ANALYTIC ELECTRON MICROSCOPY AS A MICRO-LABORATORY FOR QUALITY CONTROL OF CERAMIC PAVING AND TILING

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1. INTRODUCTION

The use of electronic microscopy along with the quantitative and qualitative microanalysis of materials, especially advanced ceramic and glass materials, has recently become very important due to the quantity of problems concerning control of composition of raw materials and finished product that can be resolved using these techniques. Equally, its use in the production control of any traditional ceramic material, such as tiles and paving, should be essential today in any modern company aspiring to high levels of production quality.

In 1969, for the first time, a detector of X-ray energy dispersion was incorporated into a conventional microprobe, verifying the great advantage that this microanalysis system had for the study of materials. Since then it has been generally used in all control and research laboratories for materials of any type. This innovation converted electron microscopes, which had been used since the previous decade,into powerful instruments of analysis and observation.

As is well known, today the control of the microstructure of the fired and unfired piece is fundamental to the production of ceramic materials. The appearance and properties of the final product depend directly on the microstructure of the material. The term microstructure is very broad and includes fundamental variables, which not only concern the relative content of the vitreous and crystalline phase but also the following characteristics: crystalline structure, chemical bonding character, and defects (such as impurities, cavities, and dislocations) that appear in the crystalline phase of the ceramic product. All these microstructural aspects can be controlled in a ceramic tile or paving piece with the use of electron microscopy techniques, which constitute, as will be seen, a very powerful tool for the ceramicist.

2. FUNDAMENTALS AND CONFIGURATION TYPES IN ANALYTIC ELECTRON MICROSCOPY. IMAGE TYPES.

All observation and microanalytical techniques that can be carried out nowadays using an analytical electron microscope are based on the interaction that an electron beam produces when it is incident on a material. The different types of signals and radiation that are obtained are presented in Figure 1 (1) (2). Images can be formed by:

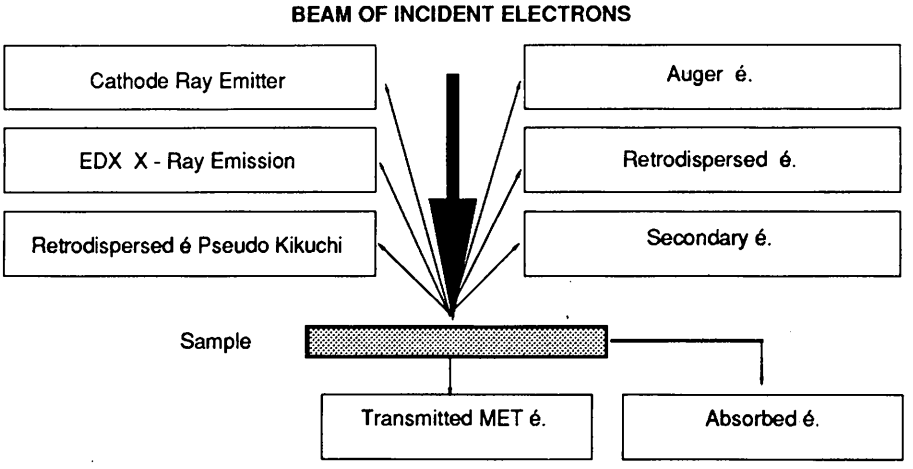

Fig. 1 - Signals that are observed in a scanning electron microscope when an electron beam is incident on the fractured surface of a ceramic material or glass.

- secondary electrons, which come from a depth of 20-30nm below the surface.
- retrodispersed electrons, which are emitted from a greater depth (approx. 50 nm).

Both these signals are the ones which are most frequently used within scanning electron microscopy (SEM).

- Auger electrons (from 1-2 nm).
- electrons absorbed into the material. In the same way chemical analysis can be performed using the following types of radiation:
- X-rays, these can be detected with a wavelength spectrometer (WDX) or with a solid state spectrometer (EDX).
- Cathode Rays
- Electromotive force generated in the material.

If the material is sufficiently thin, the transmitted electrons give rise to the name transmission electron microscopy (TEM)) through which it is possible to perform a crystallographic analysis by electron diffraction in very localized areas of the material (CBED).

Thus, electron microscopy techniques can be schematically classified according to the techniques used and to the procedure for collecting the signal that results from the interaction of the electron beam and material:

- Transmission Electron Microscopy (TEM)
- Scanning Electron Microscopy (SEM)
- Scanning transmission Electron Microscopy (STEM)
- Field Emission Electron Microscopy (FEEM) (which is possible for both TEM and SEM).

Various types of microanalysis can be carried out on tiles, paving pieces or their raw materials with the radiation emitted from the material, when it is excited by the electron beam. Although signals exist such as those from Auger electrons (AES), or those from electrons that undergo a loss

of energy crossing a sufficiently thin sample (EELS), the most common microanalysis in existing instrumental configurations on the market is that which uses X-ray emission, which is produced in a similar way as in X-ray fluorescence analysis, but in a localized area of the material (up to 1 micron in SEM system and 1nm in TEM systems). There are two different techniques for the detection of this radiation:

- WDX or X-ray analysis by wavelength; this is normally used in conventional microwave spectroscopy and uses a crystal analyser sequential detector.

- EDX or x-ray analysis by energy dispersion based on direct, simultaneous detection using a Si(Li) solid state detector.

Neither WDX nor EDX spectrometers possess all the characteristics of the ideal x-ray detector (small, cheap, easy to manage, efficient, fast and good resolution), but they do complement each other, although EDX detectors are used more generally to resolve industrial control problems due to their versatility and speed. Table I shows a comparison of the most important characteristics of the two detectors.

Table I.

Comparison of AXDLO and AXED spectrometers.

Characteristics	**AXDLO Analysing Crystal**	**AXED Semi-conductor Si(Li)**
Basic:		
Resolution at 6.4 KeV	-10eV	-150eV
Mechanical		
Efficiency	<30%	100% (for 3-15 KeV)
Solid Angle	-0.001 stereo:	-0.001 stereo: ad(variable) ad(fixed)
Focusing	maximum	minimum
Analytical:		
Elements detected	>B	>Na
X-ray peaks/troughs	200-2000	20-100
Detection Limit	10^{-15} -10^{-16} g	10^{-16}-10^{-17} g
Exactitude	0.1-0.01%	0.1-0.01%
Pressure	-5% rel.	-5% rel.
Sensitivity (% counts)	less	greater
Average analysis time	15-30 mins	0.5 - 1 min

With regard to analytical additions, various configurations are available, the following are the most frequent:

- SEM/WDK (classic spectrometry), SEM/EDX or even SEM/WDX/EDX

- TEM/WDX (little used) TEM/EDX (frequently used nowadays)

- TEM/EDX/EELS (known as analytical electron microscopy (AEM).

However, in this report the general term analytical electron microscopy will be used to refer to a TEM/EDX configuration as well as an SEM/EDX configuration.

The quantity of information that can be obtained in analytical electron microscopy, using this as a general term, is such that these instrumental configurations can be considered as control and

analysis "microlaboratories". Morphological, crystallographic, analytical, chemical bonding, electromagnetic properties and even mechanical information can be obtained using suitable detectors.

The information that can be obtained from SEM/EDX, the most used system nowadays, is:

Morphological information: can be obtained from all types of signals except X-rays and Auger electrons.

Analytical information: can be obtained from signals from

- X Rays
- Cathode rays
- Auger Electrons
- Retrodispersed electrons

Crystallographic Information, can be obtained from emissions from:

- retrodispersed electrons
- transmitted electrons (electron microdiffraction and convergent electron beam diffraction, CBED)
- X-ray channelling signal
- Electron or pseudo-Kikuchi channelling diagrams.

Chemical Bonding Information:

- Auger electrons
- X-rays

Electromagnetic Information:

- Secondary electrons
- Electromagnetic forces

Characteristics concerning resolution and detection power of microanalytical techniques are given in

Table II (3).

Table II. Fundamental Characteristics of microanalytical techniques.

Technique	Depth	Detection Limit	Resolution Lateral	Elements Analysed
MET-AXED	100nm	0.1%	40nm	>Na
MET DDDD	100nm	<0.1%	40nm	>B, C
MES-AXED	≅um	0.1%	0.1-1μm	>Na
MSE	≅um	0.1%	1μm	>C
EEA-e	0.4-2.5nm	0.1%	0.1-3μm	>Li

3. QUALITATIVE AND QUANTITATIVE MICROANALYSIS BY EDX AND EELS

An EDX detector, which has a Si crystal semi-conductor doped with Li and a 0.003 inch Be protective window, gathers practically 100% of the x-ray emission in the 2.5 - 15 keV spectral interval where practically all the elements present in ceramic materials are found. The element detection limit can be improved in Si (Li) detectors with no window or with a ultrafine window, these can analyse up

to B, C, N, and F. Thus, the efficiency of x-ray microanalysis depends on the type of detector used, as can be seen in Figure 2.

Chemical elements that constitute the support as well as the glaze of a tile or paving piece can be analysed, in general, by the different analytical electron microscopy techniques. The only element that cannot be analysed with any configuration is Lithium. The detection of Boron presents many difficulties, although its detection is possible, as some spectrometer manufacturers assert, using EDX detectors with an ultrafine Beryllium window or with no window. With this type of detector even fluorine may be analysed. For the moment, the quantitative analysis of these elements presents great difficulties. From sodium to uranium there are generally not any problems regarding the quantitative and qualitative analysis of these elements, although sodium does present problems in its exact.

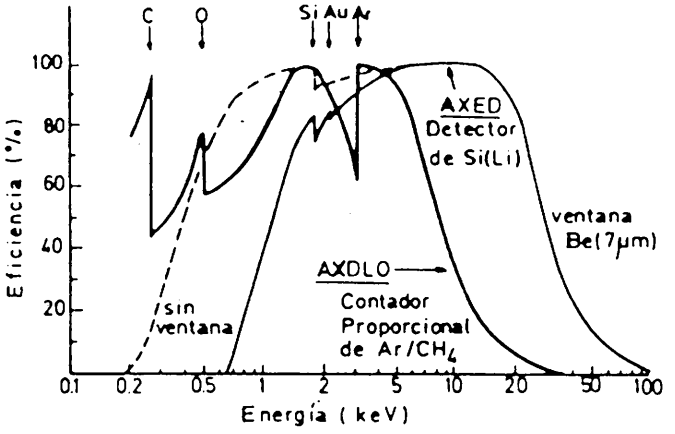

Fig. 2 Efficiency curves for different types of detectors used in MARX.

An other type of problem exists due to the overlapping of x-ray peaks or the presence of minority elements. A typical and frequent case of overlapping is that of the potassium line (K) and zirconium line (L) or that of Titanium (K) and Barium (L), (1).

Computerised systems incorporated into WDX and EDX spectrometers allow spectrums to be archived and manipulated and even allow an archive reference file of spectrums or analytical standards to be drawn up; this results in the relatively rapid quantitative analysis of any ceramic material.

An EDX spectrum represents a series of emission peaks that correspond to the lines of emission K, L, M & N for every element present in the sample against the emission energy for each spectral line. The height of the peaks after subtracting the bottom is directly related to the concentration of the elements present within the ionization volume of the sample. This ionization volume depends on the size of the electron beam. When the spectrum is obtained with a TEM/EDX configuration, the ionization volume also depends on the thickness of the thin lamina that constitutes the sample in this case. In a SEM/EDX system (1) the concentration of an element in a sample (C_A) is related to the concentration of that element in the standard sample (C_o) by the expression:

$$C_A = C_O \frac{I_A}{I_O} ZAF$$

IO where: I_A and I_0 are the intensities of the sample and the standard in the spectrum; Z is a atomic number correction factor; A is a co- efficient of absorption correction factor and F is a fluorescence correction factor. These correction factors are important for voluminous samples (cases where microanalysis using SEM/EDX is carried out), but they are practically insignificant for thin laminae (where microanalysis is carried out using TEM/EDX systems), which greatly helps quantification in the latter type of system (4). Also, in this case, EDX spectrums have hardly any base, as can be seen in the example shown in Figure 3, which corresponds to an analysis carried out on a surface with a metallic appearance and iridescent effects of a vitreous ceramic material obtained from a mixture of muscovite and amblygonite (5).

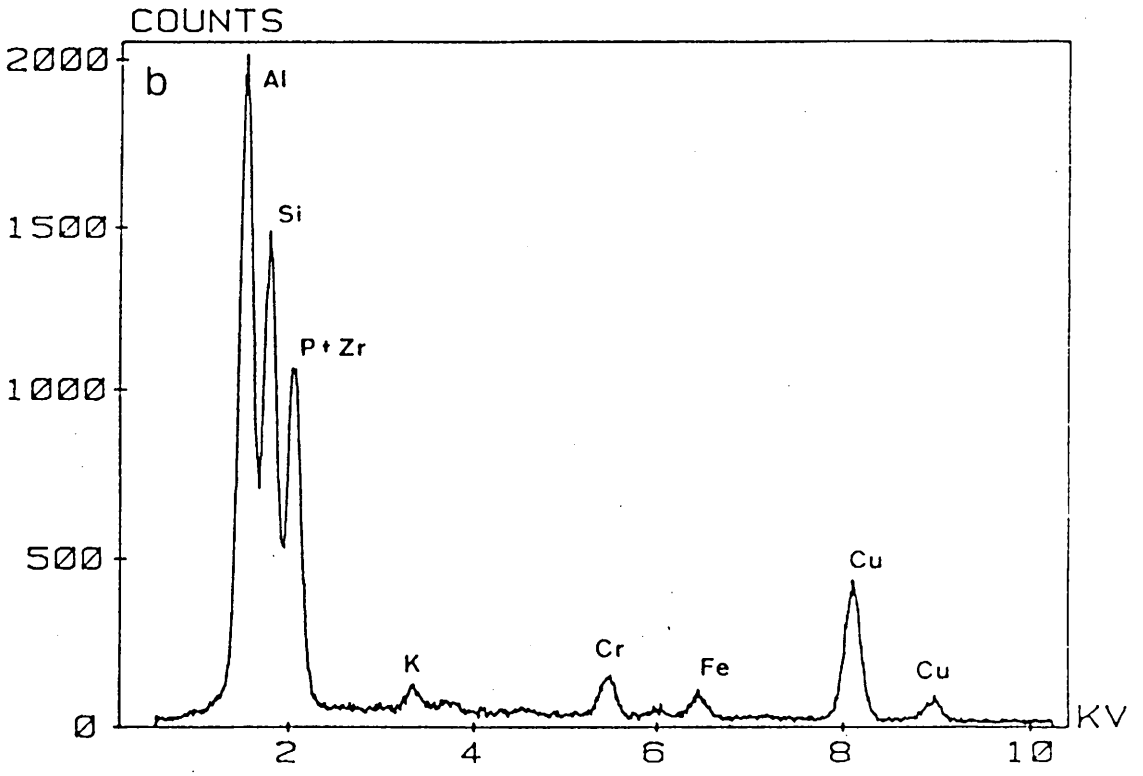

Fig. 3 - Average EDX spectrum obtained from a vitreous ceramic material with a reflective surface and an aventurine effect.

During 1972-75, Cliff and Lorimer (6) proposed that, in the case of thin laminae, the following expression could be used:

$$\frac{Cy}{Cx} = Kyx \frac{Iy}{Ix}$$

where Cy/Cx is the ratio of concentrations in % weight of an element, with respect to an x in the volume analysed, Iy/Ix is the ratio of intensities of the characteristic peaks, and kyx is a proportionality factor that can be easily calculated or obtained by a previous tabulation of standard values. In 1975, the authors mentioned above obtained a series of values for kyx for minerals whose exact chemical analysis was obtained with a Kevex detector, taking the peak for Si as a reference X. To use this method, three fundamental principals must be kept in mind:

1) The composition of the standard samples is perfectly known, invariable and homogeneous.

2) The calibration factors kyx are not universal constants and are only applicable to each specific TEM/EDX configuration.

3) The criterion of thin laminae is fulfilled, this assumes that the preparation is sufficiently thin for the effects of absorption and fluorescence to be negligible.

In the TEM/EDX configuration, it is possible, moreover, to perform an analysis of electron energy loss (EELS), if the relevant spectrometer is installed, this allows analytical data and even information about chemical bonding to be obtained, especially for lighter elements. Electrons that suffer an energy loss crossing the material are picked out with a spectrometer of a similar design to a mass spectrometer and then detected by a photomultiplier tube and a scintillation counter. The intensity of the electrons is proportional to the quantity of lost energy. Each ionization is seen in the spectrum as an absorption edge (Figure 4) (7).

In the EELS spectrum, each peak is supported by the edge of the preceding peaks. The bottom of the spectrum is defined as an exponential curve of the form Ae, where A and r are constants and E is the loss of energy. The intensity also depends in this case on the concentration of each element but, as it is still very new, there is not much quantitative experience of this technique as yet.

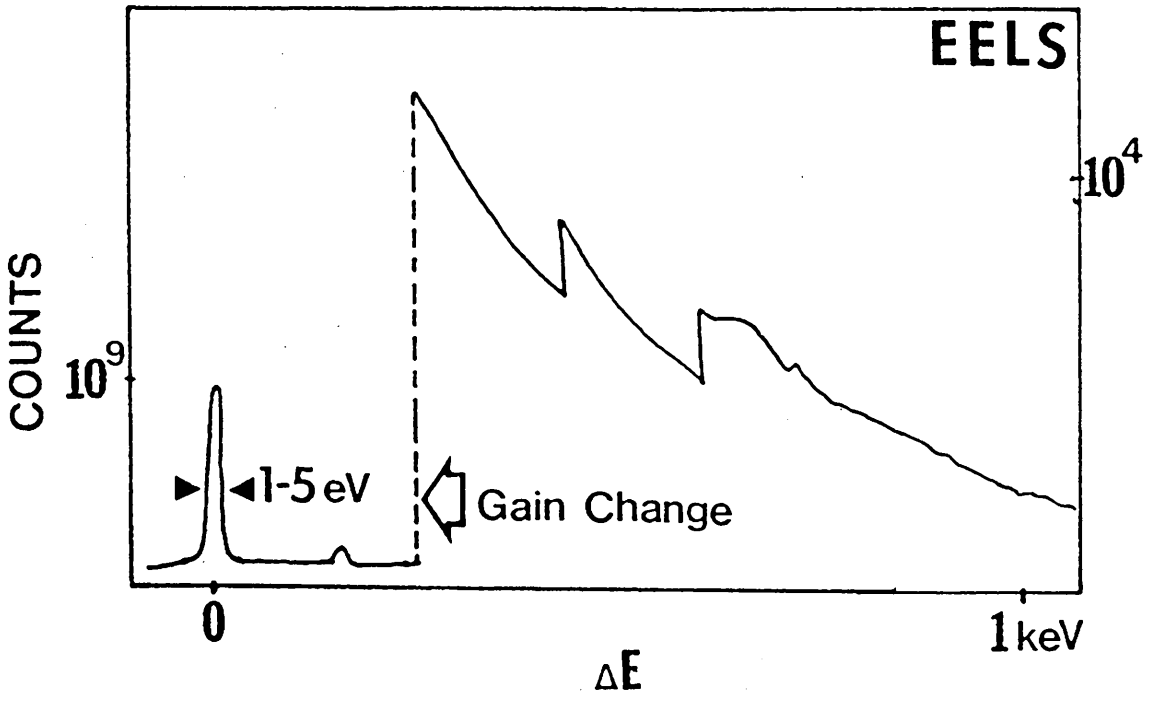

Fig. 4 Representative Model of EELS type of spectrum that is obtained from Transmission Electron Microscope.

4. FACTORS THAT AFFECT MICROANALYSIS USING ELECTRON MICROSCOPY

Analytical quantification, of the support as well as glaze, and of the volume of the sample or of a prepared thin lamina, (TEM/EDX), is affected by a series of factors and corrections that must be borne in mind. In the case where an EDX detector is used, the principal factors that affect the analysis are: time of acquisition, angle of suspension of detector, detector efficiency, overlapping of peaks, type of analytical standards, etc. If the analysis is carried out on thin laminae (TEM/EDX), the thickness of the film, the mode of acquisition (TEM or STEM), and parasitic x-rays that can be produced in the microscope column must also be taken into account.

In the case of Electron Energy Loss detectors, the quantification is basically influenced by the depth or depth-peak relationship, and scattering or multiple dispersion due to thickness and mode of operation - in other words, if the spectrum is obtained as an image or as diffraction. However, the quantitative analysis is also affected by the entrance aperture of the spectrometer, the beam current, spacial resolution, the energy window chosen, the adjustment of depth, etc.

5. METHODS FOR PREPARING SAMPLES

For the SEM/EDX technique, the preparation of the tile or paving piece is simple, since a metallization of the surface with Au, Au- Pd, Pd, or just carbon is sufficient. To facilitate the observation and recognition of the phases which compose the material, it is generally suitable to carry out a light chemical attack on the surface of the material. When it is wished to observe the glaze-support interphase, insertions of epoxy-resins or bakelite can be carried out, followed by a short traversal of the material in a perpendicular direction to the interphase.

For the TEM/EDX technique, the tile or paving piece can be observed and analysed by diverse replica techniques:

- direct or simple: this is performed with evaporated carbon.
- indirect or double, this is carried out in two stages: first with a plastic film of triazole, with which the first mould or replica is obtained, and then with an evaporated film of carbon.
- extraction: this allows particles to be pulled from the surface, their chemical content or crystallography can then be analysed.(2).

The first two types of replica allow the observation of the microstructure of the tile - in a non-destructive manner, if the double replica technique is used - but they don't allow the chemical analysis of the material by TEM, as a result, when transmission electron microscopy is used for analytical ends, the most suitable thing to do is to slim the sample down.

The slimming down of the support of a tile or paving piece is carried out in various stages, the first being the cutting of the material into slices ('wafering'), followed by a mechanical grinding with various abrasive papers. This operation can be performed manually or, less laboriously, with a machine called a "dimpler". The final thickness, which must be less than 150nm, is achieved by prolonged ionic bombardment with argon. If it is wished to observe the glaze-support interphase, this is possible by TEM/EDX, thanks to a technique elaborated by Rincon et al (8), which is shown in Figure 5. This technique has been recently developed for the study of vitreous ceramic materials with iridescent surfaces or aventurine effects, but it can be applied for the study and analysis of ceramic tiles and paving. Thanks to this preparation of samples procedure it was possible to analyze the composition of a fine surface layer on which an optic effect with a metallic appearance and iridescences were produced. The formation of a spodumene of phosphate enriched with iron oxides and not previously described in scientific literature is connected to this effect.

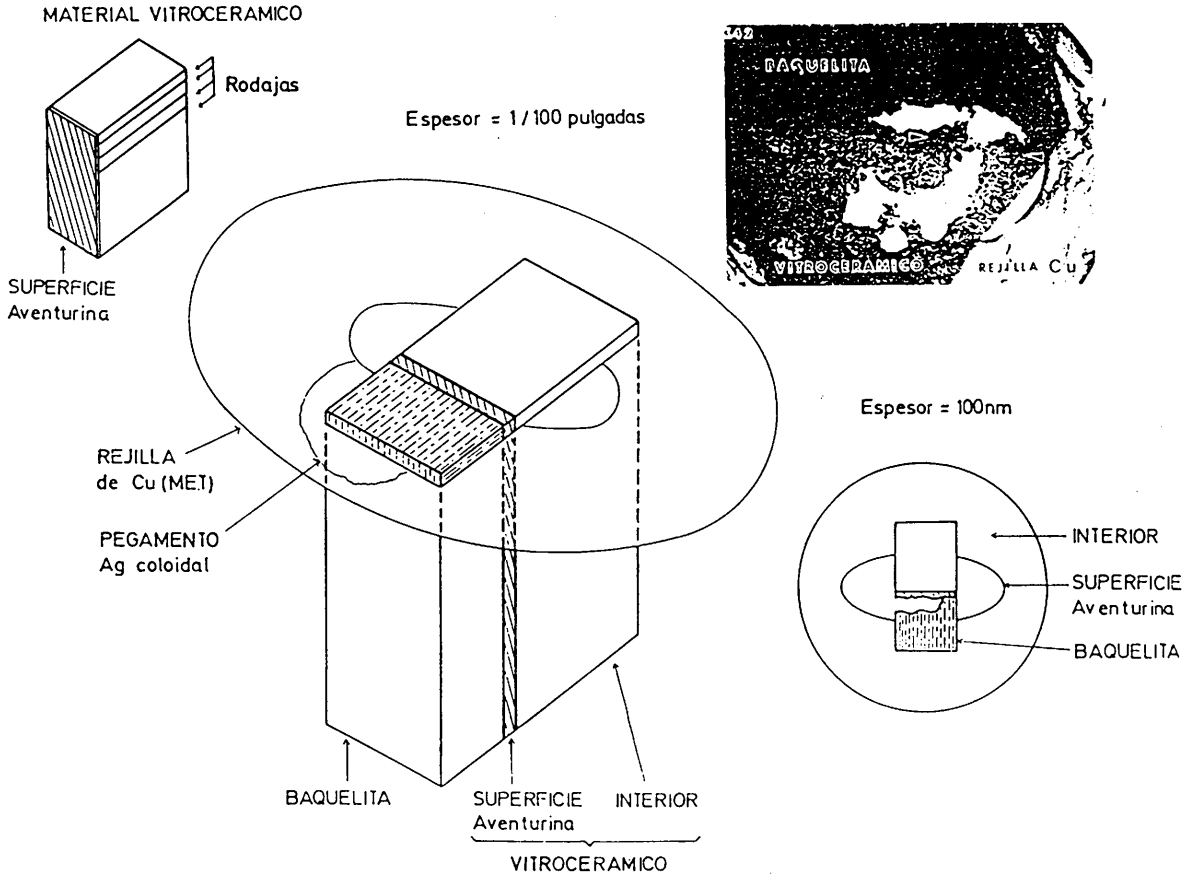

Figure 5. Diagram of transverse section obtained for the analytical electron microscopy study of both vitreous ceramic materials with a reflecting surface and aventurine effect, and the glaze-support interphase of ceramic paving and tiling.

6. CONTROL APPLICATIONS FOR TILES AND PAVING PIECES

In production control as well as quality control of ceramic tiles and paving, and in the raw materials, textural and microstructural problems can arise, as well as problems of analytical observation in certain areas. These problems normally concern not only the ceramic support and glaze, but also the interphase between both constituents of the tile or paving piece. With regard to microstructural visualization and quantification, a classification can be made as follows:

Study of raw materials:

- shape, size and distribution of clayey minerals as well as other minerals used in the support or mixture.
- shape, size and distribution of granular or enamel frits.

Study of unfired ceramic support:

- Distribution of particle sizes and pores.
- Distribution of agglomerates within the pores.
- Mutual or preferential orientation of particles. (This control is essential, since in the texture of the dried piece, the positions that the clay particles will occupy after firing are already determined.)

Thus, for example, pieces obtained by extrusion with a certain ball clay have a very different resistance if they are manufactured using 90% of the fraction of the mixture less than 1um and 10% of the fraction greater than 1um than if they are manufactured using only the latter fraction. Hence by SEM it can be verified that the fracture of the piece produced with the finer clay shows a finer more compact microstructure, while that produced with the larger particles has large laminae with little coaxiality between them. Studies have also been realized with TEM to relate the surface resulting from the powders to the dimensions of the crystals that constitute these powders (10). Thus, the physical characteristics of the raw materials seem to have more influence on the unfired piece than on the fired piece.

Study of ceramic support after firing.:

- Volume fraction of crystalline and vitreous phase.
- Shape and distribution of each crystalline phase.
- size and perfection of crystals in crystalline phase.
- borders between phases or grain borders.
- contact angles
- porosity

Study of vitreous or vitreous crystalline glazes

- texture and rugosity of the surface
- separations or immiscibilities of phases
- porosity or bubbles
- impurities, defects
- glaze-support interphase

With respect to the raw materials that are used in production of the tile and paving support, these are generally mixtures of clayey minerals. Electron microscopy is the only technique that can observe the shape of these minerals, and even help in their identification when it is possible to do this by other techniques, as, for example, in the case of the differentiation between Kaolinite (normally hexagonal crystals) and crystals of halloysite (tabular splintered crystals) (11).

Given that the glazes are generally glass, the study of their homogeneity and related effects, such as bubbles, solid inclusions, borders of immiscible solutions, corrosion figures after prolonged use with atmospheric or chemical agents, etc, is fundamental. Not only is it necessary to study the condition of the surface, it is also necessary to know the internal texture of this type of glass. The

texture of the surface as well as the internal texture can be found with replica techniques. The separation of phases and immisicibilities that produce opalescences have been known for some time in glazes (12) and take place in systems of two or more components like:

Al2O3-SiO2;
Li2O-B2O3-SiO2;
Na2O-B2O3-SiO2;
Li2O- TiO2-SiO2;
Li2O-Al2O3-B2O3-SiO2....

The opalization of these types of glass is produced by recrystallizations in some cases, and ,in others, by the separation into various amorphous immiscible phases, comparable to emulsions. These separations can take place when the glass is being cooled, in the course of "maturation" or formation of the glass, or even by a thermic treatment.

In the case of B2O-SiO2 and K2O3-B2O3-SiO2, the droplets belonging to the dispersed separated phase are enriched in silica, having an average diameter of around 100 nm. When the glass is a PbO-B2O3- SiO2 composition, rich in PbO, the droplets of the dispersed phase are released into the glass matrix during cooling, owing to their greater dilation co-efficient, and stick to the replica in the form of black spheres.

If the support is a porcelain composition, it may be composed of three principal phases: mullite, quartz and a vitreous phase, which can be perfectly differentiated by SEM/EDX. Mullite is present in two forms, one of them acicular, that can only be observed using an electron microscope. The acicular mullite comes from crystallization at the start of the vitreous liquid phase, when the content of alkaline earth silicates in the latter is not yet too high. The other form of mullite, which comes from the changes in kaolin and keeps its flaked structure, is formed by the thermic decomposition of kaolin by a solid state reaction. (13)

The electron microscope and microanalysis is also very useful in the study of the development of the glaze surface structure: surface microdefects, attack by different media, pigment composition (14), colorants, etc. It can even be used to observe the abrasion or wear undergone by the glaze in laboratory tests or in its daily use, once installed. Dry residue and dirt that are retained on the glaze surface can also be analysed and observed.

The fields of application of microanalysis in the control of tiles and paving pieces can be summarised as below:

Analysis of raw materials:

- Analysis and identification of elements present in rock minerals
- Analysis of cementations and agglomerations in rocks

Analysis of ceramic supports:

- Study of interphases
- Diffusion between oxides.
- Refractory attacks
- Glaze application
- Study and analysis of defects

Analysis of glazes:

- Diffusion profiles
- Glass -glass
- Glass - metal
- Glass - melted salt

- gas, dissolution
- Defects: Stones, strings, unmelted substances
- Refractory attacks
- Surface volatilization phenomena.
- Analysis of vitreous crystalline glazes (15).

In general, the observation and analysis of any type of defect, in the support as well as the glaze, is the principal application of both SEM/EDX and TEM/EDX systems. The analysis of small strings, grooves, and stones is impossible to carry out using traditional methods. Thus, comparing the EDX spectrum of a string and a K2O- SrO-Al2O3-SiO2 glaze matrix, it can be seen that the string contains an excess of Al2O3 and K2O. In the case of glazes, the clarity of the image when observing the glaze-support interphase section by TEM, SEM and Optic Microscopy techniques has been demonstrated in numerous cases, besides the microanalytical data that the SEM technique can provide.(16)

Finally, with respect to glaze defects such as bubbles, it has been known for some time that there is a relationship between the appearance of this type of defect and the size interval of the bubbles (17). Although optic microscopy allows the observation of these defects, it does not allow a chemical microanalysis of the areas or even of the insoluble particles or crystals adjacent to these defects. With analytical electronic microscopy techniques it is possible to follow the path of the bubbles towards the surface, relating this to the composition gradients of the glaze. Defects caused by bubbles below 80 micra, which are imperceptible to the human eye and which can be the cause of cracking and other defects, can also be located and identified by analytical electron microscopy techniques.

7. CONCLUSION

From the above, we conclude that analytical electron microscopy techniques, both the SEM/EDX configuration, for more general use, and the TEM/EDX configuration, are authentic "microlaboratories" for microstructural observation and analysis, The possibilities of analysing points, areas or across lines, which can include the crossing of interphases, make these techniques a powerful tool in quality control in the ceramics industry. Their versatility and capacity for analysis and observation, across large and small ranges, is such that they must be considered as essential for production and quality control in the manufacture of ceramic tiles and paving pieces.

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