflé, Thèse de 3ème cycle Université de Poitiers, 6 avril (1971).
18. Hassan, H.A., Smith, N.S., A.I.A.A. Journal, 8, 657, (1970).
19. Leontiev, A.J., Voltchkov, E.P., "Caractéristiques électriques et thermiques d'un plasmatron de haute enthalpie" in "Investigations expérimentales des plasmatrons" M.F. Joukov, Ed. Nauka Novossibirk (1977).
20. Kimblin, S.U., "Erosion des électrodes et processus d'ionisation entre les électrodes de l'arc dans le vide et à la pression atmosphérique". P. 226 in "Investigations expérimentales des plasmatrons." M.F. Joukov, ed. Nauka Novossibirk (1977).
21. Romalo, D.I., Revue Roumaine des Sciences et Techniques, Série électrotechnique et énergétique, 13, 415 (1968).
22. Finkelnburg, W., MAECKER, N., Elektrische Bögen und thermiches Plasmas, Handbuch der Physik, Springer - Verlag, Berlin, (1956).
23. Nachman, M., Rev. int. Htes Temp. et Réfract., 10, 65, (1973).
24. Pfender, E., Electric Arcs and Arc Gas Heaters, in Gaseous electronic (ed.) N.M. Hirsh, H.J. Oskam, Acad. Press (1978).
25. Hoyaux, M.F., Arc Physics, (Applied Physics and Engineering, vol. 8) Springer Verlag, Berlin, (1968).
26. Bourdin, E., Calcul approximatif d'une tuyère de torche à plasma par application du modèle à propriétés constantes, Rap. Int. Lab. Thermodynamique, Université de Limoges, avril (1978).
27. Schoumaker, H.R.P., Fours à chauffage plasma, in Conference Proceedings of International Round Table on Study and Application of Transport Phenomena in Thermal Plasma, Odeillo, sept. (1975).
28. Geideman, W.A., A general discussion of plasma generator design consideration and operating characteristics, Plasmadyne Corporation, PRE 107.
29. Schoeck, P.A., Ph. D. Thesis Univ. Minnesota (1961).
30. Joukov, M.F., Koroteel, Ourioukob, B.A., "Hydrodynamique appliquée des plasmas thermiques" Rédacteur : Koutatrieladze S.S. Ed. Nauka, Novossibirsk (1975).

31. Joukov, M.F., Kourotchkine, Poustagarov, A.F., "Etude des plasmatrons utilisant des gaz plasmagènes soufflés à travers un étage rapporté entre les électrodes" p. 81 in "Investigation expérimentale des plasmatrons" MF Joukov Ed. Nauka Novossibirsk (1977).

32. Schnell, C.R., Hamblyn, S.M.L., Hengartner, K. and Wissler, M. (Lonza Ltd), The industrial application of plasma technology for the production of fumed silica, presented at the Symposium "Commercial Potential for Arc and Plasma Processes", Atlantic City, N.J. 8-11 septembre (1974).

33. Fey, M.G., Kemeny, G.A., Method of direct ore reduction using a short gap arc heater, U.S. patent 3, 765, 870, oct. 16, (1973).

34. Bonet, C. and al, J. Phys. D., Appl. Phys. 9, L141, (1976).

35. Shakov, M.F., Smolyakov, V. Ya., Urgukov, B.A., Electric-Arc Heaters of Gases (ed.) Nauka, Moscow (1973).

36. Wilks, P.H. and al, Chem. Eng. Prog., 68, 82 (1972).

37. Sheer, C., Korman, S., Kang, S.F., Investigation of convective arcs for the similation of re-entry aerodynamic heating, AFOSR-TR-74-1505, Contrat F-44 620-69-C-0104 (1974).

38. Bayliss, R.K., Bryant, J.W., Sayce, I.G., Plasma dissociation of zircon sands, in the proceedings (S-5-2) of the III International Symposium on Plasma Chemistry, Limoges, France, 12-19 july (1977).

39. Kubanek, G.R., Munz, R.J., Gauvin, W.H., Plasma decomposition of molybdenum disulphide - A progress report, in the proceedings (S-5-4) of the III International Symposium on Plasma Chemistry, Limoges, 13-19 july (1977).

40. Bonet, C., Vallbona, G., Foex, M., Daguenet, M., Dumargue, P., Rev. Int. Htes Temp. et Réfract., 11, 11 (1974).

41. Pickles, C.A., Wang, S.S., McLean, A., Alcock, C.B., Segsworth, R.S., Transactions ISIJ, 18, 369 (1978).

42. Whyman, D., J. Scient. Instrum., 44, 525 (1967).

43. Tylko, J.K., High Temperature Treatment of Materials, Can. Pat. n° 957733, Granted to Tetronics Ltd, (1974).

44. Arc-Coal Process Dev., Final Report May 1966, april 1972, AVCO Corporation Systems Division, Towell, Massachussetts, USA, 91851.

45. Grosse, A.V. et al, Mater. Res. Stand., 5, 173 (1963).

46. Foex, M., Delmas, R., C.R.A.S. Paris, C1, 9 (1967).

47. Sayce, I.G., Selton, B. : Special Ceramics, British Ceramics Research Association, 5, 157 (1972).

48. Yerouchalmi, D. et al, High Temperatures - High Pressures, 3, 271 (1971).

49. Howie, F.H., Sayce, I.G., Rev. Int. Htes Temp. et Refract., 11, 169 (1974).

50. Chase, J.D., Skriven, J.F. : Process for the benefication of titaniferous ores utilising a hot wall continuous plasma reactor, U.S. Pat. 3, 856, 918 (1974).

51. M.H.D. Research Inc., U.K. Pat. 1, 205, 576 (1970).

52. Gold, R.G., Sandall, W.R., Cheplick, P.G., Mac-Rae, D.R., Plasma reduction of iron oxide with hydrogen and natural gas at 100 kW and 1 MW, International Round Table on Study and Application of Transport Phenomena in Thermal Plasmas - IUPAC Odeillo 12-16 sept. (1975) proceedings.

53. Magnolo, G., Can. Min. Metall. Bull., 57, 57 (1964).

54. Fiedler, H. et al, Results of plasma melting of steel, Fifth International Symposium on Electroslag Remelting and Other Special Melting Processes Pittsburgh (1974).

55. Schoumaker, H.R.P., Fours à plasmas, in proceedings of International Round Table on Study and Application of Transport Phenomena in Thermal Plasmas, IUPAC, Odeillo, 12-16 sept. (1975).

56. Paton, B. et al, Plasma arc remelting,in a copper water-cooled crystalliser as a new method of improving metal and alloy properties, in proceedings of the third International Symposium on Electroslag Melting Processes, Pittsburgh USA (1971).

57. Kinoshito, T., Shinka, 17, 61 (1975).

58. Sayce, I.G., Pure and Applied Chemistry, 48, 215, (1976).

59. Sheer, C., Korman, S. : Arcs in Inert Atmospheres and Vaccuum, p. 169, (ed) Wiley New-York, (1956).

60. Pfender, E., Pure and Appl. Chem., 48, 199-213 (1976).

61. Coudert, J.F., Bourdin, E., Baronnet, J.M., Rakowitz, J., Fauchais, P., Chemical kinetics study of nitrogen oxide synthesis a D.C. plasma jet, a proposed model, Journal de Physique 100, C7-355, (1979).

62. Polak, L., Ch 13, p. 141, T2 Plasma Chemistry, Wiley-Interscience, N.Y. (1971).

63. Barrere, M., Prud'Homme, R., "Equations fondamentales de l'aérothermo-chimie" Masson et Cie éditeurs Paris (1973).

64. Zeleznick, F.J., Gordon, S., Industrial Engineering Chemistry, 60, 6 (1968).

65. Storey, S.H., Van Zegeren, F., The computation of chemical equilibria, Cambridge University Press (1970).

66. Bourdin, E., Contribution à l'étude théorique et expérimentale de la synthèse de nitrures par réaction d'un jet de plasma d'azote avec des poudres d'aluminium et de silicium" Thèse de 3ème cycle, Université de Limoges (1976).

67. Fauchais, P., Baronnet, J.M., Bayard, S., Rev. Int. Htes Temp. et Réfract., 12, 221 (1975)

68. Frank-Kamenestkii, D., "Diffusion and heat transfert" in Chemical Kinetics Plenum Press. New-York - London (1969).

69. Emanuel, N., Knorre, D., "Cinétique chimique" Edition Mir. Moscou (1975).

70. Johston, H., "Gas phase reaction rate theory" Ronald Press Company, New-York, (1966).

71. Baulch, D.L., High Temperature Reaction Rate Data, n° 4, Leeds (1969).

72. Warner, D.D., The Journal of Physical Chemistry, 87, 2329 (1977).

73. Devoto, R.S., Phys. of Fluids, 10, 2105, (1967).

74. Mason, E.A., Kinetic processes in gases and plasma, (ed.) A.R. Hochstim Academic Press. N.Y. and London (1969).

75. Chapman, S., Cowling, T.G., The mathematical theory of non uniform gases (ed.) Cambridge University Press, U.K. (1970).

76. Athye, W.F., A critical evaluation of methods for calculating transport coefficients of partially and fully ionized gases, NASA TN, ND-2611 (1965).

77. Devoto, R.S., Phys. of Fluids, 9, 1230, (1966).

78. Devoto, R.S., Li, C.P., J. Plasma Physics, 2, 17, (1968).

79. Devoto, R.S., A.I.A.A. Journal, 7, 2, (1969).

80. Devoto, R.S., Phys. of Fluids, 16, 616, (1973).

81. Butler, J.N., Brokaw, R.S., Journal of Chemical Physics, 26, 1636, (1957).

82. Vanderslice, J.T., Weisman, S., Mason, E.A., Fallon, R.J., Phys. of Fluids, 5, 155 (1962).

83. Boulos, M.A., Gauvin, W.H., Can. J. Chem. Eng., 52, 355, (1974).

84. Bhattacharyya, D., Gauvin, W.H., A.I.Ch.E. J., 21, 879, (1975).

85. Boulos, M.A., IIIème Symposium International de Chimie des Plasmas, I.U.P.A.C., S-3-2. Limoges (1977).

86. Bonet, C., "Thermal Plasma Processing" Chemical Eng. Prog. USA, 72, 12, 63 (1976).

87. Yoshida, T., Akashi, K., Journal of Applied Physics, 48, 2252 (1977).

88. Fiszdon, J., Lesinski, J., International Round Table on Study and Application of Transports Phenomena in Thermal Plasmas - Odeillo 12-16 sept. (1975).

89. Mathieu, A.C., Contribution à l'étude expérimentale et théorique de la sphéroïdisation de particules d'argile réfractaire dans un four à plasma, Thèse de docteur-ingénieur, Université de Limoges 18/07/1979.

90. Fey, G., Electric arc heater for the process industries - National Industrial Electric Heating Conference Cincinnati Ohio USA, feb. 9-12 (1976).

91. Dumon, A., Inf. Chimie, 164, 101, (1977).

92. Spitz, Peter H., Inf. Chimie, 164, 101, (1977).

93. Kern, W., Rosler, R.S., Advances in deposition processes for passivation films, J. Vac. Sci. Technol., 14, 1082, (1977).

94. Sinha, A.K., Electrochemical Society Meeting Las Vegas (1976) - Plasma Enhanced C.V.D., A review.

95. Kirk, R.W. and Gurev, H., Paper presented at Am. Inst. Chem. Eng. 64th Annual meeting (nov. 1971).

96. Joyce, R.J., Steerling H.F. and Alexander, J.H., Thin Solid Films, 1, 481 (1973).

97. Gereth R. and Scherber, W., J. Electrochem. Soc., 119, 1248 (1972).

98. Reinberg, A.R., Plasma etching semiconductor manufacture. A review. Electrochemical Society Meeting Washington, mai (1976).

99. Kumar, R., Ladas, C., Hudson, G., Characterization of Plasma Etching for Semiconductor Applications, Solid State Technology, 3, 54 (1976).

100. Abe, H., Dry Process in Semiconductor Device Manufacture - Table Ronde Internationale sur les traitements de surface et la polymérisation par plasma. Limoges juillet (1977).

101. Carlson, D.E. et al, Properties of Amorphous Silicon and Solar Cells. R.C.A. Review, 38, 211, (1977).

102. Groset,M., Perez De la Sota, R., Velasco, G., Seve, G., Lassabatere, L., 1er Colloque International de Pulvérisation Cathodique, Montpellier, oct. (1973), pp. 65-70.

103. Francombe, M.H., 1er Colloque de Pulvérisation cathodique, Montpellier, oct. (1973), pp. 81-91.

104. Daviose, P.D., Maissel, L.I., Journal of Applied Physics, 37, 574, (1966).

105. Auberger, G., David, R., 1er Colloque International de Pulvérisation cathodique, Montpellier (1973), pp. 295-299.

106. Pichoir, R., 2ème Colloque International de Pulvérisation Cathodique, Nice (1976), pp. 133-136.

107. Mukherjee, J.L., Wu, L.C., Green, J.E., Cook, H.E., J. Vac. Sci. Technol., 12, 850 (1975).

108. Schintimeister, W., Pacher, O., J. Vac. Sci. Technol., 12, 743, (1975).

109. Swaroop, B., J. Vac. Sci. Technol., 13, 680 (1976).

110. Buisine, A., "Traitement industriel du polyethylène par effet couronne" ADERP Chimie des Plasmas, Dourdan Fév. (1978).

111. Amouroux, J., et al, "Propriétés adhésives des films de polyethylène soumis à l'action d'une décharge couronne" ADERP Chimie des Plasmas, Dourdan fév. (1978).

112. Rykalin, N.N., Kudinov, V.V., Pure and Appl. Chem., 48, 229, (1976).

113. Besson, J.L., Boch, P., "Plasma spraying of Ceramics" International Round Table Discussion on "Special Ceramics for Electronics and Electrical Engineering, Warsaw 8-11 oct. (1978).

114. Ingham, H.S., Shepard, A.D., Metco Flame Spray Handbook (1965).

115. Guyonnet, J., Brevet CNRS 124 111 et additifs 168 044 et 704 678.

116. Wilks, P.H. and Thorpe, M.S., The heating of solids in high temperature plasma. Paper presented at American Chemical Society Symposium on high temperature, Chicago, (1970), p. 13.

117. Fey, M. and al, "Spheroïdization of magnetite using an A.C. arc heater" International Round Table on Study and application of transport phenomena in thermal plasmas - Proceedings - Odeillo sept. (1975).

118. Landt, U. et al, Production of smouth and spheroïdal ferrosilicon particles S.A. Pat. 720850 appl. (1971).

119. Arkless, K., Ceaver, D., Brit. Patent, 1 226 082 (1966).

120. Sayce, I.G., Pure and Appl. Chem., 48, 215, (1976).

121. Magnolo, G., Can. Min. Metall. Bull., 57, 57 (1964).

122. Lachner, W. et al, "Results with plasma torch furnaces for melting high quality steels from alloy soap". Proceedings Fourth International Symposium on Electroslag Remelting Processes - Tokyo (1973).

123. Fiedler et al, "Results of plasma melting of Steel". Proceedings Fourth International Symposium on Electroslag Remelting and other Special Melting Process - Pittsburgh USA (1974).

124. Asada, C. et al, "Plasma induction Heating". Proceedings Third International Symposium on Electroslag Melting Processes - Pittsburgh USA (1971).

125. Paton, B. et al, "Plasma arc remelting in copper water-cooled crystalliser as a new method of improving metal and alloy properties." Proceedings Third International Symposium on Electroslag Melting Processes, Pittsburgh USA (1971).

126. Kinoshito, I., Shinku, 17, 61, (1975).

127. Schoumaker, H.R.P., "Fours à chauffage plasma" dans "Conference proceedings of International Round Table on Study and Application of Transport Phenomena in Thermal Plasmas", Laboratoire des Ultra-Réfractaires du CNRS, Odeillo sept. (1975).

128. Schoumaker, H.R.P., "Four à plasma triphasé" Publication Electrotherm. Communication au C.B.E.E. réunion du 30/03/(1971).

129. Rossener, H.O., Stahl O. Eisen. 95 (2), 61, (1975).

130. Davidson, R.C., I.E.E.E. - I.A.S. Conference on applied Electrostatics, Toronto (1978).

131. Gladish, H., Hydrocarbon Proc. Petrol. Ref., 41, 159, (1962).

132. Gladish, H., Chimie Ingenieur Technik, 41, 204, (1969).

133. Dupont, Arc Acetylene Process par R.A. Schulze, Chemistry and industry, 9, 1539, (1968).

134. Babcock, J.A., Chem. Eng. Process., 71, 90, (1975).

135. Eremin, E.N., Mal'Tsev, A.N. and Rusakova, L.A., Russ. Journ. of Phys. Chem. 1256, (1974) et 1129 (1974).

136. Mal'Tsev, A.N., Eremin, E.N., et Belova, V.M., Russ. Journ. of Phys. Chem., 1042 (1971).

137. Polak, L.S., Kinetika i thermodinamika khimiceskikh protsessov v nizkotemperatournoy Plazmz, (ed.) Nauka, Moscou (1965).

138. Pollo, I., 3ème Symposium International de Chimie des Plasmas, IUPAC, Limoges, G-1-9, (1977).

139. Coudert, J.F., Baronnet, J.M., Rakowitz J. et Fauchais, P., 3ème Symposium International de Chimie des Plasmas, IUPAC Limoges, G-1-7, (1977).

140. Amouroux, J., Cavadias, S., Rapakoulias, D., 3ème Symposium International de Chimie des Plasmas, Limoges (1977) G-1-5.

141. Akashi, K. et al, Seisen-Kenkyu, 22, 370, (1970).

142. Morel, S., Rudy I Metals Niezelanze, 18, 25, (1973).

143. Mac Rae, D.R. et al, Ferrovanadium production by plasma carbothermic reduction of vanadium pentoxide, XXXIV Conf. Electric. Furnace, St-Louis, USA, déc. (1976).

144. Mac Rae, D.R. et al, Ferrovanadium production by plasma carbothermic reduction of vanadium oxide. T. III - Third Int. Symp. on Plasma Chemistry, IUPAC Limoges, 13-19 juillet (1977).

145. Fey, M.G., Harvey, F.J., Plasma heating devices in the electric energy economy, Metals Eng. Q., may, 27-30 (1976).

146. Wolf, G.B., Westinghouse Electric. Private Communication feb. (1976).

147. Pickles, C.A., Wang, S.S., Mc Lean, A., Alcock, C.B., Segswoorth, P.S., IEE Transactions, 18, 369, (1978).

148. Kassabji, F., Pateyron, B., Aubreton, J., Fauchais, P., Morvan, D., Technical and economical studies for metal production by plasma steel making application, IVth International Symposium on Plasma Chemistry. Zurich. Aug. (1979).

149. Boulos, M.I., Gauvin, W.H., Can. J. Chem. Eng., 52, (3), 355, (1974).

150. Kubanek, G.A., Munz, R.J., Gauvin, W.H., Plasma decomposition of Molybdenum disulphide. A progress report, IIIème Symp. Int. de Chimie des Plasmas. IUPAC Limoges 13-19 juillet (1977).

151. Clump, W.C., Kwasnoski, D., Mac Rae, D.R., Thompson, C.D., A study of high temperature methane reforming, Interamerican Congress of Chemical Engineering, Caracas Venezuela, 13-16 (1975), p. 33.

152. Tylko, J.K., "The in-flight manufacture of irons and steels in an expanded precessive plasma reactor", IIIème Symposium International de Chimie des Plasmas. IUPAC Limoges, 13-19 juillet (1977) t. III.

153. Foster Wheeler Ltd/Tetronics Ltd : "The production of steel from coal and iron ore using the Tetronics expanded precessive plasma". Technical report dec (1976).

154. Aubreton, J., Fauchais, P., Amouroux, J., Les fours à plasmas en métallurgie extractive, Journées d'Etudes. L'industrie des Métaux. Comité Français d'Electrothermie. Versailles 5-6 avril (1978).

155. Grosse, A.V. et al., Mater. Res. Stand. 5, 173, (1963).

156. Foex, M., Delmas, R., Paris C.R. Seanc. Acad. Sci. Series, C1, 9, (1967).

157. Hamblyn, S.M.L. et al, The industrial application of plasma technology for the production of fumed silica - Symposium of the American Chemical Society on the Commercial Application of Plasma Atlantic City (1974).

158. Yerouchalmi, D., et al, High Temperatures - High pressures, 3, 271, (1971).

159. Sayce, I.G., Selton, B., Special Ceramics. British Ceramics Research Association, 5, 157, (1972).

160. Burov, I.T., Bysyuk, V.V., Zabrodin, V.K., Mosse, A.L., Rev. Int. Hautes Temp. Réfract., 15, 201, (1978).

161. Bayliss, R.K. and Derry, R., J. Appl. Chem., 16, 114, (1966).

162. Everest, D.A., Napier, E. and Wells, R.A., "Processes for the extraction of beryllium from flotation concentrates of beryl. in High Temperature Refractory metals, Krinvsky, W.A. ed. (New-York : Gordon and Breach, 1978), 113-28.

163. Shelley, T.R. and Charles, J.A., Trans. Instn. Min. Metall. (Sect. C : Mineral Process. extr. Metall.), 79, C259 (1970).

164. Barett, M.F. et al, Trans. Inst. Min. Metall. 84, C231, (1975).

165. Shelley, T.R. and Charles, J.A., Trans. Instn. Min. Metall. (Sect. C : Mineral Process. Extr. Metall), 78, C177, (1969).

166. Recasens, J., Bortaud, P. and Bonnier, E., Revue Int. Hautes Temp. Réfract., 4, 281, (1967).

167. Demoustiez, A., Hanon, J. and Winand, R., Industrie Chim. Belge, 32, special, 144 (1970).

168. Dumas, J.L., Garnier, B., J. Chim. Phys., 72, 1045, (1975).

169. Dumas, J.L., Revue de Physique Appliquée, 12, 1035, (1977).

170. Carbough, D.C. et al, J. Chem. Phys., 47, 5211, (1967).

171. Willis, C., Can. J. Chem., 51, 3605, (1975).

172. Dumas, J.L., communication privée (1975).

173. Griem, M.R., Plasma Spectroscopy, Mc Graw Hill, New-York (1964).

174. Mac Whirter, R.W.P., Plasma diagnostics, ed. by W. Lochte-Holtgreven, North-Holland, Amsterdam, (1968).

175. Drawin, H.W., High pressures - High temperatures, 2, 359, (1970).

176. Baronnet, J.M., Contribution à l'étude spectroscopique des plasmas d'azote produits par un générateur à arc soufflé, Application à la chimie des plasmas : Synthèse des oxydes d'azote, Thèse de Doctorat ès Sciences Physiques, Université de Limoges, nov.(1978).

177. Fleurier, C. et al, Computer Phys. Com., 7, 200, (1974).

178. Mermet, J.M. et al, Rev. Int. Htes Temp. et Réfract., 10, 133, (1973).

179. Andanson, P., et al, J. Phys. D. : Appl. Phys., 11, 209, (1978).

180. Engelsht, V.S. et al, J. Quant. Spectrosc. Radiat. Transfer, 21, 65, (1979).

181. Birkeland, J.W., Applied Optics, 7, 1635, (1968).

182. Myers, B.R. et al, Rev. Sci. Instrum., 49, 610, (1978).

183. Olsen, H.N., J. Quant. Spectrosc. Radiat. Transfer, 8, 1419, (1968).

184. Sebald, N., Proc. XII Int. Conf. Phen. Ion. Gases Endhoven (1975), p. 187.

185. Pickalov, V.V. et al, Journal de Physique, 40, C7-855, (1979).

186. Bauder, U.H., Journal de Physique, 38, C3-135, (1977).

187. Schlüter, D., Z. Astrophysik, 56, 43, (1962).

188. Schlüter, D., Z. Astrophysik, 61, 67, (1964).

189. Fauchais, P., Journal de Physique, 11, C2-137, (1973).

190. Ranson, P., Thèse de Doctorat ès Sciences, Université d'Orléans (1978).

191. Wiese, W.L., Plasma diagnostic techniques, ed. by Huddlestone R.H. et al., Academic Press (1965).

192. Wiese, W.E., Phys. Rev., A11, 1854, (1975).

193. Fauchais P., Lapworth, K.C., First report on spectroscopic methods of temperature measurement - IUPAC Plasma Chemistry Subcommission.

194. Cabannes, F., Analytical Uses of Plasmas, ed. by R.M. Barnes Wiley.

195. Waszink, J.H. et al, J. Appl. Phys., 42, 3374, (1971).

196. Meubus, P. et al, Canad. J. Chem. Eng., 49, 797, (1971).

197. Brünger, M. et al, Z. Naturforsch., 30a, 1560, (1975).

198. Lesage, A. et al, Journal de Physique, 40, C7-805, (1979).

199. Weiss, C.O. et al, Opt. Com., 16, 399, (1976).

200. Baum, D. et al, Plasma Physics, 17, 79, (1975).

201. Meiners, D. et al, Z. Naturforsch, 28a, 1294, (1973).
202. Czernichouski, A., Acta Physica Polonica, A40, 283, (1970).
203. Schreiber, P.W. et al, Plasma Physics, 15, 635, (1973).
204. Yasuda, A. et al, Proc. XIII Int. Conf. Phen. Ion. Gases, Berlin (1977) 0240.
205. Helbig, V. et al, Proc. XIII Int. Conf. Phen. Ion. Gases, Berlin (1977), 0239.
206. Kafrouni, H. et al, Congrès National de Physique des Plasmas, Paris (1976).
207. Cheng, T.K. et al, J. Appl. Phys., 46, 1961, (1975).
208. Glasser, J. et al, J. Phys. D. App. Phys., 11, 1703, (1978).
209. Apostol, D. et al,Infrared Physics, 16, 269, (1976).
210. Vasil'eva, I.A. et al, Teplefizika Vysokikh Temperatur, 13, 1242, (1975).
211. Veron, D., Opt. Com., 10, 95, (1974).
212. Tishchenko, E.A. et al, Journal de Physique, 40, C7-859, (1979).
213. Zatsepin, V.G. et al, Journal de Physique, 40, C7-857, (1979).
214. Sprousse, J.A., A.E.D.C. Rept n° AD-781-064 (1974).
215. Kolevov, A.N. et al, Teplofizika Vysokikh Temperatur, 16, 642, (1978).
216. Corti, S. et al, Proc. XIII Int. Conf. Phen. Ion. Gases, Berlin (1977), 0257.
217. Buchenauer, C.J. et al, Rev. Sci. Instrum., 48, 769, (1977).
218. Djordjevic, D. et al, Proc. XIII Int. Conf. Phen. Ion. Gases, Berlin (1977) 0241.
219. Filenko, Y.A. et al, Journal de Physique, 40, C7-873, (1979).
220. Barkhudarov, E.M. et al, Journal de Physique, 40, C7-869, (1979).
221. Radley, R.J. Jr., Phys. Fluids, 18, 175, (1975).
222. Attwood, D.T., Appl. Phys. Letters, 26, 616, (1975).
223. Ineichen, B., Applied Optics, 12, 2554, (1973).
224. Matulka, R.D., J. Appl. Phys., 42, 1109, (1971).
225. Kunze, H.J., Plasma diagnostics, ed. by W. Lochte-Holtgreven, North-Holland, Amsterdam (1968).
226. Chan, P.W., I.E.E. transactions of plasma science, PS-3, 174, (1975).
227. Karpov, O.V. et al, Teplofizika Vysokikh Temperatur, 13, 232, (1975).
228. Barbian, E.P., Proc. XIII Int. Conf. Phen. Ion. Gases, Berlin (1977) 0247.
229. Oepts, D., Journal de Physique, 40, C7-793, (1979).
230. Van der Sidge, B., Journal de Physique, 40, C7-851, (1979).
231. Döbele, H.F., Proc. XIII Int. Conf. Phen. Ion. Gases, Berlin (1977), 0245.
232. Alayli, Y. Journal de Physique, 40, C7-817, (1979).
233. Vriens, L., Journal of Appl. Phys., 45, 4422, (1974).
234. Vriens, L., Physical Review Letters, 30, 585, (1973).
235. Batenin, V.M. et al, High Temperature, 15, 208, (1977).
236. Margolin, L.Y. et al, Proc. XIII Int. Conf. Phen. Ion. Gases, Berlin (1977), 0246.
237. Pyatnitskii, L.N. et al, Teplofizika Vysokikh Temperature, 16, 202, (1978).
238. Lapp, M. et al, Laser Raman Gas Diagnostics, Plenum Press, New-York (1974).
239. Lapp, M. et al, Proceedings of the dynamic flow conference on dynamic measurement in unsteady flows (1978) Marseille and Baltimore, p. 665.
240. Measures, R.M., Analytical laser spectroscopy, ed. by Omenetto N., Wiley (1979).
241. Druet, S., Mesures. Régulations. Automatisme, 71, (oct. 1978).
242. Herzberg, G., Molecular spectra and molecular structure. Vol I, Van Nostrand Toronto (1967).
243. Lapp, M. et al, Advances in Infrared and Raman spectroscopy, vol. 3, ed. by Clark R.H.J. et al (1977) Heyden and Son Ltd.
244. Inaba, H. et al, Opto-Electron., 4, 69, (1972).
245. Murphy, W.F. et al, Appl. Spectrosc., 23, 211, (1969).
246. Péalat, M. et al, Optics communications, 22, 91, (1977).

247. Bailly, R. et al, Proceedings of the Sixth International Conference on Raman spectroscopy ed. by Schmid E.D. et al, Heyden and Son Ltd. (1978).

248. Aeschliman, D.P. et al, J. Quant. Spectrosc. Radiat. Transfer, 21, 293, (1979).

249. Vriens, L. et al, J. Appl. Phys., 46, 3146, (1975).

250. Hill, R.A. et al, J. Quant. Spectrosc. Radiat. Transfer, 21, 213, (1979).

251. Lederman, S. et al, Rept AD/A-005 000 (1974).

252. Péalat, M. et al, 16th Int. Symposium on Combustion, Pittsburgh (1977).

253. Taran, J.P., IIIth Int. Conf. on Laser Spectroscopy (TICOLS) Jackon Lodge (1977).

254. Moya, F. et al, XIVth Conference on Aerospatial Sciences. AIAA. Washington (1976).

255. Pealat, M. et al, XVIth Int. Symposium on Combustion. Pittsburgh (1977).

256. Omenetto, N. et al, Atomic fluorescence spectrometry. Basic principles and applications. Pergamon Press (1979).

257. Omenetto, N. et al, Analytical Laser Spectroscopy. Wiley (1979).

258. Dayly, J.W. et al, J. Quant. Spectrosc. Radiat. Transfer, 17, 327, (1977).

259. Daily, J.W., Applied Optics, 16, 568, (1977).

260. Daily, J.W., Applied Optics, 17, 225, (1978).

261. Daily, J.M., Applied Optics, 17, 1610, (1978).

262. Catherinot, A. et al, Phys. Rev., A18, 1097, (1978).

263. Daily, J.W., Applied Optics, 15, 955, (1976).

264. Stepowski, D. et al, Applied Optics, 18, 354, (1979).

265. Betchel, J.H., Optical Society of America Annual Meeting. San Francisco (1978).

266. Blasckburn, M.B., Applied Optics, 18, 1804, (1979).

267. Haraguchi, H., Spectrochimica Acta, 35A, 391, (1979).

268. Van Calcar, R.A. et al, J. Quant. Spectrosc. Radiat. Transfer, 21, 11, (1979).

269. Smith, B.W. et al, Canad. J. Spectrosc., 22, 57, (1977).

270. Haraguchi, H., Canad. J. Spectrosc., 22, 61, (1977).

271. Haraguchi, H., Applied Spectroscopy, 31, 156, (1977).

272. Haraguchi, H. et al, Applied Spectroscopy, 31, 195, (1977).

273. Boutilier, G.D., Applied Optics, 17, 2291, (1978).

274. She, C.Y. et al, Optics Letters, 2, 30, (1978).

275. Vardelle, A., "Contribution à la mesure statistique des vitesses et des températures de surface de particules injectées dans un jet de plasma d'arc", Thèse de 3ème cycle, Université de Limoges (1979).

276. Cambray, P., "Contribution à l'étude des processus de relaxation dans les jets de plasma, d'hélium à basses pressions", Thèse de Doctorat d'Etat ès Sciences Physiques Université de Poitiers, janv. (1980).

277. Fiszdon, J., Gauk, Daniault, Rev. Int. Htes Temp. et Réfract., 13, 11, (1976).

278. Hare, A.L., Velocity measurements in plasma flows using cooled pitot tubes : an unsolved problem, Proceedings G.3.9., IIId International Symposium on Plasma Chemistry, Limoges (1977).

279. Cambray, P., "Contribution à la mesure des flux de chaleur et de la vitesse d'écoulement du plasma dans un générateur à arc soufflé", Thèse de 3ème cycle, Poitiers (1971).

280. Guyonnet, J., Borie, A., Fauchais, P., "Projection au chalumeau à plasma de revêtements céramiques à coefficients de frottement variables", In proceedings IV-5 of International Round Table of Transport Phenomena in Thermal Plasmas, IUPAC, Odeillo, 12-16 sept (1975).

281. Durst, F., Melling, A., Whitelaw, J.H., Principles and practice of laser-doppler anemometry, Academic Press, (1976).

282. Perugini, G., Analysis of dynamic fusion phenomena of ceramic and metallic powders injected into an argon plasma jet, 3d International Meeting on Modern Ceramics Technologies, Rimini, Italy, (1976).

283. Fiszon, J., Lesinski, J., International Round Table on Study and Application of Transports Phenomena in Thermal Plasmas. Odeillo 12-16 sept. (1975).

284. Tõdorovic, P.S. and al, Spectrochimica Acta, 313, 103, (1976).

285. André, M., Les techniques de cinématographie ultra-rapide, CEA, Centre de Limeil, France (1977).

286. Gold, D., J. of Physics E : Scientific Instruments, 10, 395, (1977).

287. Yeh, Y., Cummins, H.Z., Appl. Phys. Lett., 4, 176, (1964).

288. Durst, F., Zare, M., Bibliography of laser doppler anemometry litterature, University of Karlsruhe, published by DISA Information Department.

289. Barrault, M.R. et al, J. Phys. E., 7, 663, (1974).

290. Irie, M., Barrault, M.R., J. Phys. D., 10, 1599, (1977).

291. Gouesbet, G., Thèse d'Etat, Université de Rouen, 21 déc. (1977).

292. Bayliss, R.K., Sayce, I.G., Durao, D., Melling, A., Measurement of particles and gas velocities in a transfered arc heater using laser doppler anemometry. 3d International Symposium on Plasma Chemistry, Limoges 13-19 july (1977).

293. Lesinski, J., Mizera-Lesinska, B., Fanton, J.C., Boulos, M.I., LDA Measurements under plasma conditions. 4th Symposium on Plasma Chemistry, Zurich, August 27, sept 1st(1979).

294. Wilson, J., J. of Phys., E11, 555, (1978).

295. Abbiss, J.B. et al, Optics and laser technology dec. 249 (1974).

296. Lesinski, J., Mizera-Lesinska, B., Fanton, J.C., Boulos, M.I., LDA measurements in gas-solid flows. 2nd Multiphase flow and heat transfer symposium. workshop. Miami, Florida, USA, april (1979).

297. Torobin, L.B., Gauvin, W.H., Can. J. Chem. Eng., 37, 129, (1959).

298. Lewis, J.A., Gauvin, W.H., A.I.Ch.E.J., 19, 982, (1973).

299. Bonet, C., Description d'une méthode de mesure de la température d'une particule en mouvement, Réunion RCP/Gas Ionisés Réactifs, Paris le 10 février (1978) (ed.) P. Fauchais, Limoges University.

300. Kruszewska, B., Lesinski, J., Rev. Phys. Appliquée, 12, 1209, (1977).

301. Allen, I., Particle size measurement, Halsted Press, New York (1975).

302. Kerker, M., The scattering of light and other electromagnetic radiation, Academic Press, New-York (1969).

303. Holve, D. et al, Applied Optics, 18, 1632, (1979).

304. Holve, D., et al, Applied Optics, 18, 1646, (1979).

305. Holve, D., et al, Meeting of the Western States Section of the Combustion Institute, La Jolla California (1976).

306. Farmer, W.M., Appl. Opt., 13, 610, (1974).

307. Farmer, W.N., Proceedings of the Dynamic Flow Conference (1978).

308. Self, S.A., Proceedings of the Dynamic Flow Conference (1978).

309. Royer, H., Opt. Com., 20, 73, (1977).

310. Trolinger, I.D., App. Opt., 18, 1758 (1979).

311. Zeldovich Ya. B. et al, The oxidation of Nitrogen by Combustion, Izdat. Akad. Nauk SSSR, Moscow, (1947).

312. Zeldovich, Ya. B. et al, Physics of Shock Waves and High Temperature Hydrodynamic Phenomena, Academic Press, (1966).

313. Glick, H.S. et al, J. Chem. Phys., 27, 850, (1957).

314. Duff, R.E. et al, J. Chem. Phys., 31, 1018, (1959).

315. Bunker, D.L. et al, J. Am. Chem. Soc., 80, 5085, (1958).

316. Kistiakowsky, G.B. et al, J. Chem. Phys., 27, 1141, (1957).

317. Kaufman, F. et al, J. Chem. Phys., 23, 1702, (1955).

318. Polak, L.S. et al, Kinetics and Thermodynamics of Chemical Reactions in Low Temperature Plasma, Moscow - Nauka (1965) (en russe).

319. Vetter, K., Elektrochem., 53, 369, (1949).

320. Wise,H., Frech, M.F., J. Chem. Phys., 20, 22, (1952).

321. Wise, H., Frech, M.F., J. Chem. Phys., 20, 1724, (1952).

322. Rozlowski, A.I., Russian Journal of Physical Chemistry, 30, 1349 (1956) (en russe).

323. Ammann, P.R., Timmins, R.S., A.I.Ch.E.J., 12, 956 (1966).

324. Baronnet, J.M., Coudert, J.F., Rakowitz, J., Bourdin, E., Fauchais, P., Nitrogen oxides synthesis in a D.C. plasma jet, 4th international Symposium on Plasma Chemistry, Zurich, August 27, sept. 1st (1979).

325. Coudert, J.F., "Contribution à l'étude de la synthèse des oxydes d'azote par chalumeau à plasma", Thèse de 3ème cycle, Université de Limoges (1978).

326. Cavadias, S., Synthèse directe des oxydes d'azote dans un réacteur à plasma basse pression hors équilibre. Thèse de 3ème cycle, Université de Paris VI - 11 juin (1979).

327. Fauchais, P., Bourdin, E., Aubreton, J., Amouroux, J., L'actualité chimique, 4, 36, (1978).

328. Rapakoulias, D., Etude des processus de fixation de l'azote dans un réacteur chimique à plasma hors équilibre. Mise en évidence de processus catalytique, Thèse de Doctorat ès Sciences Physiques, Université de Paris VI, 11 juin (1979).

329. Madejski, J., Int. J. Heat and Mass Transfer, 19, 1009 (1976).

330. Madejski, J., Bull. Acad. Pol. des Sciences, 24, n° 1 (1976).

331. Guyonnet, J., Brevet C.N.R.S. 124 111 et additifs 168 044 et 7044678.

332. Asada, S., Yeguski, I., Adaski, T., Japan Inst. Metals, 34, 128, (1970).

333. Capitelli, M. et al, Combustion and plasma, 15, 23, (1970).

334. Meyer, H., Über das Schelzen von Pulvern in Plasmatrahl. Mitteilung aus dem Max-Planck-Institut für Silikat. Forshung, Würtzbury (1969).

335. Pfender, E., Pure and Appl. Chem., 48, 199 (1976).

336. Kansawa, A., Pfender, E., I.E.E.E. Transactions on plasma Sciences. Vol. PS-6 n° 1 March (1978).

337. Bonet, C., Chemical Eng. Prog. USA, 72, 63 (1976).

338. Ecker, G., Electrode components of the arc discharge, Ergebnisse d. exakten naturwiss. Vol. 33, p. 1, Springer, Berlin (1961).

339. Kimblin, C.W., I.E.E.E. Trans. plasma Sci., PS-2 (4), 310 (1974).

340. Eckert, E.R.G., Pfender, E., Advances in plasma heat transfer, in Advances in Heat Transfer vol. 4 Academic Press, New-York (1967).

341. Incropera, F.P., Leppert, G., Int. J. Heat Transfer., 10, 186, (1967).