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A structural approach of the critical behavior of coalescence and electroconductivity in the electrolytic thin layers

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The purpose of this paper is to study the critical behavior of electroconductivity in thin layers deposited on a cold support made of thermoresistent glass, in a mixture of H_2O and SO_3, by burning rich sulphur (2.5-4.5%) fuels. From an ecological perspective, this is a highly important issue because this mixture generates acid-sulphur rains. In this sense, using the method of condensation of the H_2O and SO_3 mixture in the form of a solution of H_2SO_4 in water, a measuring of the temperature dependence of electroconductivity of a thin layer has been made. There is a big interest in determining the acid dew point temperature, T_{PRA}, and the possibility of controlling it. One of these methods is the blasting of MgO powder, of different dimensions of granulation, at the end of the flame of the 4 vapor-tones/hour boiler, resulting in a very important change of the critical behavior of the studied system.

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1. Introduction

The interest in this issue is based on the concern for the ecological implications of the fuels containing sulphur (2.5 - 4.5%) in a heat environment and the generation of electrical energy. In the same time, such a matter is of great importance in defining the dew acid point. The usage of rich sulphur fuels in thermal installations consisting in a heating apparatus presents certain implications in the phenomenon of corrosion at low temperatures. During the combustion, the most important parameter which influences the corrosion is the SO_3 content [1,2]. Its presence is mainly determined by the oxygen amount in the burning room. In the stoechiometric burning conditions, the conversion of sulphur from fuels to sulphur dioxide in the presence of the oxygen excess, results in SO_3, which is highly corrosive. The mixture of SO_3 and H_2O (as vapors) behaves as a binary mixture and when the temperature reaches the acid dew point temperature, the sulphuric acid H_2SO_4 condenses on a cold surface. This phenomenon determines the corrosion of metallic pieces and the sulphating of refractive materials [2,3,5].

In order to reduce the corrosion, using sulphur rich fuels, the following measures are taken: the avoidance of sulphur in the fuel, the improvement of burning results by using additive substances, the burning of the fuel in a reduced excess of the air, the air dilution of the burning gases in the chimney [3,4]. The additives, solid, liquid and gas, are products which, introduced in the fuel or in the burning gases, reduce the corrosion and deposition effects. [5]

Solid additives used with very important results are oxide powders (e.g. magnesium oxide). These can be introduced on the burning gases way in order to reduce the SO_3 by transforming it in $MgSO_4$.

2. Experimental approach

Given a support temperature $T_S < T_{PRA}$, the result is a condensation of electrolytic mixture of $H_2SO_4 + H_2O$ in thin layer. The raising of the support temperature over T_{PRA} results in the evaporation of the electrolytic layer between the electrodes. In this way, the temperature at which the conduction in the thin layer obtained by the acid sulphuric condensation appears or disappears is revealed. The distribution of the electrolytic thin layer on “cold” support ($T_S < T_{PRA}$) depends on the support form, the geometry of the system “cold support - chimney” and on the burning conditions of fuels [1,5].

A measuring check rod is used in order to obtain the experimental value of acid dew point temperature T_{PRA} in burning gases. The check rod consists of a metallic carcass (1) kept cold using a water flow to protect it against the heated burning gases, an air pipe to cool the support (2) and to command the support temperature T_S. In the head of the check rod (5), which represents the cold support for the sulphuric acid condensation, two platinum electrodes (4), connected by wires with the conductivity measuring device (6), are implanted. The temperature is measured using a thermocouple (7), placed on the head of the check rod. The cold air (3) conducted to the head of the check rod determines the temperature $T_S < T_{PRA}$ and a thin electrolytic layer is laid on the cold support.

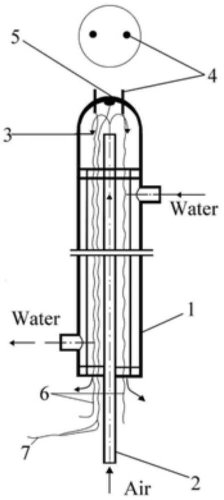

Fig. 1. The measure check rod.

Reducing the flow of the cold air, the support temperature increases $T_S > T_{PRA}$ and the electric conductivity of the layer decreases because of the evaporation of the deposited electrolyte [5].

3. Results and discussion

The values of the electroconductivity determined with the check rod presented in Fig. 1 allows us to obtain the critical dew acid temperature from the curves σ = f (T_S), with three important regions: saturation S, active A and critical region I. The theoretical explanation of such a system is given in the Kuramoto model of weak related oscillators [7-9] and with switch model function [10]. At low densities of H_2O and SO_3 resulted from the burning gases responsible for the thin electrolytic layer, the number of condensed molecules is determined by [6].

$$N = c\tau_s \cdot \left[1 - \exp\left(-\frac{T}{T_s}\right)\right],$$

with

$$\tau_s = \tau_o \cdot \exp\left(-\frac{E_d}{RT}\right),$$

where τ_0 represents the oscillation period of the molecules, E_d – the molar adsorption energy on the support, R – the molar constant, and T – the temperature of the burning gases. The concentration of critical ionic nanostructures of electrolytic thin layer depends on the temperature support T_S, as follows:

$$N_i = N_{\exp}\left(-\frac{G_i}{k \cdot T_s}\right),$$

where G_i is the critical value of free energy.

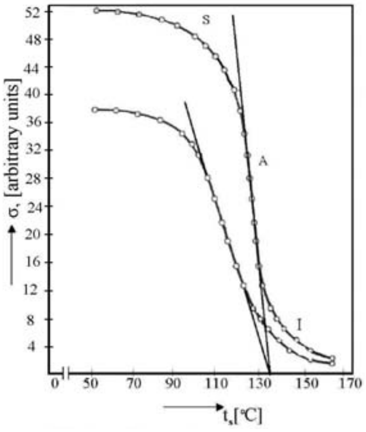

Fig. 2. The electric conductivity versus support temperature $\sigma = f(T_S)$.

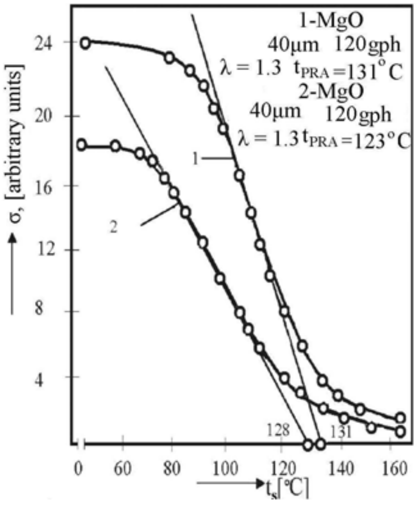

Fig. 3. The influence of injected MgO flowing on the acid dew point for a constant air excess λ = 1.3.

The critical radius of these insular structures of critical coalescence is expressed through:

$$R_c = \frac{const.}{k \cdot T_s \cdot \ln\left(\frac{p}{p_e}\right)},$$

where p is the pressure of saturated acid vapors, and p_e is the equilibrium pressure at the temperature of the T_S support.

Thus, the multiplication of these insular structures is reached and the expansion of their dimensions leads to a growth in the conductibility of the thin layer until a maximum value σ_{max}, depending on many factors, is attained.

In the same time, with the determination of the dew acid point from the curve representing the variation of the electroconductivity versus the support temperature, the results obtained by blasting the magnesium powder oxide of different granulation in the focus of the boiler's vapors become visible.

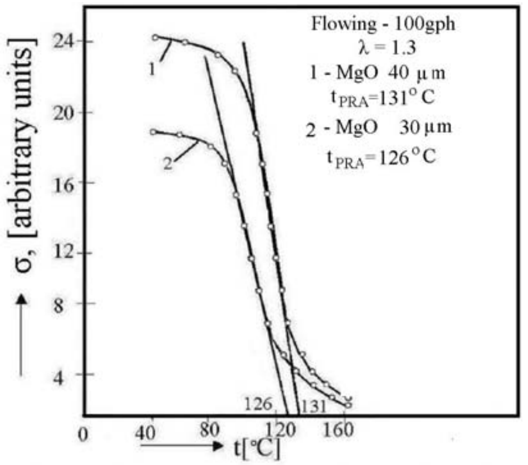

Fig. 4. The granulation influence of injected MgO on the acid dew point temperature for a constant air excess $\lambda = 1.3$.

The condensation resulted on an electroinsulator material (thermoresistent glass) was measured by the electroconductivity and the results are as given in Fig. 4. The first thing determined was the behavior of the electrolytic thin layer, given the same concentration of $H_2SO_4 + H_2O$ electrolytic mixture, but of different thickness. The experimentally determined results represented graphically from the curves $\sigma = f\,(T_S)$, express the same critical dew acid temperature T_{PRA}, because the physical conditions in the system are the same. Consequently, the modification of one of these conditions leads to a change in the dew acid temperature and consequently in the distribution of electrolytic nanostructures in the thin layer obtained.

4. Conclusions

The measuring of the electro conductivity of thin acid layers with the original method and device as presented in the paper, allows us to determine the dew acid temperature and to study the possibilities of its modification by the introduction of MgO of different granulation in the acid burning atmosphere. The critical behavior of the electro conductivity of the thin layers enables the existence of critical nanostructures very close to the dew acid temperature value, theoretical explanation of such a system beeing given in Kuramoto model of weak related oscillators correlated with the switch model function.

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