CALCULATION OF PARTICLES DENSITY DISTRIBUTION OF CALCIUM IN A DC ARC FREE BURNING IN AIR IN PRESENCE OF FLUORINE

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Abstract

Calculations of the particles density distributions of calcium in a dc arc free burning in the air with and without presence of fluorine are performed employing a new approach for solution of the mass transport equation. The approach is based on the Galerkin's method, well known in the theory of variational calculus, and enables us to achieve a solution of the mass transport equation in its general form. Experimentally derived values for the diffusion coefficient and the axial transport velocity are employed in calculations of spatial particles density distributions.

1. INTRODUCTION

The effect of the added fluorine on the spectrochemical detection of elements, especially calcium, in a dc arc free burning in the air has been subject of extensive both experimental and numerical investigations in our laboratory[1-6]. It has been found that in the presence of fluorine the radial temperature distribution is characterized with a higher maximum at the arc axis and a steeper decline towards the outer arc zones. The values of the diffusion coefficient and of the axial transport velocity of calcium [2,3], as well as the radial distribution of Ca, CaO, Ca+ and CaF particles have been experimentally determined, too [4]. The later results combined with the calculations of the plasma composition [5] have enabled an estimation of the radial distribution of the calcium particles regardless of the particular
species (Ca, Ca⁺, ...). It has been found that the presence of fluorine causes a larger radial gradient of the calcium concentration. The influence of chemical reactions between fluorine and calcium on the intensities of calcium spectral lines and molecular bands has been investigated theoretically in papers [6].

On the basis of all these findings it has been concluded that the effect of fluorine on the intensities of spectral lines and bands of the investigated element must be connected with a change of the mass transport in the presence of fluorine. Therefore in the present paper the experimentally obtained data concerning the arc parameters are employed to calculate the concentration distribution of the investigated substance in the arc plasma without and with fluorine.

2. METHOD FOR SOLUTION OF THE MASS TRANSPORT EQUATION

The mass transport equation for a vertical axially symmetrical free burning arc (in cylindrical coordinates) and for steady state, has the form:

\[
D \frac{\partial^2 n}{\partial r^2} + (D + r \frac{\partial D}{\partial r}) \frac{\partial n}{\partial r} + D \frac{\partial^2 n}{\partial z^2} - \frac{\partial n}{\partial z} - \frac{\partial v}{\partial z} = 0
\]  

(1)

where \(n\) represents the particles' concentration, \(D\) diffusion coefficient assumed to be radially dependent, \(v\) is axial velocity. An approximate treatment of mass transport equation in arc was a subject of several papers as [7,8] where the attention was paid to the central arc zones. In order to find a more general solution of the mass transport equation the method proposed in [9] was used. It represents an application of the Galerkin's method [10] for solving of differential equations. Let us suppose that the differential equation to be solved has the form:

\[
L \{n\} = 0
\]  

(2)

where \(L\) represents some operator and \(n\) required function which has to satisfy some boundary conditions. We seek for an approximate solution of eq. (2) in the form:
\[ n(r,z) = \sum_{n=1}^{N} \sum_{m=1}^{M} c_{nm} f_n(r) \varphi_m(z) \quad (3) \]

where \( f_n(r) \) and \( \varphi_m(z) \) are basis functions and \( c_{nm} \) coefficients to be determined. We assume that the function \( n(r,z) \) satisfies the following boundary conditions:

\[ n=0 \quad \text{if} \quad \frac{z}{r} = \infty \quad (4.1) \]

and

\[ -D \frac{\partial n}{\partial z} + \nu n = f(r) \quad \text{for} \quad z = 0 \quad (4.2) \]

Substituting (3) in (2), taking into account (4.1) and (4.2) and projecting so obtained expression on each of the basis functions, the system of equations equivalent to (5) is obtained:

\[ \sum_{n=1}^{N} \sum_{m=1}^{M} c_{nm} I_{i,j,nm} + \lambda_i h_j = 0 \quad (5) \]

with

\[ I_{i,j,nm} = \int_0^\infty \int_0^\infty f_i(r) \varphi_j(z) L f_n(r) \varphi_m(z) r dr \]

and Lagrange multipliers \( \lambda_i \).

Solving the system of \( N(M+1) \) linear equations we obtain the \( N \times M \) coefficients \( c_{nm} \), determining the spatial particles distribution \( n(r,z) \) and \( M \) Lagrange multipliers \( \lambda_i \).

The basis functions dependent on \( r \) \( f_n(r) \) are chosen to be:

\[ f_n(r) = N_n \ {}_1F_1(a,1,dr^2) \exp(-\frac{1}{2} dr^2) \quad (7) \]

with \( N_n = \sqrt{2a} \) and \( d\nu = dr \). \( {}_1F_1 \) represents the confluent series \( (a=0, -1, -2, \ldots) \) and \( a \) is a parameter which should be optimized for the concrete problem. The \( z \)-dependent basis functions are taken in the form:

\[ \varphi_m(z) = N_m H_m(\sqrt{2}z) \exp(-\frac{1}{2} \beta z^2) \quad (8) \]

whereby \( N_m = \sqrt{2} (\beta m!)^{1/4} / (2^m m!)^{1/2} \), \( d\nu = dz \) and \( H_m(\sqrt{2}z) \) are Hermite polynomials. Both of the particular basis sets are orthonormal.
3. EXPERIMENTAL DETERMINATION OF DIFFUSION COEFFICIENT AND AXIAL TRANSPORT VELOCITY

Experimental determination of the diffusion coefficient of substances in the arc plasma is described in details in [2,11]. The substance whose diffusional coefficient has to be measured is injected into the plasma in the form of liquid Bullets of its aqueous solution - in the present case Ca(NO₃)₂. The arc is photographed with a high speed camera using an interference filter to separate the radiation emitted by the investigated substance. The diffusion coefficients were determined from spatial intensity distribution of the characteristic radiation, found for a number of successive photos by photometric measurements. Since the clouds of injected substance appear at various distances from the arc axis, it was possible to determine also an approximate temperature dependence of D. The dependence D on T in high temperature regions is extrapolated using $D \sim T^{1.2}$ dependence. The transformation of $D = D(T)$ into $D = D(r)$, Fig. 1a, is performed employing experimentally found radial temperature distribution [4]. No systematic change of the value for D in the presence of fluorine was stated [3]. The directed transport velocity was determined [12,3] by registering the positions of the clouds of excited substance on successive photos obtained with high speed camera. It was found that the axial velocity increases considerably in the presence of fluorine to about 400 cm s⁻¹ compared to 200 cm s⁻¹ without fluorine.

The last parameter which must be specified in the calculations is the shape of the flux - profile of the substance at the top of the lower electrode. An exponential dependence $f(r) = \exp(-20 \ r^2)$ shown in Fig. 1b. is employed.

4. RESULTS AND DISCUSSION

In the calculations of the particles density distribution a set of 25 basis functions was used. The value of the parameter $\lambda$ determining the form of the r-dependent basis is fixed to 20. Two values for $\beta$ (0.1 and 1.0) are used, both of them giving similar final results.
The results are shown in Fig. 2. Full lines correspond to the absence \((v = 200 \text{ cm/s})\), dashed to the presence of fluorine in the plasma \((v = 400 \text{ cm/s})\). As expected, a decrease of

![Graph](image1)

**Fig. 1a.** Radial dependence of diffusion coefficient of calcium

**Fig. 1b.** Assumed flux-profile at the top of the lower electrode

![Graph](image2)

**Fig. 2.** Calculated radial distribution of calcium particles

--- without fluorine ; --- with fluorine
the particles density along the z-axis and a simultaneous flattening of the radial distribution is evident. The particles concentration is generally smaller in the presence of F (e.g. at faster axial transport) in accordance with findings of other authors [7].

On the basis of these calculations we can now explain a much more pronounced radial decline of the calcium concentration in the presence of F, observed experimentally[4] in the following way: i) As a consequence of chemical reactions involving fluorine a narrower arc core with higher temperature (compared with the case when F is absent) is formed. ii) larger temperature gradient causes higher axial (convection) velocity iii) due to higher axial velocity the substance is more spread longitudinally, the latter diffusion being less pronounced.

REFERENCES