Electrophysical Characterisation of Powders†

R. Ciccu, M. Ghiani and A. Serci
University of Cagliari, DIGITA Dpt.*
G. Ferrara
University of Trieste, DICAMP Dpt.**
P. Massacci
University of Rome “La Sapienza”, ICMMPM Dpt.***

Abstract

The paper reviews methods for the electrophysical characterisation of powders and particles and describes in detail many of the laboratory units especially designed for this purpose at the Cagliari University. In particular, the following characteristics can be measured or calculated for powders and particles: (a) electrical conductivity as a function of temperature; (b) thermoelectric potential difference; (c) Seebeck coefficient; (d) electron work function; (e) position of the Fermi level referred to the valence band upper edge; (f) width of the forbidden energy gap; (g) either type of charge carrier concentration (n concentration of electrons in the conduction band, p concentration of free holes in the valence band); (h) either type of charge carrier mobility; (i) electrical charge of powders or single particles; (j) triboelectric charging with different systems. Detailed drawings of the laboratory equipment are provided for each unit used to measure the above-mentioned characteristics, as well as the experimental procedure for both fine powders and single particles. The paper also provides the theory on which the experimental procedure is based and the calculation methods.

1. Introduction

The electrophysical characterisation of powders is highly important in a number of processes involving mineral separation, dust collection, coating materials, handling bulk solids, transporting and mixing powders and particles, and agriculture among others. The influence of the powders' electrophysical characteristics on most of these processes was studied empirically in the past; more intensive studies were conducted only about 30 years ago using the solid-state physics. The most significant early studies dating back to the sixties, in particular related to flotation, electrostatic and triboelectric separation, are those by Plaksin et al. [1, 2], Hoberg [3], Carta et al. [4, 5, 6], Revniytsye et al. [7], reported also by Schubert [8].

Since the sixties, the University of Cagliari has devoted great effort to conducting both theoretical and experimental research on the electrophysical characteristics of powders and particles and their influence on electrostatic and triboelectric separation, as well as on wet separation systems such as flotation. The collaboration of Professor P. Manca [9, 10, 11] at the Institute of Solid State Physics has been of great importance in this effort. A number of new laboratory units were designed and set up to measure certain physical quantities that make it possible to calculate the electrophysical parameters which describe both surface and bulk energy states of minerals, and powders and particles in general.

After a concise preliminary review of the solids' energy bands theory, this paper describes the laboratory equipment in detail; the mathematical relationships between the relevant physical quantities are also provided and discussed. In addition, the correlation between the electrophysical parameters and the energy exchange phenomena on which the behaviour of solid particles during the separation processes is based is explained and discussed. The laboratory equipment described in this paper was already presented in 1974 (Ciccu et al., [12]), although it had a very limited audience as it was published in Italian.
2. Energy Level Band Theory

The behaviour of solids in electric conduction can be described with the energy level band model [13, 14]. In solids, the electron energy levels can lie in allowed energy bands that may overlap or be separated by forbidden gaps. The uppermost allowed band is the conduction band where electrons move freely under the action of an electric field; in metals this band is only partially filled, while in semiconductors and insulators it is empty. A more or less wide forbidden gap separates the conduction band from the underlying valence band where the electrons are strictly bound to the atoms. At temperatures above 0 K, some electrons may acquire enough energy to jump up to the conduction band (if the forbidden gap is not too wide as in insulators), leaving holes in the valence band. In this way, electric conduction occurs through the movement of electrons in the conduction band and holes in opposite direction in the valence band, even if their mobility differs, as will be explained later.

The description above refers to ideal solids whose crystal lattice is perfect, i.e. it extends indefinitely and has no defects or impurities (intrinsic semiconductor). Actually, localised energy levels lie in the forbidden gap in real solids due to impurities or imperfections in the crystal lattice (natural or intentionally produced) [11, 15, 16], or due to the abrupt interruption of crystal lattice periodicity [17, 18]. These energy levels may be donor levels if occupied by electrons or acceptor levels if empty and hence able to receive electrons coming from the valence band. Accordingly, semiconductors are called n-type or p-type and the electric conduction occurs involving electrons in the conduction band and holes in the valence band. The two types of energy levels may also coexist in the forbidden gap: in this case, both electrons and holes independently contribute to electric conduction. In any case, the minimum energy needed for starting conduction equals the energy difference between the lower limit of the conduction band and the donor level, or between the acceptor level and the upper limit of the valence band.

The Fermi level $E_F$ encompasses the energy status of a solid. It gives the average energy of the electrons involved in the exchanges taking place in electric and electrochemical phenomena. In a semiconductor without defects or impurities, the Fermi level lies exactly at the centre of the forbidden gap (intrinsic semiconductor). In a more general case, $E_F$ may lie in the upper part of the forbidden gap if donor levels prevail or in the lower part if acceptor levels prevail (extrinsic semiconductor).

In addition to the Fermi level $E_F$, the other electro-physical parameters needed to define the energy status of a solid more completely are:

- the work function, $\Phi$, the energy required to remove an electron from the Fermi level to the vacuum level (reference level);
- the width of the forbidden energy gap, $E_g$;
- the charge carrier concentration of either type ($n$, concentration of free electrons in the conduction band; $p$, concentration of holes in the valence band);
- the charge carrier mobility of either type, $\mu_n$ or $\mu_p$.

Fig. 1 shows the energy band model where localised levels in the forbidden band occur as a consequence of impurities or crystal lattice defects. Figs. 1a) and b) refer to an n-type semiconductor: at ambient temperature, electric conduction is only due to electrons which have jumped from the donor level to the conduction band where they move freely under the action of an electric field. As absolute temperature $T$ increases, an increasing number of electrons in the valence band receive enough energy to overcome the energy gap $E_g$, so they jump to the conduction band. Thus, the semiconductor becomes an intrinsic semiconductor when electrons which have jumped from the valence to the conduction band prevail over the electrons coming from the donor levels in the forbidden gap (whose quantity is obviously limited). At the same time, a number of holes equal to the number of electrons which have jumped are generated in the valence band, further contributing to electric conduction with p-type carriers. The Fermi level initially lies between the donor level and the bottom of the conduction band; as the temperature increases, it gradually moves downwards towards the centre of the forbidden gap, which is reached when the ratio of electrons/holes involved in conduction practically reaches unity.

![Fig. 1](image-url)

Fig. 1 Energy band model for: (a) n-type semiconductors; (c) p-type semiconductors. Figures (b) and (d) show how the Fermi level moves towards the centre of the forbidden band as absolute temperature increases.
Likewise, the acceptor levels lie in the lower part of the forbidden energy gap in p-type semiconductors (Figs. 1c and d). Therefore, electrons in the valence band with relatively low energy can jump and fill the acceptor level, thus producing holes in the valence band capable of p-type electric conduction in the same band. As the absolute temperature T increases, an increasing number of electrons in the valence band receive enough energy to overcome energy gap $E_g$, and thus jump to the conduction band. The semiconductor becomes an intrinsic semiconductor when the electrons which have jumped from the valence band to the conduction band prevail over the holes left by the electrons which have jumped from the valence band to the acceptor energy levels in the forbidden gap (which can be rapidly filled). The Fermi level, initially lying between the top of the valence band and the acceptor level, gradually moves upwards towards the centre of the forbidden band as the temperature increases.

Fig. 1 also shows the energy levels (referring to the vacuum level) corresponding to work function $\phi$; this gives the mean energy needed to extract an electron from the crystal lattice. Fig. 1 provides a simplified explanation of these phenomena as it refers only to the semiconductor surface, even if the internal part of the solid close to the surface is also involved. For a more detailed explanation, see the papers of Carta et al. [5], Revnivtzev et al. [7], and Schubert [8].

The relevant parameters can be determined by measuring electrophysical quantities such as:
- the difference in contact potential between the sample and a reference electrode; work function $\phi$ can be calculated from this;
- the electric conductivity in the intrinsic zone of the semiconductor, whose gradient gives the forbidden gap width;
- the thermoelectric effect which makes it possible to determine the Fermi level and, hence, calculate the charge carrier concentrations and also to define the type of conduction.

Methods and units used for measuring such electrophysical quantities are illustrated in the following sections. The values of the parameters describing the surface energy status of powders and particles of solids can be calculated from these quantities. In addition, a special section is devoted to measuring the contact electric charge, a phenomenon that can be well explained by using the band energy model.

3. Measuring Electric Conductivity and Forbidden Gap Width

Electric conductivity depends on the number of charge carriers and their ability to move under the action of an electric field. It is expressed as [10, 19]:

$$\sigma = q \cdot n \cdot \mu_n + q \cdot p \cdot \mu_p$$  \hspace{1cm} (1)

where:
- $\sigma$: electric conductivity \hspace{1cm} (S·cm$^{-1}$)
- $n$: concentration of free electrons \hspace{1cm} (electrons·cm$^{-3}$)
- $p$: concentration of holes \hspace{1cm} (holes·cm$^{-3}$)
- $\mu_n$: mobility of free electrons \hspace{1cm} (cm$^2$·V$^{-1}$·s$^{-1}$)
- $\mu_p$: mobility of holes \hspace{1cm} (cm$^2$·V$^{-1}$·s$^{-1}$)
- $q$: electron charge \hspace{1cm} (1.602·10$^{-19}$ C)

Eq. (1) is valid in the semiconductor’s intrinsic zone. However, it is also valid in the extrinsic field when the number of minority charge carriers is significant compared with the number of majority carriers.

As in the intrinsic zone $n=p=n_i$, Eq. (1) becomes:

$$\sigma = n_i \cdot q \cdot (\mu_n + \mu_p)$$  \hspace{1cm} (2)

and, if the electron mobility is much higher than hole mobility:

$$\sigma = n_i \cdot q \cdot \mu_n$$  \hspace{1cm} (3)

Since:

$$n_i = \frac{2(2\pi mkT)^{3/2}}{h^3} \left( \frac{m_n \cdot m_e}{m^2} \right)^{3/4} \exp(-E_g/2kT)$$  \hspace{1cm} (4)

where:
- $m$: free electron mass \hspace{1cm} (9.11·10$^{-31}$ kg)
- $h$: Planck’s constant \hspace{1cm} (6.624·10$^{-34}$ J·s)
- $m_n$: effective mass of an electron \hspace{1cm} (kg)
- $m_p$: effective mass of a hole \hspace{1cm} (kg)
- $T$: absolute temperature \hspace{1cm} (°K)
- $k$: Boltzmann’s constant \hspace{1cm} (1.38·10$^{-23}$ J·K$^{-1}$)
- $E_g$: forbidden gap width \hspace{1cm} (eV)

Eq. (3) becomes:

$$\sigma = q \cdot \frac{2(2\pi mkT)^{3/2}}{h^3} \left( \frac{m_n \cdot m_e}{m^2} \right)^{3/4} \exp(-E_g/2kT) \cdot \mu_n$$  \hspace{1cm} (5)

If the product of the effective masses is constant and the mobility of free electrons is proportional to $T^{-3/2}$ (lattice diffusion), the result is:

$$\sigma = A \cdot \exp(-E_g/2kT)$$  \hspace{1cm} (6)

where:
- $A$: constant
- $E_g$: $E_{g0} + aT$
- $E_{g0}$: forbidden gap width at 0°K
According to Eq. (6), if conductivity \( \sigma \) is plotted in a logarithmic scale against the reciprocal absolute temperature, a straight line is obtained whose slope in the high temperature zone (where the semiconductor is intrinsic) gives the width of the forbidden band \( E_g \) (e.g., see Fig. 1 of paper [6]).

The apparatus described in Fig. 2 was developed to measure \( \sigma \) in powders. The sample is introduced into a cylindrical cavity delimited by a high-resistivity ceramic body between two cylindrical copper electrodes. The axes of the electrodes have been bored; so thermistors can be inserted to measure the temperature at the electrodes’ ends (Fig. 3). The powder sample with the desired size composition is then pressed between the two electrodes. These electrodes can be heated up to 600-700°C with an electric resistance around a ceramic sleeve. The compression of the powder is obtained by applying a pressure with maximum load of 10 kN. The apparatus is located inside a vacuum-sealed stainless steel vessel with a control window. After the vacuum has been achieved, the vessel is filled with an inert gas (argon) and the heating of the electrodes begins.

The relevant data are measured forwards (as temperature increases), and backwards (as temperature decreases). Electrodes a, b, c, d, e, and f are connected to the circuit (b) in Fig. 2 to measure the electric conductivity.

All the connections are made with shielded cables and Amphenol connectors. Earthing resistance must be less than 2 \( \Omega \).

Electric conductivity \( \sigma \) (S \( \cdot \) cm\(^{-1} \)) is calculated with the following equation:

\[
\sigma = \frac{I \cdot l \cdot s}{V_+ + V_-} 
\]

where:
- \( I \) electric current (mA)
- \( l \) distance between the electrodes (cm)
- \( s \) electrode’s cross-section (cm\(^2\))
4. Measuring the Thermoelectric Effect

The thermoelectric potential difference between two extremities of a solid depends on the diffusion of electrons and holes inside the solid where a temperature gradient exists. The Seebeck coefficient $\alpha$ (mV/°C) is the ratio between the thermoelectric potential difference and the temperature difference between the extremities of the sample, connected to a high impedance voltmeter.

The Seebeck coefficient may be from 100 to 1,000 times higher in semiconductors than in metals. Hence, the metals in the circuit do not influence the measurement. This coefficient may vary rapidly with temperature and greatly depends on the concentration of impurities in the semiconductor. There are equations that give the Seebeck coefficient for both intrinsic and extrinsic semiconductors. For extrinsic semiconductors, Putley [20] gives:

$$\alpha = -\frac{k}{q} \left[ \frac{P+5/2-E_v}{kT} \right]$$  \hspace{1cm} (8)

where $P$ is a constant and $E_v$ is the Fermi level (eV) (referred to the valence band upper edge) given by:

$$E_v = kT \cdot \ln \frac{n \cdot h^3}{2(2\pi m^*_v)3\frac{3}{2}}$$  \hspace{1cm} (9)

The symbols are the same as in the preceding section.

When impurities prevail, the Seebeck coefficient is:

$$\alpha = \pm \frac{k}{q} (A-\eta)$$  \hspace{1cm} (10)

where:

$$\eta = \frac{E_g}{kT} \quad \text{for p-type semiconductors}$$

$$\eta = \frac{E_g-E_v}{kT} \quad \text{for n-type semiconductors}$$

In Eq. (10), the + sign refers to p-type and the − sign to n-type semiconductors. Given $\alpha$ and $E_g$ (eV), it is possible to calculate Fermi level $E_v$. Constant $A$ is assumed equal to 2 in the case of diffusion processes due to thermal vibration of the crystal lattice, and equal to 4 in the case of diffusion processes due to impurities and crystal defects.

For intrinsic semiconductors, Johnson [21] developed an expression incorporating: ratio $b$ between the mobility of electrons and holes, forbidden gap width and the ratio between the effective masses of electrons and holes:

$$\alpha = -\frac{k}{q} \left[ \frac{b-1}{b+1} \frac{E_v/2kT}{2(b-1)+\frac{3}{4} \ln(m^*_h/m^*_e)} \right]$$  \hspace{1cm} (11)

If the forbidden band amplitude and temperature are assumed to have a linear relationship, according to an arithmetic scale diagram where the Seebeck coefficient is plotted against the reciprocal absolute temperature, one can obtain slope $\Theta$ and intercept $c$ which defines the straight line:

$$\alpha = \Theta/T + c$$  \hspace{1cm} (12)

where:

$$\Theta = -\frac{k}{q} \left[ \frac{b-1}{b+1} \right] \frac{E_g/kT}{2(b-1)+\frac{3}{4} \ln(m^*_h/m^*_e)}$$

and

$$c = -\frac{k}{q} \left[ \frac{b-1}{b+1} \right] \frac{a}{2k} + \frac{3}{4} \ln\left( \frac{m^*_h}{m^*_e} \right)$$

Since $E_g$ is known (calculated by measuring the electric conductivity), one can obtain ratio $b$ between the electron and hole mobility using the equation:

$$b = \frac{E_g-2\Theta q}{E_g+2\Theta q}$$  \hspace{1cm} (13)

or the approximate equation:

$$b = \left| \frac{m^*_h}{m^*_e} \right|^{\frac{5}{2}}$$  \hspace{1cm} (14)

The thermoelectric potential difference can be measured with the same cell used for the electric conductivity according to circuit (c) of Fig. 2. The sample with the desired size composition is introduced into the measurement cell between the two copper electrodes: after the vacuum is achieved and the inert gas is introduced, only one electrode is heated up to 300-400°C. The thermoelectric potential difference is measured when the temperature decreases. The temperature difference between the electrodes is measured by the thermistors connected with an electrometer. All the connections are made with cables and Amphenol-type connectors. Grounding resistance is lower than 2 Ω. An example of determining the Seebeck coefficient is given in Fig. 2 of paper [6].

5. Measuring the Electric Charge

When two solids (metals or semiconductors) are placed in contact, a flow of electrons moves from the material with the higher Fermi level (lower work function) to the other until the Fermi level energies of
both materials are equalised. For example, a semiconductor whose Fermi level is lower than a metal will extract electrons from the metal, and assumes a negative charge (not only on the surface but also in the layer near the contact). Conversely, a semiconductor whose Fermi level is higher than a metal will supply electrons to the metal, and assumes a positive charge.

In a nutshell, if $\Phi_m$ and $\Phi_s$ are the work functions of the metal and the semiconductor, we will have the following when the solids are placed in contact:

positive semiconductor
negative metal for $\Phi_m > \Phi_s$

negative semiconductor
positive metal for $\Phi_m < \Phi_s$

More details on this phenomenon and on the distribution of charges near the contact zone in semiconductors can be found in the paper of Carta et al. [5].

The contact charge can be obtained in the lab by letting the particles slide on vibrating chutes or by injecting them into an air cyclone where friction occurs in the inner wall.

5.1 Vibrating Chute Method

In general, the contact charge must be measured in a controlled atmosphere. The device sketched in Fig. 4 has been used to achieve this. The compressed air, partially dehumidified in two collecting reservoirs (not shown in the figure), is fed into vessel G (controlling the pressure with needle valve V and manometer M), and is dehumidified to about 3% by passing it through many silica gel beds. Then, the air is fed to an electrically heated coil where the temperature can reach about 70°C, and finally it is fed into a Perspex box (internally shielded through an earthed copper cage) where the vibrating chute and the Faraday well are located (Fig. 5). This apparatus lies on a non-vibrating table. The air enters the vessel through many inlets in order to rapidly obtain constant characteristics inside the box. The requested conditions are controlled by a thermometer and a hygrometer. The chute on which the particles slide is earthed and rigidly fixed (though electrically insulated) to a vibrator capable of variable amplitude by means of a rheostat. The Faraday well consists of a metal cylinder (10 cm diameter, 30 cm height) shielded by an earthed coaxial cylinder with a conical frustum-shaped cover with a circular hole on top for the passage of the particles. A Teflon block insulates the two coaxial cylinders. The particles fall into the Faraday well connected to an electrometer, which measures the electric charges in coulomb. The electrometer is connected to a recorder. The Faraday well rests on a high-accuracy scale in order to weigh the particles and calculate the specific charge (C/g).

The charge of differently sized individual particles can be measured from about 2 mm down to 0.5 mm with statistical procedures. After at least one hour under controlled atmosphere, particles are fed through a suitable dosing device on the chute where they slide and fall one at a time into the Faraday well.

The particle charge can be determined under controlled atmosphere in air or inert gas with the apparatus of Fig. 5. A more recent version of the apparatus has been constructed for measurements in vacuum as well, and for a larger range of vibration frequency and amplitude, as well as contact time. In this way, different rubbing systems can be simulated from gentle sliding, to high-velocity impingement [22, 23, 24, 25, 26].
Fig. 6 shows a photo of the apparatus consisting of three parts: a system for charging the particles, a device for feeding charged particles into the Faraday well, and a system for containing particles before processing. This apparatus is hosted in a vacuum vessel.

The charging system consists of a vibrating plate suspended on two springs and actuated by a set of two opposite main electromagnets. The plate can be heated to a desired temperature controlled by a thermocouple, and an interchangeable surface manufactured using whatever material can be fixed over it for triboelectric charging. Surface vibration amplitude is set in each test, while frequency can vary between 2 and 24 Hz during the test. Retention time of the particle on the charging surface can vary from one second to one hour. The surface is kept horizontal during the charging phase, at the end of which it is inclined downwards, thus directing the particles towards the Faraday well when the electric charge must be measured.

Two additional electromagnets feed charged particles into the Faraday well. One of them inclines the surface, the second produces a controlled vibration. When particles stick to the surface due to the high acquired electric charge, the two main electromagnets can be deployed to detach these particles.

The particle dispenser consists of two independent superimposed stainless steel discs. The top disc has steel brushes attached under it that delimit a number of places (between the brushes) where single particles or groups of particles can be placed in a round channel engraved in the bottom disc. The bottom disc is fixed and has a hole where the particles fall onto the vibrating charging chute which drives them into the Faraday well. The top disc rotates by steps through a driving gear controlled by a photoelectric cell, so that particles are sent to the charging chute at spaced time intervals.

All the operations in the steel vacuum vessel are controlled and monitored, and charges are measured by means of an electrometer and a recorder.

5.2 Air Cyclone Method

The air in the apparatus sketched in Fig. 7 comes from a compressor with automatic pressure control and oil filter, and it is directed into two passive accumulators with total capacity of 0.1 m³. A set of valves discharges the condensed water. A constant pressure of 0.5 MPa is obtained in the last accumulator. The air dehumidification system is indicated in Fig. 7, which also shows the hygrometer (4) for monitoring air humidity. The air flow rate is controlled by means of a rotameter and then sent to the cyclone charging system where the particles from the cyclone apex go directly into the Faraday well. Temperature and pressure are monitored in the charging system, and there are two systems for feeding particles: the first (12) for bulk feeding of fine powders and the second (13) for feeding single particles. In system (12) the particles are conditioned either with the air circulating in the cyclone or in the Perspex vessel; system (13) gives only the last possibility. In any case, particles should be heated at a given temperature before each test. Other gases can be used as an alternative to compressed air.

The terminal part of the apparatus, shown on the right in Fig. 7, can be manufactured with different materials; in particular, the cyclone can be replaced to study the behaviour of various materials in the contact charging as well as to study the influence of the cyclone geometry. Preferably, the solid to be charged must be classified in narrow size ranges, especially for study of charging single particles. Statistical significance for determining the average charge of single sized particles requires measurements on at least 200 particles.

The measurement results of the triboelectric charge may vary widely depending on different factors, for example:

- the contact system used and its energy: gentle or stronger sliding in a chute, rubbing in an air cyclone or rotating device, charging by impact;
- the crystal size, orientation and surface affected by charging;

![Apparatus for measuring the triboelectric charge on individual particles. This apparatus is contained in a Leybold-Heraeus steel vacuum vessel.](image-url)
the surrounding atmosphere in equilibrium with the crystal surface.

Therefore, different systems give different charge values [27]. For example, in an air cyclone, one obtains electric charges ten times higher than in a sliding chute [24]. However, the polarity of the charge chiefly depends on the work function difference between the solids in contact.

Recently, other charging systems have been studied, sometimes according to the needs of the research: charging single particles by impact [28], charging powders in pipes during pneumatic transport [29].

6. Measuring the Work Function

The Fermi level position, defined by the Work Function $\Phi$, determines the polarity of electric charges. In the triboelectric charging of two solids, the one with the higher Fermi level (i.e., the lower work function) gives electrons to the other which becomes negatively charged, while the first solid becomes positively charged. The following methods can be used to determine the work function:

- photoelectric method,
- thermoionic method,
- ionisation method
- Kelvin method.

6.1 Fundamentals for Measuring the Work Function

a) Photoelectric Effect

The energy of electrons emitted from a surface subsequent to an incident monochromatic radiation can be determined by measuring the potential $V$ needed to decrease down to zero the photoelectric current:

$$V \cdot q = h \cdot v - \Phi$$

where:

- $v$ wavelength of the incident radiation (cm);
- $h$ Planck's constant ($6.624 \cdot 10^{-34}$ J·s);
- $\Phi$ work function (eV);
- $q$ electron's charge ($1.602 \cdot 10^{-19}$ C).

b) Thermoionic Effect

Electrons are spontaneously emitted from a high-temperature solid. The current density of this emission is given by the Richardson-Fermi expression:

$$J_s = A \cdot t^2 \cdot e^{-\Phi/kT}$$

where:

- $A$ constant;
- $T$ absolute temperature (°K);
- $k$ Boltzmann's constant ($1.38 \cdot 10^{-23}$ J·K$^{-1}$);
- $t$ time (s);
- $\Phi$ can be calculated by measuring $J_s$ and plotting log $J_s$ against 1/T.

c) Ionisation

When ionised gas is present between two facing solids, the ions are attracted depending on the Fermi levels: positive ions migrate towards the surface with the higher Fermi level, negative ions towards the surface with the lower Fermi level. Consequently, ions act as an electric connection allowing the Fermi levels of the two solids to equalise. The contact potential difference between the solids is:

$$V_c = (\Phi_1 - \Phi_2)/q$$

where $\Phi_1$ and $\Phi_2$ are the work functions of the reference solid and unknown solid, and $q$ is the electron charge.
d) Kelvin Method

According to the classical Kelvin method [30] (Fig. 8a), two facing samples A and B (A with known work function; B, unknown) form a capacitor with capacitance $C_1$. The two capacitor plates are electrically connected with switch K so that negative charge $Q$ flows from A (with the lower work function) to B until the Fermi levels of the two solids equalise. In this way, the contact potential difference $V_0$ is established between the two plates.

When switch K is closed, the moved charge will be $Q = C_1 V_0$. When switch K is open and the distance between the plates is increased, the capacitance will be strongly reduced to $C_2$. Therefore, since $Q$ is constant, the potential difference $V_E$ becomes much higher than $V_0$ according to:

$$V_E = V_o(C_1/C_2)$$  \hspace{1cm} (18)

The increasing distance between the capacitor plates only serves to increase the potential difference measured by electrometer E.

Another measuring system consists of inserting a potential difference just equal to $V_0$ into the circuit of Fig. 8a) to counteract the contact potential difference. This way, the increased distance between the plates with K open will not effect any increase in the potential difference measured by the electrometer, as the voltage applied to the circuit exactly compensates the contact potential difference. Hence we know $V_0 = (\phi_1 - \phi_2)/q$, and we obtain $\phi_2$ if $\phi_1$ is known.

The modified Kelvin methods involve producing a relative motion of the plates (or the samples acting as plates) of the capacitor, thus generating an alternating current that can be nullified by applying a given voltage (counteracting the contact potential difference) (Fig. 8b) [31].

The following methods were set up to determine the work function:
- vibrating capacitor;
- rotating capacitor;
- ionisation.

6.2 The Vibrating Capacitor Method

If $V_c$ is the contact potential difference between the plates of a vibrating capacitor, its capacity varies according to the equation $C(t) = C_0 \cos mt$ and the electric current will be:

$$i = V_c \frac{dC}{dt} = -V_c \omega C_0 \cos mt$$

The following potential difference can be measured at the extremities of resistance $R_1$:

$$V_1 = -V_c \omega R_1 C_0 \cos(mt + \phi)$$

where $\omega$ is the angular frequency, and $\phi$ the phase shift produced by circuit capacitance $C$ depending on capacitor $C_s$ and $R_1$.

Potential difference $V_1$ is generally much lower than $V_c$ because capacitance $C$ is only a few pF; the vibration frequency $f = \omega/2\pi$ is about 100 Hz; the maximum value of $R_1$ is limited by $C_s$. In general, the required signal is highly disturbed subsequent to undesired noise in the apparatus. A phase-sensitive detector is used to eliminate the signals which do not correspond to the vibrating capacitor frequency, thus discriminating the signal from disturbances.

Fig. 10 shows the measuring circuit. The low-frequency oscillator (<100 Hz) (1) actuates the electromagnetic vibrator (9) through the power amplifier (2). Potential difference $V_1$ occurring at the extremities of resistance $R_1$ is amplified in the low-noise amplifier (5). As indicated before, the phase shifter (3) and the phase-sensitive detector (4) are needed.
During measurements, the phase shifter is used to maximise the phase-sensitive detector deviation. In fact, this maximum deviation is proportional to the contact potential difference, provided that other conditions are equal. The measuring method consists of using the potentiometer (6) to balance the contact potential difference $V_c$ until the signal from the phase-sensitive detector reaches zero. The instruments used in the circuit in Fig. 10 are:
- a high-frequency-range video oscillator (model TF 88S A/1, Marconi Instruments) with amplifier and continuously variable output;
- a cathode-ray oscilloscope with 1 MΩ input impedance (model 104, Hewlett-Packard);
- an electrometer with input impedance up to $10^{14}$Ω (model 610 B, Keithley Instruments);
- a potentiometer that can produce a minimum of $10^{-3}$ of the battery voltage; it is equipped with a voltmeter whose sensitivity is $10^{-3}$ V (model 2227, Yokogawa Electric Works);
- a phase shifter that can shift the phase by about 180° (model 421, Brookdeal);
- a phase-sensitive detector with a 1 Hz to 1 MHz frequency range (model 471, Brookdeal).

In practice, only gold or platinum can be used as reference metals to measure the work function of different materials due to their resistance to oxidation. In our case, gold was preferred as its work function is well known: measurements made by many researchers indicate that the gold work function is 4.71 eV, which is assumed as the reference value.

In Fig. 11, the reference electrode (1) is fixed at the lower extremity of a hollow Teflon rod and connected to the potentiometric circuit with a cable passing through the same rod. The sample (2) is pasted with a suspension of colloidal silver to a gold disc (3) which is fixed through the screw (4) to a site made in the support arms (6). The Teflon block (7) is an insulator; the shielded cable and amplifier connection is shown in (8). The disc (3) and the support arms (6) are gold-plated to avoid superimposing the potential contact differences of other metals. This apparatus is inside a vacuum container with vacuum-sealed electric connections.

6.3 The Rotating Capacitor Method

Fig. 12 shows the electric circuit. As in the vibrating capacitor method, a periodic current is generated with the rotating capacitor. Since the periodic current...
is weak, the signal must be amplified before being displayed on the oscilloscope. If a voltage balancing the contact potential difference $V_c$ is applied to the plates of the rotating capacitor through a potentiometer, one obtains:

$$i = dq/dt = V \cdot dc/dt = 0$$

Hence, when the sine wave displayed by the oscilloscope is minimised by acting on the potentiometer, the voltage will equal the contact potential difference.

Since the voltage of the battery may not be constant, the potential difference must be measured in the potentiometric circuit using a high-precision electronic voltmeter. To reduce high-frequency disturbances, the signal is sent in a low-pass filter before the oscilloscope. The instruments used in the measuring circuit are:

- a potentiometer that can provide a minimum of $10^{-3}$ of the battery voltage; it is equipped with a voltmeter with sensitivity of $10^{-3}$ V (model 2227, Yokogawa Electric Works);
- an electronic voltmeter whose sensitivity is $10^{-4}$ V (model 419 A DC null voltmeter, Hewlett-Packard);
- an electrometer with input impedance up to $10^{14}$ Q (model 610 B, Keithley Instruments);
- a cathode-ray oscilloscope with 1 MΩ input impedance (model 104, Hewlett-Packard).

**Fig. 13a** shows the assembly of the rotating capacitor and **Fig. 13b** shows the gold rotating electrode with two symmetric reliefs on the plate (A electrodes). Plate B rotates through plate shaft D, joint E and drive shaft D. The electric connection with the electrodes A is obtained through a sliding contact (graphite brush). The connection with sample P is made through a shielded cable in T. H and F are insulating Teflon blocks. Sample holder S is gold-plated to avoid superimposing the potential contact differences of other metals. The rotating capacitor is shielded with an earthed Faraday cage; chassis L and the motor are earthed as well. The measurements can be made under ambient conditions or inside a vacuum container with vacuum-sealed electric connections.

### 6.4 Ionisation Method

**Fig. 14** shows the electric circuit. The contact potential difference is:

$$V = i_1 \cdot R + e_1 = e_1(1 + R/r_1) \tag{19}$$

where:
- $R$ ionised air resistance ($\Omega$);
- $e_1$ voltage drop at the extremities of the $r_1$ resistance (mV);

Replacing resistance $r_1$ with resistance $r_2$ one obtains:

$$V = i_2 \cdot R + e_2 = e_2(1 + R/r_2) \tag{20}$$

and by equating expressions (19) and (20), $R$ can be calculated:

$$R = (e_1 - e_2)/(e_1/r_1 - e_2/r_2)$$

By substituting $R$ in Eqs. (19) or (20), the contact potential difference $V$ can be obtained. To this end, measuring the voltage drops $e_1$ and $e_2$ is sufficient.
The measuring circuit includes:
- a resistance varying from $10 \Omega$ to $10^{14} \Omega$;
- an electrometer with input impedance up to $10^{14} \Omega$ (model 610 B, Keithley Instruments);
- a low-impedance voltmeter recorder;
- an ionising source, consisting of a tablet activated with Radium-226 inserted into an Ag base plate and an Au plate, with a specific activity of 185,000 disintegrations per second.

Fig. 15 shows the assembly of the ionisation chamber. It consists of a metallic cylinder with two vacuum-sealed caps and four vacuum-sealed windows to inspect the ionising zone. Two pipes connect the vacuum pump and fill the cylinder with a gas as required. The sample is fixed to a holder in a colloidal silver paste. This holder is suspended by three adjusting screws and earthed. The ionising source is inserted into a cavity on a gold plate under the sample in order to reduce the radiation angle. In this way, only the space in front of the sample is irradiated. The base plate of the ionising source lays on a Teflon block and is connected to the external electric circuit by means of a shielded cable. The electric connection is vacuum-sealed. Measuring the distance between the electrodes and their parallel setting is very important. This can be obtained optically through the windows using a light source, a lens and a screen, where the distances are indicated.

The sample whose work function is being determined may be a metal, a mineral or a compacted powder. A powder can be compacted by using a press capable of reaching 60 MPa.

7. Measuring the Concentration of Electrons and Holes

The electrophysical characteristics below are necessary to define the energy structure of semiconductors in terms of average behaviour:

- $E_t$ Fermi level, referred to the valence band upper edge (eV);
- $E_g$ forbidden gap width (eV);
- $n, p$ concentration of charge carriers, n-type (electrons) and p-type (holes), expressed in number of charge carriers per cm$^3$;
- $\mu_n, \mu_p$ mobility of n-type and p-type charge carriers, expressed in cm$^2$.V$^{-1}$.s$^{-1}$

The concentration of charge carriers $n$ and $p$ and their ratio can be determined by both indirect and direct (Hall effect) methods.

7.1 Indirect Method

The following equation links the quantities $E_t$, $E_g$ and $p/n$ [32]:

$$E_t = \frac{1}{2} E_g - \frac{1}{2} kT \cdot \ln \frac{p}{n}$$  \hspace{1cm} (21)

where $k$ is Boltzmann's constant and $T$ the absolute temperature.

Therefore, after calculating $E_t$ and $E_g$ through the experimental procedures described in sections 3 and 4, the $p/n$ ratio can be calculated. In addition, if $p/n$ is known, the absolute values of the charge carrier con-
Concentrations \( p \) and \( n \) can be calculated with the following equation [16, 19].

\[
p \cdot n = (2U \cdot T^{3/2})^2 \exp \left( - \frac{E_g}{kT} \right)
\]

where \( U \) is a constant equal to \( 2.42 \cdot 10^{15} \text{ cm}^{-3} \text{ K}^{-3/2} \).

### 7.2 Direct Method

If an electric current \( I_x \) (x axis) flows in a semiconductor (Fig. 16) of size \( d \) (y axis) and thickness \( h \) (z axis), a potential difference forms along the z axis when a magnetic field \( H_y \) is applied [19]:

\[
V_H = 10^{-12} \frac{R_H I_x H_y}{d}
\]

where:
- \( V_H \) Hall voltage (mV);
- \( I_x \) Hall current (mA);
- \( H_y \) magnetic field strength (T);
- \( d \) size of the sample (cm);
- \( R_H \) Hall coefficient (cm$^3$/C)

\( R_H \) value (constant) depends on the material, the temperature and the impurity content.

Measuring the sign of the \( V_H \) voltage makes it possible to determine the conduction type: p-type (positive sign) or n-type (negative sign). \( R_H \) gives information on the sample characteristics. The general expression of \( R_H \) is:

\[
R_H = -\beta \frac{\mu_n \mu_p - \mu_p^2}{\mu_n + \mu_p}
\]

where \( \beta \) equals 3\pi/8 for diffusion due to thermic vibrations, and 1.93 for diffusion due to impurities.

When the semiconductor is in a temperature range where one type of charge carrier concentration predominates over the other, the following simple equations can be used to determine the charge carrier concentration \( n \) and \( p \):

\[
n = -\beta \left( \frac{1}{q R_H} \right) \quad \text{for n-type semiconductors}
\]

\[
p = +\beta \left( \frac{1}{q R_H} \right) \quad \text{for p-type semiconductors}
\]

The charge carrier mobility can be calculated with the equations:

\[
\mu_n = -\frac{R_H \sigma}{\beta} \quad \text{for n-type semiconductors}
\]

\[
\mu_p = +\frac{R_H \sigma}{\beta} \quad \text{for p-type semiconductors}
\]

where \( \sigma \) is the electric conductivity determined as explained in section 3.

For intrinsic semiconductors, where \( n=p=n_i \), we have:

\[
\sigma = n_i q (\mu_n + \mu_p)
\]

\[
n_i = 2 \frac{(2\pi m_k T)^{3/2}}{h^3} \left( \frac{m_n m_p}{m^2} \right)^{3/4} \exp \left( - \frac{E_g}{2kT} \right)
\]

\[
R_H = -\beta \frac{\mu_n^2 - \mu_p^2}{n_i q (\mu_n + \mu_p)^2} = -\beta \left( \frac{b-1}{q \cdot n_i \cdot b+1} \right)
\]

where:
- \( m \) mass of the electron (9.11$\cdot 10^{-31}$ kg);
- \( h \) Planck's constant (6.624$\cdot 10^{-34}$ J$\cdot$s);
- \( m_n \) effective mass of an electron (kg);
- \( m_p \) effective mass of a hole (kg);
- \( b \) ratio between the mobility of electrons and holes.

Combining Eq. (29, (30) and (31), one obtains:

\[
R_H = -\beta \frac{h^2 \exp \left( E_g / 2kT \right)}{q \cdot b+1} \quad \text{that can be written in the form}
\]

\[
R_H T^{3/2} = \left( \text{constant} \right) \exp \left( E_g / 2kT \right)
\]

The slope of line log \( R_H T^{3/2} \) versus \( T^{-1} \), gives the value of \( E_g \)/4.61-k, where \( k \) is Boltzmann's constant.

When both types of charge carriers have to be taken into consideration, the following equations can be used:

\[
n \cdot p = \text{constant}
\]

\[
\begin{align*}
\frac{n \cdot \mu_n + p \cdot \mu_p}{n \cdot \mu_n^2 + p \cdot \mu_p^2} &= \frac{\sigma}{q} \\
\frac{n \cdot \mu_n^2 + p \cdot \mu_p^2}{\beta \cdot q} &= \frac{R_H \cdot \sigma^2}{\beta \cdot q} \\
n \cdot p &= \text{constant}
\end{align*}
\]

Bearing in mind the equation:

\[
p - n = 2 \cdot M \exp \left( - \frac{E_g}{2kT} \right) \sqrt{\frac{p}{n}}
\]

(where \( M=U \cdot T^{3/2} \) deriving from Fermi-Dirac's statistics, the equation system (34), (35), (36) and (37) can be solved.

The Hall effect can be detected using direct or alternating current. Due to the system asymmetry, a
small potential difference between the z-axis electrodes can be observed when voltage is applied to the x-axis electrodes (Fig. 16) using the direct current, even without a magnetic field. When the Hall effect is small, this potential difference may exceed the Hall voltage.

The following procedure can be used to overcome this drawback: when a direct current flows through the sample (x-axis electrodes), one measures voltage \( V_0 \) between the z-axis electrodes with a high-impedance voltmeter when the magnetic field is zero. The magnetic field is then applied and one measures \( V_1 = V_0 + V_H \), where \( V_H \) is the Hall voltage. Reversing the magnetic field, the Hall voltage reverses as well and one measures \( V_2 = V_0 - V_H \). Hence:

\[
V_1 - V_2 = (V_0 + V_H) - (V_0 - V_H) = 2V_H
\]

(38)

The Hall effect measurements with direct current were made using a DC generator (Keithley, model 240 A) and an electrometer (Keithley, model 610 B or model 640). Measurements were made in the vacuum with the cell illustrated in Fig. 18, on samples of minerals or other materials and compacted powders, up to temperatures of 700-800°C.

The use of alternating current is preferable when measurements are made on compacted powders [33]. The measuring circuit is sketched in Fig. 17 and consists of the following units:
- a phase-sensitive detector with frequency range from 1Hz to 1 MHz (model 471, Brookdeal);
- an amplifier (model 450, Brookdeal);
- a phase shifter that can shift the phase by about 180° (model 421, Brookdeal);
- a signal generator (model 142, Watevek);
- an electronic filter (model 3750, Krohn-Hite), frequency range 0.02-20 kHz;
- an electromagnet (Systron-Donner) with low residual flux density (0.03 Tesla), capable of providing a magnetic field intensity up to 3 Tesla;
- a Hall probe (model 505, RFL Electronics) for measuring the magnetic field intensity.

When an alternating potential difference is applied to the x-axis electrodes (Fig. 16), an alternating current occurs in the sample. Since the magnetic field is along the y axis, an alternating voltage with the same frequency can be detected at the z-axis electrodes. In addition, a voltage with magnetic field zero as well as a voltage due to capacitive and inductive disturbances coming from the generator and connectors develops between the same electrodes. The electric signal at the z-axis electrodes is amplified and sent to the phase-sensitive detector. The reference signal is emitted by the generator through the phase shifter. When the magnetic field is reversed, the Hall voltage phase changes through 180°, and the signal component due to the Hall effect changes sign. The difference between the two measurements in the phase-sensitive detector is proportional to the Hall voltage only. Since the voltage at zero magnetic field does not change phase when the magnetic field is reversed, it does not influence the measurement. Likewise, capacitive and inductive disturbances do not change sign when the magnetic field is reversed. The reference signal must be in phase with the Hall effect signal to obtain a
maximum intensity signal from the phase-sensitive detector.

The sample is placed in a special ceramic holder (Fig. 18a) and covered with a plate of the same material. The current and voltage electrodes have been printed in this holder using a laser procedure. There is also a thermistor for measuring the temperature. The sample holder is placed in the Hall effect measuring cell (Fig. 18b), where the vacuum is created and there is the electric resistance needed to increase the temperature.

Acknowledgements

This paper summarises the results of long-term research on the electrophysical characterisation of minerals and powders, and describes the main units of the DIGITA Dpt. developed to achieve this under the aegis of MURST (Ministry of the University) and CNR (Italian Research Council) programmes.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>coefficient</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>ratio between the charge carrier mobilities $\mu_e/\mu_h$</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$C_0$</td>
<td>capacitance</td>
<td>[F]</td>
</tr>
<tr>
<td>$e_1$, $e_2$</td>
<td>voltage drop</td>
<td>[mV]</td>
</tr>
<tr>
<td>$E_f$</td>
<td>Fermi level (referred to the valence band upper edge)</td>
<td>[eV]</td>
</tr>
<tr>
<td>$E_g$</td>
<td>width of the forbidden gap</td>
<td>[eV]</td>
</tr>
<tr>
<td>$E_{g0}$</td>
<td>width of the forbidden gap at 0 °K</td>
<td>[eV]</td>
</tr>
<tr>
<td>f</td>
<td>vibration frequency</td>
<td>[Hz]</td>
</tr>
<tr>
<td>h</td>
<td>Planck's constant</td>
<td>[J·s]</td>
</tr>
<tr>
<td>$H_x$</td>
<td>intensity of the magnetic field</td>
<td>[T]</td>
</tr>
<tr>
<td>$I, I_x$</td>
<td>current</td>
<td>[mA]</td>
</tr>
<tr>
<td>$i, i_1, i_2$</td>
<td>current</td>
<td>[mA]</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann's constant</td>
<td>[J·K$^{-1}$]</td>
</tr>
<tr>
<td>l</td>
<td>distance</td>
<td>[cm]</td>
</tr>
<tr>
<td>m</td>
<td>free electron mass</td>
<td>[kg]</td>
</tr>
<tr>
<td>$m_e$</td>
<td>effective mass of an electron</td>
<td>[kg]</td>
</tr>
<tr>
<td>$m_h$</td>
<td>effective mass of a hole</td>
<td>[kg]</td>
</tr>
<tr>
<td>q</td>
<td>charge of electron</td>
<td>[C]</td>
</tr>
<tr>
<td>$r_1$, $r_2$</td>
<td>electric resistance</td>
<td>[\Omega]</td>
</tr>
<tr>
<td>R</td>
<td>resistance of ionised air</td>
<td>[\Omega]</td>
</tr>
<tr>
<td>$R_H$</td>
<td>Hall coefficient</td>
<td>[cm$^{-3}$·C$^{-1}$]</td>
</tr>
<tr>
<td>s</td>
<td>area</td>
<td>[cm$^2$]</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>[s]</td>
</tr>
<tr>
<td>T</td>
<td>absolute temperature</td>
<td>[°K]</td>
</tr>
<tr>
<td>U</td>
<td>constant</td>
<td>[cm$^{-3}$·K$^{-3/2}$]</td>
</tr>
<tr>
<td>$V_H$</td>
<td>Hall voltage</td>
<td>[V]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Seebeck coefficient</td>
<td>[V·K$^{-1}$]</td>
</tr>
<tr>
<td>$\beta$</td>
<td>constant</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>mobility of free electrons</td>
<td>[cm$^2$·V$^{-1}$·s$^{-1}$]</td>
</tr>
<tr>
<td>$\mu_h$</td>
<td>mobility of holes</td>
<td>[cm$^2$·V$^{-1}$·s$^{-1}$]</td>
</tr>
<tr>
<td>$v$</td>
<td>wavelength</td>
<td>[cm]</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>work function (Fermi level)</td>
<td>[eV]</td>
</tr>
</tbody>
</table>

referred to the vacuum level)

References


12) Ciccu, R.; Del Fa, C.; Ghiani, M.; and Massacci, P.: Metodologie sperimentali per lo studio dei fenomeni all’interfase, dei relativi parametri influenti e del loro...


Author's short biography

Raimondo Ciccu

Raimondo Ciccu graduated in Mining Engineering at the University of Cagliari in 1965. Shortly after he served the National Research Council covering the position of Senior researcher until 1973. From 1974 to 1981 he was Chief Sector at the Sardinian Mining Board (EMSa) and meanwhile he acted as Managing Director of a major mining Company in Italy. In 1982 he joined the University of Cagliari as Associate Professor and from 1983 as Full Professor of Surface Mining and Land Reclamation.

The fields of interest range from excavation and cutting of rocks using traditional and advanced technologies (diamond tools and waterjet) to various subjects of mineral processing, especially electrostatic separation and comminution. Presently his research, teaching and consulting activity is chiefly focussed on stone quarrying and processing.

Professor Ciccu Authored about 200 scientific and technical papers, most of them discussed at International Conferences, and he is responsible of many research contracts with the industry as well as scientific coordinator of EEC-supported projects. He shares many patents for electrostatic separators of mineral matter.

Languages spoken: Italian, English, French, Portuguese and Spanish.

Marcello Ghiani

Marcello Ghiani graduated in Mining Engineering at the University of Cagliari in 1958 and developed his entire Academic career at the same University. In 1966 he was abilitated as lecturer in the field mineral processing, and in 1975 he was appointed professor of mineral processing at the University of Cagliari, where from 1985 until 1992 was director of Mining and Mineral Processing Department. He carries out on a scientific activity within the frame of the research programs of the Department of Geoenrineering and Environmental Technologies and of the Mineral Science Study Centre of National Research Council at the University of Cagliari. He partecipated in various national and international conferences giving numerous contributions. He is author of more than 200 papers in the field of mineral beneficiation. As a consultant Dr. Ghiani has cooperated in the development of various projects and as a member of the scientific committee he is involved with the development of a general plan concerning the Sardinina mining sector.

Antonello Serci

SERCi ANTONELLO graduated in Mining Engineering in 1982 at the University of Cagliari (Italy) where he obtained the Ph.D. degree in 1988. Formerly junior researcher of the National Research Council, presently senior researcher at the Department of Geoeengineering and Environmental Tecnologies of the University of Cagliari.

His research activity covers many fields of mineral processing with special focus in electric separation and flotation.

Dr. Serci is author of about 20 papers and shares a patent for a new electrostatic separator with researchers of the Department and of CSGM (National Research Council).
Gianfranco Ferrara obtained his degree in Mining Engineering in 1954 at the University of Cagliari (Italy). At the same University he was appointed Research Assistant in 1955 and Assistant Professor in 1960. In 1971 he was appointed to his present position of Professor of Mineral Processing at the University of Trieste, where from 1979 to 1992 he was Chairman of the Mineral Engineering Division. Consultant for the evaluation of the research activities financed by the European Community in the framework of the Primary Raw Materials and Recycling programme from 1980 to 1989. Member of the Steering Committee of the IMPC's. Regional Editor for Europe of the journal “Minerals Engineering” from 1988 to 1997. Member of the Editorial Board of the journals “Coal Preparation”, “KONA-Powder and Particle” and “Minerals & Metallurgical Processing”. For the research activity he has been appointed Adjunct Professor of the West Virginia University, USA. To date he has produced more than 120 publications concerning mineral and coal processing research, characterisation of particulate solids, mineral liberation, comminution, mechanical, hydraulic and pneumatic classification of solids, dense medium separation processes in centrifugal field of ores and coals, rheology of dense suspensions, electrostatic separation, modelling and simulation of the separation processes of minerals, coals and particulate solids, treatment of post-consumer plastics and recycling. Author of a number of patents in the field of dynamic dense medium separation processes, which are applied in industrial plants operating in many countries of Europe, in Canada, South Africa, South America and China.

Paolo Massacci obtained his degree in Mining Engineering in 1964 at the University of Cagliari (Italy). At the same University he was appointed Research Assistant in 1964 and Assistant Professor in 1970. In 1975 he was appointed to his present position of Professor of Raw Material Engineering at the University of Rome (Italy), where since 1978 has been Chairman of the Mineral Engineering Division. He is currently member of the Scientific Committee of the International Mineral Processing Congresses, designed as Chairman for the XXI Congress which will be held in Rome in 2000. His research interests are principally concerned mineral processing, characterisation of particulate solids, recycling of secondary raw materials, flotation and comminution.