LOCAL ELECTRICAL RESISTANCE CHARACTERIZATION OF ARCHEOLOGICAL METALLIC FINDS CRUST BY AN ELECTROLITHIC METHOD

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Abstract: This work deal with the problem of locally characterize, by electrical parameters, crusts of archeological metallic finds that would allow, if performed, a better restoration procedure plan. Referring to resistance, a brief list of lead crust that is possible to meet, to which experimental data are referred, is done. A description of density current focusing apparatus is given, with the phenomenological behavior of density current. The data processing to extract local information is also presented.

Keywords: Resistance and voltage measurements, Ionic beam focusing in electrolithic solution.

1   INTRODUCTION

The problem of characterization the oxidation crust is one of most involved in studies of metals put through environmental pollution, mainly archeological finds. For example, lead, that one studies, furnishes a great variety of substances on oxidized crust: cerusite $[PbCO_3]$, brown plattnerite $[PbO_2]$, yellow massicot and brown lethargy $[PbO]$, cotunnite $[PbCl_2]$, white phosgenite $[Pb_2(CO_3)Cl_2]$, white anglesite $[PbSO_4]$, hydrocerussite $[Pb_3(CO_3)_2(OH)_2]$ [1]. One starts exploiting classical procedure of reduction, that consists in putting the archeological metallic find as cathode in an electrolithic solution, checking reduction current. Current spreads find with an unknown density depending on local oxidation crust structure making reduction not uniform. To have a very useful diagnosis system to establish the local chemical nature of oxidized crust in view to project a procedure of reduction, is necessary to locally control current density.

2   THE METHOD

If ionic reduction current could be managed on surface, assuring the find be protected from acid action, such an apparatus is able to pick up local information on crust. The scanning of all the find's surface by a mechanical system controlled by a computer, allows to obtain better results in reduction procedure.
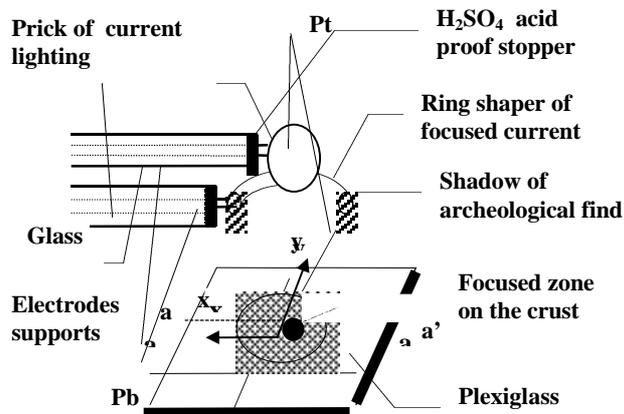

Fig. 1: Skeleton of electrical surface measurement system utilizing focused current : all it is soaked in sulfuric acid
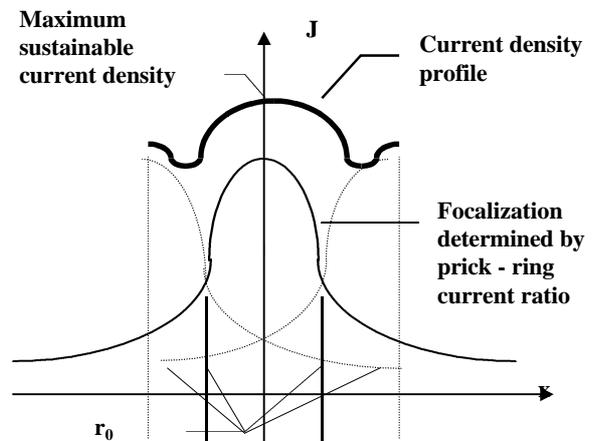

Fig. 2: hypothesized reflective characteristic of find edge

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The basic idea is in modulation of a current flux supplied to the find by a prick. Such a modulation is obtained by a ring, properly positioned in space, supplying an inverse current: its spatial configuration is displayed in Fig. 1, in which, one supposes the find like a coin, i.e. of circular shape. The electrodes structure try to obtain an intrinsically focalized current density (gaussian) that is deformed by the edge current conditions introduced by the coin. The real density current on the find is, in case of centered position of electrodes, shown in Fig. 2, in which is displayed the queues reflections of original gaussian current density distribution.

3   CURRENT DENSITY

The spatial overlaying of current fields, develops a ionic current density on the find [2], ranged under the prick. The current density distribution, in absence of crust, is settled by simulations, starting from a method utilized in a different context implying a gaussian distribution [3], in view of an analytical review of experimental data acquisition to isolate local electrical characteristic of crust. The find edge can be considered as a reflecting wall of current density distribution: queues are overlapped in the central zone as shown in Fig. 2. The maximum current density must be lower than 50 μA/mm^2: the superficial layer doesn't detach and consolidation is putted of successive restoration procedures. It is very difficult try to calculate analytically, the real current distribution in the operation geometry and in absence of crust, because contour conditions are very hard to consider. In fact the dimension of electrodes are comparable with the find ones, magnifying edge effect in collecting current. To face this problem a simulation has been carried out, in which the working area is represented by little cubes in which electrical characteristic of solution are taken into account, by resistance from center to each face. A spatial grid of 25x25x15 has been considered with elementary spatial step of 1mm. The experience across many simulations assures this spatial arrangement, gives sufficient accuracy in determining current density. Simulations are been developed by MICROCAP™ and in Fig. 3 and 4 are shown to limit cases.
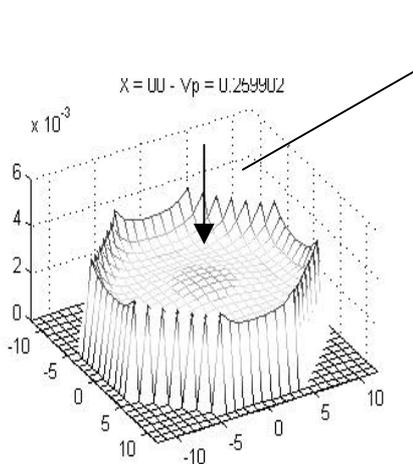

Fig. 3: current distribution, in arbitrary units,
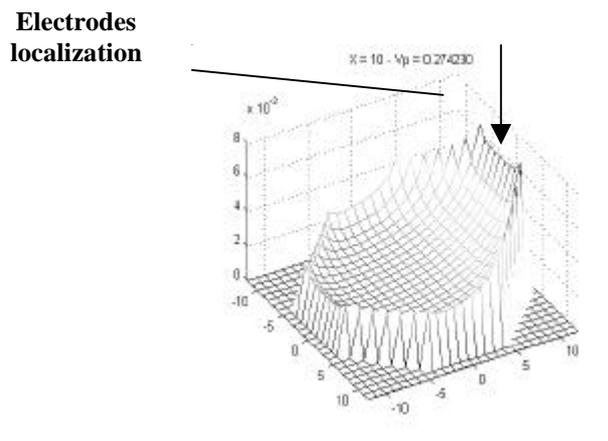with electrodes centered on the find

Fig.4: current distribution, in arbitrary units, with
electrodes at the boundary of the find

As foreseen, they have an high current density at the edge and are almost flat inside the find. This is, also, because the current distribution taken into account, is not focalized: resistance values, one will see, depends by alternate component of current alone, that is present only in the prick and for a.c. component there is not present the focalization effect. Obviously is no convenient to calculate current distributions for all possible position of electrodes, that, later, will be necessary: considering the cylindrical symmetry of system, they are deducible from few ones, picked up by the axial displacement of electrodes from the center of find.

4   ELECTRICAL MODEL OF THE CRUST

The most simple electrical model of crust can be hypothesized as potentials E_r (E_v) and a resistance R_r (R_v), in Fig. 5. If we apply, in parallel to I current generator, an a. c. i square current generator (little compared with I: about 10%, with a frequency of few Khz), the potential of the prick, will allow to determine the potential crust-solution relative to the "lighting" surface , by the relations:

$$E_{r,v} = V_{r,v} - \frac{I}{i} v_{r,v} \qquad (1)$$

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while the a.c. relation furnishes

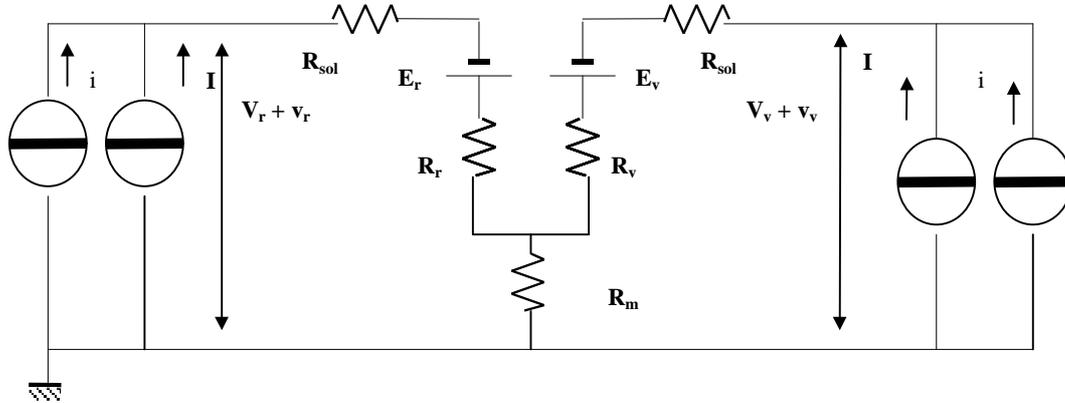$$R_{sol} + R_{r,v} + 2R_m = \frac{v_{r,v}}{i} \tag{2}$$

Fig 5: model of reduction zone and underlining of crust potential $E_{r,v}$

Currents flowing from recto and verso side of the find, can interfere each other by R_m, making necessary to clean reciprocal noise. Considering S surface of find, the coefficient of interference can be obtained minimizing the value

$$\frac{\partial}{\partial k} \sum_S \left(v_r - kv_v \right)^2 = 0 \tag{3}$$

that furnishes

$$k_{r,v} = \frac{\sum_S v_r v_v}{\sum_S v_{r,v}^2} \tag{4}$$

allowing to write

$$v'_{r,v} = k_{r,v} v_{v,r} \tag{5}$$

5   EXTRACTING LOCAL INFORMATION FROM DATA COLLECTED

Considering j,k indexes referred to the prick position and m,n indexes of current density on find, values of measured a.c. voltages of the prick, in absence of crust, can be written as:

$$v^{j,k} = z_{m,n}^{j,k} I_{m,n}^{j,k} \tag{5}$$

where $z_{m,n}^{j,k}$ is the resistance of generic current flux tube artificially determined by ionic beam modulation. Local characteristic of the density current are modified by presence of crust, that manages $v^{j,k}$, causing a variation with respect to the voltage foreseen by (5).

$$\ddot{A}v^{j,k} = \ddot{A}z_{m,n}^{j,k} I_{m,n}^{j,k} + z_{m,n}^{j,k} \ddot{A}I_{m,n}^{j,k} \tag{6}$$

In (6), $\ddot{A}z_{m,n}^{j,k}$ represent the modulation of current flux tube, by the crust, independent from position of reduction electrodes position, managed by j,k indexes. It is so possible rewrite (6) in the form:

$$\ddot{A}v^{j,k} = r_{m,n} I_{m,n}^{j,k} + z_{m,n}^{j,k} \ddot{A}I_{m,n}^{j,k} \tag{7}$$

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Putting in evidence $\ddot{A}I_{m,n}^{j,k}$, it is possible to write:

$$\ddot{A}I_{m,n}^{j,k} = \frac{\ddot{A}v^{j,k} - r_{m,n} I_{m,n}^{j,k}}{z_{m,n}^{j,k}} \tag{8}$$

Replacing in (7), the $z_{m,n}^{j,k}$ extracted from (5), one has:

$$\ddot{A}I_{m,n}^{j,k} = \frac{\Delta v^{j,k} I_{m,n}^{j,k} - r_{m,n} \left(I_{m,n}^{j,k}\right)^2}{v^{j,k}} \tag{9}$$

Current density variations must be the smallest considering physical structure of the apparatus that try to focalize current density in a spot. So must be respected the relation

$$\sum_m \sum_n \left(\ddot{A}I_{m,n}^{j,k}\right)^2 \to min \tag{10}$$

this means

$$\frac{\partial}{\partial r_{M,N}} \sum_m \sum_n \left(\frac{\Delta v^{j,k} I_{m,n}^{j,k} - r_{m,n} \left(I_{m,n}^{j,k}\right)^2}{v^{j,k}}\right)^2 = 0 \tag{11}$$

that furnishes the system

$$\sum_m \sum_n \left(\frac{\Delta v^{j,k} I_{m,n}^{j,k} - r_{m,n} \left(I_{m,n}^{j,k}\right)^2}{v^{j,k}}\right)\left(-\frac{I_{M,N}^{j,k}}{v^{j,k}}\right) = 0 \tag{12}$$

that can be reduced to

$$\ddot{A}v^{j,k} \sum_m \sum_n I_{m,n}^{j,k} = \sum_m \sum_n r_{m,n} \left(I_{m,n}^{j,k}\right)^2 \tag{13}$$

Considering that in any case the total current collected by the find is constant, the double summation in the first member of (13) is ever equal to I, the system allowing to calculate $r_{m,n}$, is

$$\ddot{A}v^{j,k} I = \sum_m \sum_n r_{m,n} \left(I_{m,n}^{j,k}\right)^2 \tag{14}$$

It is worth of mention that the spreading in current density caused by the crust can be evaluated by the (9), known $r_{m,n}$, allowing archeologists to follow the reduction current density shape, to optimize the process.

6   PRELIMINARY RESULTS

To control the correct procedure application, one doesn't apply the procedure to all over the surface of a find, but only to its central part. This reduce calculations of about a factor 4, limiting elements of matrixes of 16 times. In debugging phase this allows to lighten all problems of testing the procedure, without loss in generality. In order to obtain results foreseen by section 5., firstly one applied the cleaning algorithm of section 4. formula (5). Effectively is possible to see how the potentials picked up in verso and recto of the find interfere between. In Fig. 6 and 7 are reported potentials in recto, before and after the cleaning procedure .

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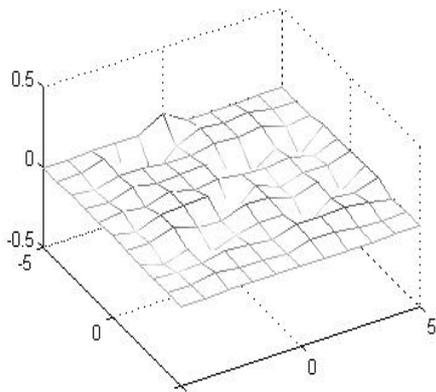Vienna, AUSTRIA, 2000, September 25-28

Fig. 6: oscillations of potentials picked up from
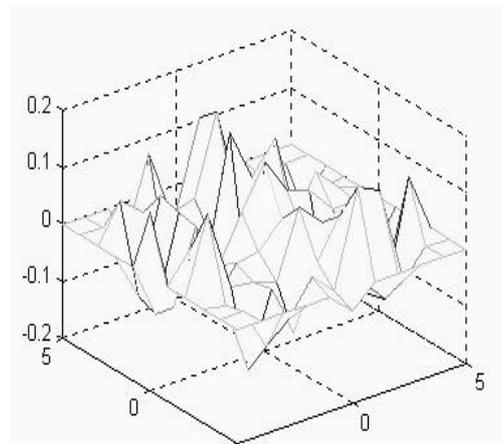recto of the find, before cleaning
procedure (arbitrary units)

Fig. 7: oscillations of potentials picked up from
recto of the find, after the cleaning
procedure (arbitrary units)

Operating all shift combinations in horizontal and vertical directions between superficial profile of signals on recto and verso of the find it is possible to obtain the coherence factor behavior. Great value of coherence factors signify a similar structure of signals in verso and recto.
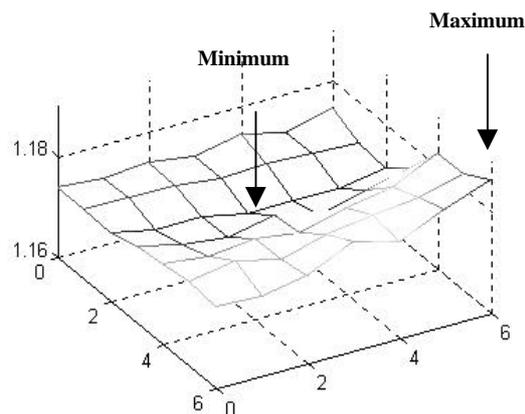

Fig. 8: spatial coherence coefficient
for a quarter of find surface

Looking at Fig. 8, it is possible to see how this happens in the center of find where it is possible to forecast the maximum value of resistance caused by oxidation. Low values of coherence function signify a separation of signals in recto and verso and suggest a spatial displacement between pricks that explore surfaces of find. This can also suggests that there exists a spatial displacement caused by mechanical arrangement.

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