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Building Materials :

Polarizing Microscope in the Study of Building Materials

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"To-day with microscopic data reinforced and extended by other analytical tools such as X-ray diffraction, differential thermal analysis and absorption spectroscopy, the microscope still retains a unique position as the universal analytical instrument and a valuable tool of the modern laboratory. On the one hand, it is the most versatile of instruments, serving widely different ends as mineral identification, particle size analysis, strain measurement, the study of porosity, texture and preferred grain orientation, quantitative analysis of material in terms of the phases or minerals present and the measurement of optical constants. On the other hand, it stands guard over the more elaborate analytical methods to ensure that their results are properly interpreted and that they are being applied in their proper sphere".

(Insley & Frechette)

The Polarizing Microscope

Although this instrument contains several additional features, the basic difference between the standard compound microscope and the petrological microscope is that the latter is equipped with a revolving stage and a pair of polars. A polar is a device which has the property of obstructing the passage of all light except that vibrating in one plane. One such polar is mounted above the objective. They are oriented with their vibration direction at right angles so that all light which is transmitted by the lower polar is obstructed by the upper one. If an object placed on the stage of the microscope is entirely glassy, the beam of light from the lower polar passing through this object will not be altered in any way, and the whole of the light will be stopped by the upper polar. The field seen through the eye piece will thus be entirely black. If, however, the object on stage is crystalline, the beam of light from the lower polar will in most cases be split into two beams as it passes into the object. One of these beams will meet with more resistance to its passage than the other. The beam emerging from the object will thus be out of phase. Some of the light from each beam will pass through the upper polar to form the final image. The interference between these two beams will result in the final image showing a characteristic "interference colour." The specific colour seen depends upon the relative retardation between the two emergent beams—that is, as the nature, optical orientation and thickness of the object on the stage.

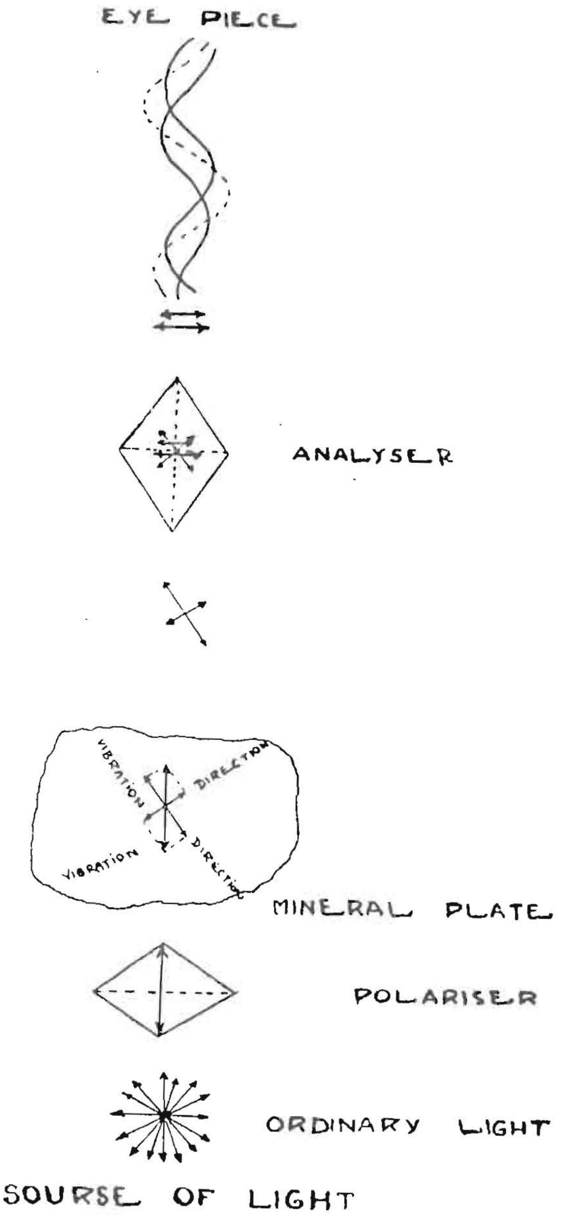

Fig. 1.

Happening in a mineral plate viewed between X-nicols

Thus in addition to its use as a magnifying and measuring instrument, a petrological microscope can be used to distinguish between glass and crystalline material and in most cases to indentify the material.

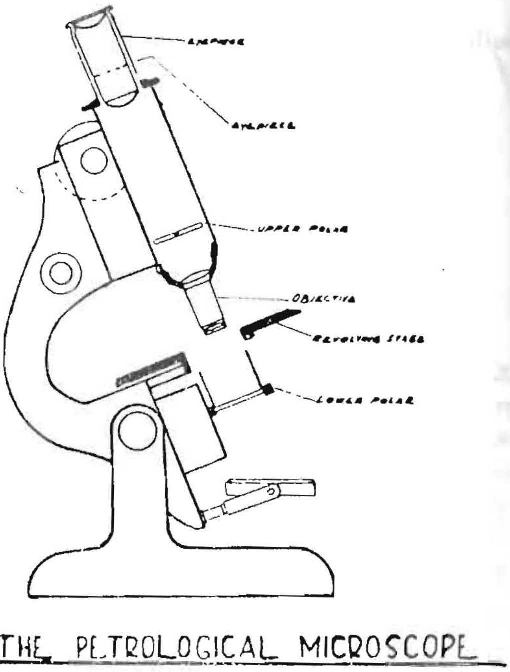

Fig. 2

(Names applied to the various parts of a polarizing microscope of simple type. Advance research models are more elaborate instruments with various accessories).

The Examination

Identification under polarizing microscope is an important part of any petrographic examination. Although the microscope is used to identify many and varied features of physical and chemical nature the primary use remains the mineral phase identification.

The success of identifying a particular object depends on proper illumination and no instrument can be expected to give proper results unless this point has received careful consideration. Various methods of illumination are used according to the nature of the object examined.

Transmitted Illumination

In a majority of cases the object is transparent and can be illuminated from below, the light rays passing through the object into the objective. This is known as transmitted or direct illumination. The object and its structural detail will be only visible if they are naturally coloured or they are artificially stained or their refractive indices are different from those of the mounting medium.

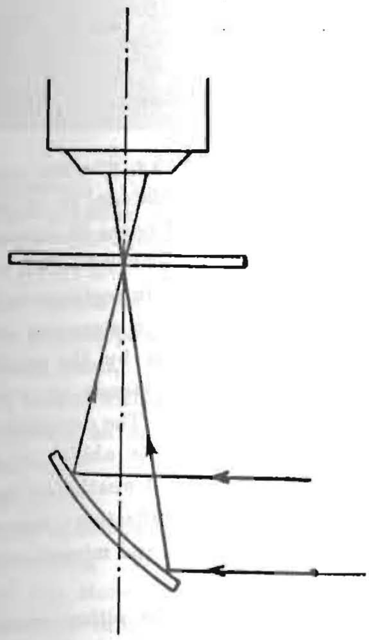

Fig 3
Trasmitted illumination

Reflected Illumination

When opaque objects are to be examined, the substage mirror or transmitted illumination can no longer be used. The illumination must be derived from rays of light thrown on to the specimen from above and thence reflected into the instrument.

Reflected light technique gives more information relating to the distribution of phases than to the indentification of minerals although the reflective powers of the various minerals have important diagnostic properties.

In order to identify a mineral phase it is necessary to ascertain certain properties, the most important of which are as follows :—

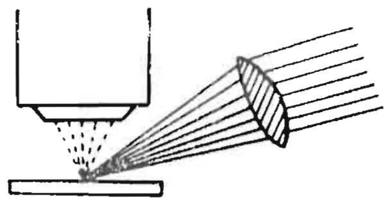

Fig 4
Reflected Illumination

1. *Refractive Indices :* Values of the refractive indices of a mineral can only be obtained in a qualitative manner by the examination of the thin section in ordinary transmitted light. In a thin section the various minerals are usually embedded in canada balsam which has a refractive index of 1.54. The amount of relief shown by the mineral depends upon its refractive index value.

2. *Birefringence :* Under crossed nicols most sections of uniaxial and biaxial crystals exhibit colour except when turned to their extinction positions. Since properly ground thin sections are about 0.03 to 0.035 m.m. thickness, the double refraction may be estimated from the interference colours. The exact position of the polarization colour can be determined by means of quartz wedge.

3. *Interference Figure :* Whether the mineral is isotropic, uniaxial positive, uniaxial negative, biaxial positive, biaxial negative is seen under convergent light and in crossed nicols.

Preparation of Material

This consists of the preparation of material for the examination under microscope. Depending upon the nature of substances and the mode of examination materials are prepaed in many ways, but the most common and important one is mentioned below.

Thin Sections

For the examination of materials under the microscope thin sections are required. A chip of the rock is rubbed perfectly flat on one side, with emery or carborundum powder on a glass or metal plate. At first coarse grinding powder may be used. After a surface is obtained it must be polished by using finer, and then very fine powder. The flattened and smoothed surface of the fragment is then cemented firmly to a glass plate by means of properly cooked canada balsam.

The next operation consists in grinding down the thick chip as in the first pocess. Great care is necessary during the final stages or the rock will be completely rubbed away. The thickness of the slice can be judged by the polarization colours of some recognisable minerals. The slice is then covered with fresh canada balsam which is again cooked but slightly to a less extent than before and a cover slip is cemented.

The preparation of thin sections of cements and the building materials offers problems not encountered in the preparation of standard thin sections of most rocks. Building materials in general have various ranges of porosity and hardness, and cements frequently hydrate and disintegrate in the presence of aqueous abrassive carriers. Portland cement clinker must be ground to half or less of the standard 30 thin section thickness in order to distinguish individual particles without confusing overlap. In case of porous, pliable material it is sometimes necessary to impregnate the specimen, with resins before sawing to prevent dust from remaining in the pores of t… section after sawing.

The use of polarizing microscope in building materials covers a very wide range of application. Starting from the correct assessment of natural materials to the quality and quantitative check of manufactured products and by-products microscope is of exceptional value and it shall be beyond the scope of these pages to enumerate all these applications. However, few important ones like building stones, raw materials, cement clinker, cement hydration, alkali aggregate reaction, etc., have been briefly treated.

Natural Materials

Natural rocks whether used as primary constructional material or as raw material for industry should never be selected haphazardly. The factor of durability which should be regarded as of primary importance in the selection of a building stone is strangely enough given the last consideration by the purchaser. Many a costly structure stands as a witness to this neglected aspect. The durability of a building stone depends on its ability to resist successfully the attacks of weathering agents, and the natural factors affecting this property are structure, texture and mineral composition.

A stone may be either coarse or fine and even grained or it may be porphyritic (Inequigranular i.e. large crystals are enveloped in a groundmass which may be microgranular or glassy). It may also be dense or porous. Considering the texture, we find that stones tend to disintegrate somewhat under changes of temperature, and that coarse grained rocks are affected more than fine grained ones depending further on the interlocking arrangement of all mineral constituents. A dense rock, other things being equal, will break down less rapidly than a pervious one. Porosity is the result of the space left between various

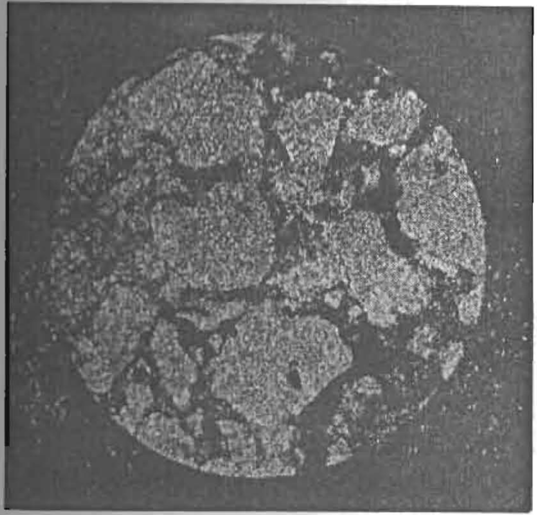

Fig 5
Photo micrograph : Coarse grained sandstone showing quartz grains (seen white) cemented in a ferrugenous mass

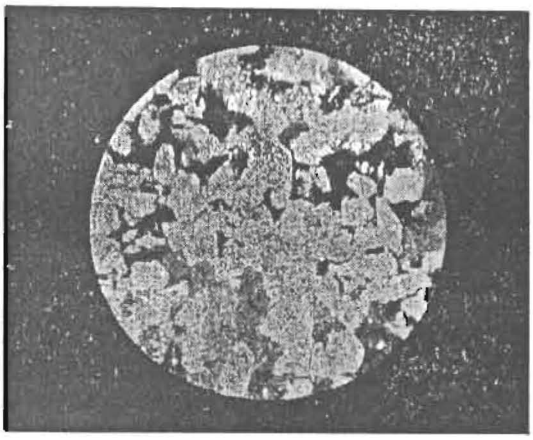

Fig 6.
Photo micrograph : Coarse grained sandstones showing angular quartz pieces (seen white) cemented in ground mass of silica mainly chalcedony with limonito staining

mineral constituents of rock and can best be determined microscopically. Several varieties of sandstones occur, some with a porous texture and others with an interstitial matrix of material such as carbonate of lime, ferric oxide, silica, etc.

The degree of compaction, and the strength of the cementing medium determine the strength of the stone. The specific gravity varies from 2.65 in highly siliceous stones to 2.95 in those containing ferruginous matter. The colour of sandstone depends on the cementing material : ferruginous sandstones are red to brown ; argillaceous earthy to buff ; siliceous, generally white ; carbonaceous mostly black. Ferruginous sandstones of yellow or greenish tint may change colour on exposure, because of the oxidation of the iron. Siliceous cement generally makes the stone strong but difficult to work whereas argillaceous cement tends to make the stone weak, while calcareous cement is liable to chemical attack.

Since different minerals show different degrees of resistance to the attacks of weathering agents, it is obvious that the rocks because of their varying mineral composition will also vary in their weather resisting qualities. Further, certain minerals are to be regarded as injurious under all circumstances, while others like mica can be considered so only when occurring in abundance in some rocks such as sandstones and marbles. Flint and chert interferes with cutting and dressing and being more resistant to weathering stands out on the weathered surface. Pyrite which can be readily recognised by its brass yellow colour in reflected light, and other iron mineral on oxidation and further leaching leave unsightly and unwanted stains. Again in the decomposition some sulphuric acid is formed and if the rock contains carbornates these are attacked by the acids set free. Tremolite-pale green variety of amphibole found in some magnesian, crystalline limestone decompose to a greenish-yellow clay. This washes out, leaving pits on the surface of stone. The mineral can be readily recognised by its high refractive index ($\alpha = 1.600$, $\beta = 1.616$, $\gamma = 1.627$), strong birefringence ($\gamma - \alpha = .027$) and its optically biaxial negative character with $2V = 80°$.

Raw Materials: One of the most important application of the polarizing microscope is in the examination of raw materials used in building industry. For identification, analysis, control of grain size and uniformity microscope can be applied conveniently in research and developments of material. Requirements for one application may be quite different from those that will apply when the materials are to be used for another purpose.

Texture, porosity, grainshape, and grain size are important factors in their behaviour during grinding, mixing and later processing. The thermal behaviour of raw materials and their microscopic character resulting from heat treatment is closely connected with the suitability of the materials for specific application.

Manufactured Products

Polarizing microscope technique has brought many fruitful results both in knowledge of the constitution of clinker and in technological improvement in the cement industry. Le Chatelier was the first to use the polarizing microscope extensively on cement clinker. With its help he discovered tricalcium silicate as the principal constituent of cement clinker. Later on Tornebohm used the microscope and observed that the cement clinker was composed of five principal constituents which he named alite, belite, celite, felite and isotropic residue. Since the time of this basic work, the microscope has been an important tool in research on cement clinker and its hydration.

The basic problem of portland cement research is concerned with the chemical nature of the substance. The success of the problem depends upon the accurate identification of compounds or other phases after they are produced. Chemical analysis is inadequate to determine the manner of combination of the constituent elements. Microscopic methods are best suited in this type of work.

The phases normally found in a Portland cement clinker of average composition are tricalcium silicate ($3\ CaO.SiO_2$), dicalcium silicate ($2\ CaO.SiO_2$), tricalcium aluminate ($3\ CaO.Al_2O_3$), brown millerit (approx. $4CaO$-$Al_3O_2.\ Fe_2O_3$), free CaO, free MgO, and glass. Tricalcium silicate in clinker occurs as well developed six sided crystals. The refractive indices of pure $3\ CaO.SiO_2$ are $NE = 1.718$ and $No. = 1.723$ and the indices in Portland cement clinker do not deviate much from the values.

The more usual form of tricalcium aluminate, a material relatively common constituent of Portland cement clinker is one which occurs in normally cooled alkali containing cement clinker. This may be a polymorphic form of tricalcium aluminate. It occurs as long prismatic crystals in the interstitial material. Its double refraction is low and its mean refractive index about 1.72. Extinction is parallel. Its etching reaction with water, prismatic form and occurrence as an interstitial material serve to distinguish other clinker constituents.

Portland cement clinker frequently contains free CaO. Crystalline CaO is cubic, but it is always found as spheroidal particle in cement clinker and never with crystal faces. It is difficult to see it in thin sections under cross-nicols of clinker because of its isotropic character. In ordinary transmitted light it may be missed in thin sections even with its high refractive index (1.836 for sodium light). It may be identified by staining technique.

MgO (periclase) is isotropic and its refractive index (1.736) is very close to the indices of the principal silicates and aluminates in clinker. Therefore, it is very likely to be confused with tricalcium silicate or tricalcium aluminate when examined under transmitted light either in powder preparation or in thin sections. It is best recognized in polished specimens by reflected light where its relatively great hardness makes it stand out in relief.

The only important iron bearing constituent of Portland cement clinker is "4 $CaO.Al_2O_3.Fe_2O_3$". This compound can be readily identified by microscopic examination in either transmitted or reflected light because of its distinctive properties. It has much higher refractive index about 2.03 than any other clinker constituent.

Careful microscopic search of Portland cement clinker containing fairly large amount of K_2O has revealed the presence of crystals of K_2SO_4. This material occurs in equidimensional grains. It has a very low birefringence of about 0.004 with $Nx=1.493$, $Nz=1.497$ biaxial positive, $2V$=approximately 67°.

Although polarizing microscope has added much to the information still our knowledge concerning other possible compounds in clinker is very fragmentary. Much work has been done and is being done on the very completed phase relationships of the alkalies with the essential oxides of the Portland cement. The existence and the identification of possible compounds in clinker have not been completely established.

Microscopic studies of aluminous cements have been reported by P.H. Bates and B. Tavasci. Compounds practically identical with the "unstable 5 $CaO.3Al_2O_3$, CaO Al_2O_3 and $CaO.2Al_2O_3$ have been identified petrographically in aluminous cements. Microscopic examination of some cements subjected to severe reducing action has revealed globules of metallic iron.

There have been many microscopic studies of Porland cements in the process of hydration and of set and hardened Portland cement pastes, mortars and concretes. During the hardening the tricalcium silicate present hydrolyses to form crystalline calcium hydroxide and a microscopically amorphous calcium silicate hydrate. Under normal conditions of hardening, the calcium hydroxide generally occurs as minute hexagonal plates which are only visible microscopically. These have the normal optical properties : Uniaxial negative with $No=1.574$, $NE=1.545$.

If pure substance tricalcium aluminate is observed microscopically in the presence of water it is seen to hydrate immediately to form a crystalline, platy, hexagonal material with indices about 1.53 and 1.52. When the tricalcium aluminate as it occurs in Portland cement is hydrated, however, the formation of the crystalline calcium aluminate hydrate is only temporary and it reacts with the saturated solution of *calcium sulphate*, formed by solution of the gypsum in the cement, to crystalize as calcium sulfo aluminate 3 CaO $Al_2O_3.3CaSO_4.31H_2O$. This occurs as long hexagonal needles which are uniaxial negative with refrative indices $No=1.464$, $NE=1.458$ (in sodium light).

Alkali Aggregate Reaction in Concrete

The harmful effects of certain substances in concrete aggregate have been recognized since early times, but the application of petrographic methods has thrown great light on these substances. Identification of the nature of the coated material which in most cases is harmful aggregate materals requires petrographic examination. The surfaces of aggregate particles may become altered or decomposed due to weathering processes. In addition to their poor bonding properties such materials may be chemically reactive with cement alkali. Petrographic examination is necessary to assess the deletorious nature of altered material.

Concrete, the artificial rock, can deteriorate as a result of freezing and thawing and attacks of sulphate solutions as well as by cement-aggregate reaction. Several forces contributing to the deterioration may operate concurrently in a concrete structure. Decline in strength, expansion, development of surface cracks and similar manifestations of deterioration may accompany any of these processes. Petrographic examination of deteriorated concrete reveals characteristics which distinguish break down resulting from cement aggregate reaction from that due to other causes. The microscope is particularly useful for this interpretation of textural relationships and for the identification of the various disintegration products.

The most reliable criterion for recognizing the cement aggregate reaction in concrete—both in thin section and hand specimen—is the presence of alkali-silica gels. These gels result from inter-action between cement alkali and susceptible rocks and minerals of the aggregate. They occur within porous particles of aggregate, in voids in the cement paste, in fractures, etc.

The gels observed in deteriorated concrete vary considerably in physical properties. These products of cement aggregate reaction may be watery, viscous or even hard and brittle, all in close association. Petrographic study indicates that prior to fracturing of the concrete the gels are highly viscous.

The index of refraction of siliceous gels in concrete is low, but varies with the water content. Desiccated gels have indices which range from about 1.46 to about 1.49. They show a varying degree of transparency and commonly contain cracks resulting from drying shrinkage. Microscopically the gels are often cloudy and brown in transmitted light due to the presence of fine inclusions. Sometimes very small particles with high birefringence are suggestive of calcium carbonate.

Microscopic study of thin sections of deteriorated concrete often reveals the presence of siliceous gels which are not readily observable in the hand specimen. Because random thin sections may not intersect gels, it is not safe to conclude that gel is absent except after detailed study of many sections. Occasionally no definite deposits of gel are found by any of these methods although other evidence may strongly suggest cement-aggregate reaction. Under these circumstances, the cement paste has a peculiar mottled aspect in thin sections.

The occurrence of alteration rims on aggregate grains of certain rock types, when properly interpreted may be diagnostic of cement aggregate reaction. These alteration rims appear distinctly different depending on the manner in which they are examined. If a fractured surface of an affected aggregate grain is observed with reflected light, the rim appears dark in contrast to the interior of the grain. When examined in thin sections with petrographic microscope using transmitted light, the rims usually have a higher transparency than the interior portion of the rock particles. For this reason these peripheral zones have been called "clarified rims". The clarification probably results from a combination of two processes, viz., the removal of some of the rock constituents by dissolution, and an increase in optical *homogeneity* by virtue of the penetration of the alkali silica gels into the interstices of the rock. This type of rim has been observed in glass andesites and rhyolites.

Summary

The paper aims at pointing out the potentialities of the polarizing microscope in the study of building materials. Intention is to help the engineers and other technicians who directly or indirectly are concerned with the nature of building materials. General optics of the

instrument, method of operation and preparation of their sections have been briefly stated.

Natural materials comprising mainly of building stones and raw materials for cement etc. can be assessed successfully for their qualitative and quantitative properties. Mineral phase identification of cement clinker has contributed greatly to the advance of cement technology. Polarizing microscope has now very recently played a great role in the study of Alkali Aggregate reaction and the study of cement hydration.

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