EVALUATION AND ADAPTATION OF THE DOBROLUBOV AND ROMER METHOD OF MICROSCOPIC EXAMINATION OF HARDENED CONCRETE

Interim Report

Methods and Equipment Used in Preparing and Examining Fluorescent Ultrathin Sections

by

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and

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(The opinions, findings, and conclusions expressed in this report are those of the authors and not necessarily those of the sponsoring agencies.)

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SUMMARY

This report explains the methods and equipment used to produce fluorescent, impregnated, polished, ultrathin sections of portland cement concrete. These sections are used in the study of the microstructure of concrete and are examined with a microscope which combines the features of a petrographic microscope with those of a microscope having incident fluorescing capabilities. The unusual features of this microscope are detailed and brief instructions for the use of the instrument are given. A few of the features of the concrete made visible by use of this preparation method and microscope are shown in photomicrographs.

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INTRODUCTION

The optical examination of the microstructure of portland cement concrete is difficult because of wide differences in sizes between the components of the concrete and the poor crystallization of the hydration products. The aggregates are measured in centimeters and the cement and hydration products in micrometers and angstroms. The poorly crystallized material is difficult to distinguish from void areas.

The distribution of the aggregate and its relationship to the main body of paste can be discerned with low power magnification or with the unaided eye. The distribution of the air voids is determined by magnifications of about 100x. The identification of the fine hydration products and study of their habit require magnifications, up to several thousand, of the electron microscopes. The relationship of the coarse hydration products to the aggregate boundaries and to the void structure, and the location and distribution of the small irregular voids and large capillaries require examination in the 100x to 500x range.

At these intermediate magnifications, rocks are generally examined in petrographic thin sections with a polarizing microscope. The standard petrographic thin section of a rock is a slice of specimen cemented to a microscope slide, ground to a thickness of 20 to 30 μm, and generally covered with a thin glass coverslip to protect the specimen and enhance its optical properties by preventing the scatter of light. Thin sections generally reveal a great deal of the microstructure of most rocks and permit the identification of most of their components. The grinding and cutting methods used in producing rock thin sections

have not changed much over the last 75 years. Sections thinner than 25 μm generally sustain a great loss of area because the edges grind faster than the center, and often soft, friable, highly fractured areas of a specimen are lost. Many materials are so fine-grained that all detail is obscured in thin sections as thin as 20 μm.

In concrete research it has been found that important microstructural details of cement paste and of some of the aggregate rocks are 2 to 20 μm in size. In standard thin sections, such small details are obscured by overlapping material and the boundaries between phases of larger components overlap and are indistinct. Most rocks are composed of well-crystallized materials that can be distinguished from each other with the analyzing polarizer and retardation plates of the standard petrographic microscope. Portland cement concrete contains many poorly crystallized and low birefringent materials that cannot be identified by the aid of the standard accessories, and are extremely difficult to distinguish from void areas.

Recently, new methods and procedures for the preparation and examination of thin sections to delineate microstructural details have been developed. One of these is a spin-off of the space program, having been developed for the examination of lunar rock specimens by Beauchamp, Williford, and Gafford of the Pacific Northwest Laboratories of Battelle Memorial Institute. It utilizes the production of ultrathin sections down to 5 μm thick.[1,2,3] The other, developed by Wilk, Dobrolubov, and Romer of Betonstrassen AG Switzerland,[4,5,6] enables the fine void, crack, and capillary system of portland cement concrete to be easily examined. This method employs fluorescent impregnation and requires a microscope equipped to illuminate the specimen with violet or blue light that will cause the fluorescent dye to emit light.

SCOPE

This present report deals with the methods and equipment used to produce fluorescent impregnated, polished, ultrathin sections of portland cement concrete, and describes the microscope used in the examination of these thin sections. Throughout this report, various proprietary names and distributors are mentioned. Such names are used for reference only, and should not be construed as being the only sources or even the best sources of these materials, but merely items that worked in this laboratory.

PROCEDURES FOR PREPARING SPECIMEN

1. Select and mark the specimen area. Generally the area selected should be centered on mortar rather than on coarse aggregate. The area should be about 16 x 32 mm to fit the well area of the final mounting glass.

2. With the small diamond blade saw (Table 1*, item 1), and, preferably, an oil lubricant, cut a small slab 4 mm thick from the specimen area. Extremely fragile specimens may require thicker slabs.

3. Rinse slab well in acetone** or 1,1,1- trichloroethane.** Air dry or oven dry thoroughly and mount with quick-set glue to work glass (Table 2, item 1). Use a thin, even layer of glue so the specimen will be parallel with and tight on the glass.

4. Mount in vacuum chuck of Ingram Ward grinder (Table 1, item 5) and grind with the diamond wheel until the entire surface of the specimen has been cleaned of saw-damaged material.

5. Wash by soaking in 4 changes of acetone over a period of two or three hours. Air dry.

6. Dehydrate in vacuum oven at 80°C overnight (Figure 1). Maintain vacuum of 10 µm Hg for about an hour before leaving for the night. In the morning, turn the heat off and allow the closed oven and specimen to come to room temperature before releasing the vacuum.

7. Pot specimen with ground surface up in the fluorescent epoxy (Table 2, item 5) to which has been added some 0.3 Linde, a grinding compound, to protect the edges during later polishing. At the Council, disposable plastic petri dishes (5 cm diameter) are used as potting containers. The corners of the work glass must be snapped off to make the specimen fit. The use of larger containers would result in a waste of epoxy. The containers holding the specimens covered with epoxy are placed in the vacuum oven at room temperature and the vacuum is intermittently and slowly brought down as low as possible (10 µm Hg) and kept there until gassing has stopped. This step takes about 3 or 4 hours and is best done in stages to prevent overflow of the bubbling epoxy and to allow it time to penetrate the specimen. Release the vacuum and allow air pressure to force epoxy into all portions of the void system.

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*Tables and figures are appended.

**Persons unfamiliar with the hazards of these compounds are referred to the Chemical Safety Data Sheets published by Manufacturing Chemists Association, Inc., 1825 Connecticut Avenue, N.W., Washington, D. C., 20009.

8. Cure at room temperature for 36 hours, or until epoxy is hard and brittle and does not show any plasticity when tested with a pick. (It is necessary that the grinding procedures to follow remove the epoxy by the same infinitesimal chipping method as used for removing the aggregate rock and cement paste.)

9. Trim excess epoxy and glass from specimen with a saw. Clean bottom of glass of plastic and epoxy by peeling, and mount on additional work glass with quick-set glue. (This work glass is required to fully cover the vacuum chuck in next step.)

10. Clean the final mounting surface by placing the new work glass on the vacuum chuck of the Ingram grinder and carefully grind off the epoxy coating on the specimen surface. A change in sound of grinding will be noticed when the epoxy is gone. Remove as little of the specimen as possible. This highly impregnated area is the best portion of the specimen for use as the thin section.

11. Lap the mounting surface by hand with a 5 μm Al_2O_3 water slurry on glass. Clean in ultrasonic cleaner with acetone solvent. Place under 10 μm vacuum at 50°C for 3 or more hours to remove all oil and water. (Do not soften epoxy at high heat.)

12. Mount the lapped, impregnated surface in a well petrographic slide (Table 2, item 9) with undyed epoxy. (Resiweld 7120, Table 2, item 10, produces a better bond than does the epoxy used for impregnating.) It is very important that the mounting step be performed carefully to eliminate air pockets and ensure a good bond. Place the mounted sample in a clamp on clamp-stand to cure overnight as shown in Figure 2.

13. Cut off the excess thickness of specimen by mounting the final well slide against the vacuum chuck of the Ingram trimmer, as shown in Figure 3. Thus the speciman is made reasonably thin and the two work glasses are removed.

14. Reduce the specimen to about 30 μm thickness in the Ingram grinder. Rinse well with acetone or 1, 1, 1-trichloroethane.

15. Lap by hand with 5 μm Al_2O_3 water slurry on glass. Clean in ultrasonic cleaner with acetone.

16. Polish on Syntron vibratory polisher (Figure 4 and Table 1, item 7) by attaching slide to flat side of weights with double-sided adhesive tape. Place rubber bumper rings on

weights and, using 3 μm diamond compound (Table 2, item 12), and lapping oil (Table 2, item 13), vibrate for about 16 hours, or until thickness is reduced to 10 μm, and the surface is polished and free of scratches. Certain types of aggregate will necessitate further polishing, after thorough cleaning, with 1 μm diamond compound in a second Syntron bowl. Clean sections carefully.

17. When not in use, store sections in a dark, airtight cabinet with ascarite and drierite to prevent carbonation.

The method any particular laboratory uses to produce thin sections will depend on the equipment available and the preference of the technical personnel. Pacific Northwest Laboratories of Battelle recommends the use of a belt sander and a bench lapping machine with diamond impregnated laps. Romer of Labor fur Praparation and Methodik, Switzerland, recommends the use of a diamond tooled milling machine. Council experience has been with the Ingram thin section machines. The ultrathin sections are being examined by eye rather than with an electronic image analyzing device. It has been found that sufficient flatness, for the Council's present studies, has been obtained with the listed equipment.

THE MICROSCOPE

The microscope used in the Council laboratory is an Olympus Vanox II with the standard attachments and accessories for research in polarized light microscopy with the addition of a vertical illuminator for fluorescent light. The transmitted light is from a low voltage halogen source and the incident light from a 200-watt mercury burner. It was necessary that the microscope stand be factory altered to allow sufficient space for mounting the analyzer above the vertical illuminator. The vertical illuminator has a built-in turret for exciter filters UG-5, ultraviolet light (U engraving); BG-3, violet light (V engraving); BG-12 blue-violet light (B engraving); and IF 545 & BG-36, green light (G engraving). There is a slide containing the complementary dichroic mirrors and barrier filters controlled by a lever in a slot: Position U = DM 400, barrier L 410; Position V = DM 455, barrier Y 455; Position B = DM 500 with barrier 0-515. Position G was altered by removing DM 580 and barrier 0-590 to provide a path for ordinary polarized light microscopy.

For the dye used, the exciter filters built into the turret in the vertical illuminator, especially the BG-3 and the BG-12, were usually sufficient. Occasionally it has been convenient to have an extra BG-12 available for use in the exciter filter slot. The only additional barrier filters used have been a Y-485, Y-495, and an 0-515.

Figure 7 illustrates the relationship of the filters to the dye emittance spectrum. A different dye would have required different filters. The various filter combinations shown produced slightly different colors as mentioned below.

Quantitative examination of specimens with reflected fluorescent light was best accomplished with the addition of transmitted plane polarized light filtered with a large, 3.0 mm thick BG-12. A special swing-out mount for this filter was fabricated in the Council shop, Figure 8. For this examination, the illuminator was adjusted for violet light (V settings) and the accessory barrier Y-485 was employed. The fluorescence was greenish yellow and the aggregates dark blue.

The incident microscope accessories used include a Swift automatic point counter, several other push botton counters (for counting voids, cracks, and traverses), a filar micrometer, and a Berek compensator.

The best black and white photomicrography was obtained when the BG-12 exciter (B engraving) and the dichroic mirror DM-500 with the barrier 0-515 (B slot)were employed. When viewed by eye the fluorescence was orange yellow and the aggregates were black. The contrast was better, but some paste details were lost.

Color photomicrography requirements varied with the intensity of fluorescence but was generally good with the violet settings (BG-3, DM-455, and Y-455) and the addition of Y-485. No transmitted light was used in the photomicrography.

Initially, difficulty was encountered in centering the condenser for transmitted light and it was necessary to return the microscope to the supplier to have the substage altered. Problems were also encountered in aligning the polarization. This defect also was corrected.

Completely satisfactory exposures for photomicrography with fluorescent light or with crossed polarization have not been obtained. In both cases it has been necessary to use many different exposure times, or, if the automatic exposure meter is used, to photograph with many different ASA numbers fed into the machine.

The parts of the microscope are listed in Table 3.

RESULTS

The described method produces a sample preparation which has given the researchers new insights into the nature of portland cement concrete when the specimens are examined with the

special microscope system. Ultrathinning of the section to about 10 μm eliminates much of the overlap of the components but retains sufficient thickness for examination of the optical properties of the birefringent crystalline portions. Vibratory diamond polishing of the surface allows examination in reflected light without distortion and light scatter in transmitted light. Impregnation with a fluorescent dye allows differentiation between low index isotropic components and void areas. Some of these features are illustrated in Figures 9 through 15.

ACKNOWLEDGMENTS

The authors are most grateful to J. C. Stulting, laboratory instrument maker; and J. L. Mills, laboratory mechanic, for the fabrication of the swingout filter holder, the vibratory lap table, the clamp stand, laboratory benches, and the microscope work table. The encouragement and advice of H. H. Newlon, Jr., associate head of the Council, is also gratefully acknowledged.

The study is being conducted under the supervision of H. E. Brown, assistant head of the Council.

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Table 1

Equipment for Specimen Preparation

Item #

1. Rock saw (many sources of supply), fitted with a 6" blade, metal bonded diamond rim. Felker (Rimlock blade), Torrence, California.

2. Electric drying oven (NAPCO) ± 1°C controller, range to 200°C; VWR Cat. No. 52345 107 or equivalent.

3. Vacuum oven (NAPCO) ± 0.5°C, range to 200°C, vacuum to 10 μm; VWR Cat. No. 52344-002 or equivalent.

4. Vacuum pump, Duo Seal, two stage Welch, model 1400, Arthur H. Thomas Cat. No. 1055-G35 or equivalent.

5. Ingram-Ward thin section cut-off saw.

6. Ingram-Ward thin section grinder; both items #5 and #6 require coolant pumps and traps and a vacuum pump for the chuck. Both from Ward's Natural Science Establishment, Rochester, N.Y. Use an oil coolant such as Bayol.

7. Vibratory Polisher, Syntron, Model LP-01-C.
   including one 12" diam. stainless steel bowl, one cloth clamping ring, five mettalographic holding fixtures for 1 1/2" OD specimen.
   Controller, Syntron, Model LPC-01
   One additional stainless steel bowl with cloth clamping ring
   FMC Corporation, Homer City, PA; for Council procedures, the holding fixtures are used only as weights and additional weights of similar size should be fabricated locally.

8. Rubber "O" bumpers for weights;fabricated locally.

9. Ultrasonic cleaner; many sources of supply.

10. Clamp stand; fabricated as in Figure 2.

Table 2

Expendables for Specimen Preparation

Item #

1. Work slides - standard petrographic size, 26 x 46 mm, microscope slides; many suppliers.

2. Quick-set glue — any one of the new super glues with quick-set, 1 minute.

3. Potting containers — disposable plastic 5 cm petri dishes. Only bottoms are used.

4. Acetone for cleaning and drying (1, 1, 1-trichlorethane can be used for certain steps).

5. Epoxy formulation

Resin XB 2697	50 gm
Hardener HY 2962	32 gm
Thermoplast Yellow (5G)	1 gm (mix with hardener)
Dibutyl Phthalate	5 gm

Resin and hardener are available as experimental products produced in Switzerland and obtainable through Ren Plastics, Lansing, Michigan, attention A. N. Cianciarulo.
Thermoplast Yellow (5G) is available as samples from BASF Wyandotte Corp., Parsipany, N. J., attention Tom McCormick.
Dibutyl Phthalate is available from many chemical supply houses.

6. Filler (for epoxy), Linde A Alumnia, 0.3 μm, sold as a polishing compound by many suppliers.

7. Alumina 5 μm for hand lapping, Crane Packing Co., Morton Grove, Illinois.

8. Glass plate for lapping, any local glass supply.

9. Well petrographic slides, AB Buehler, Evanston, Ill.

10. Mounting epoxy, Resiweld 7120, H. B. Fuller Co., Fridley, Minnesota.

11. Double-sided adhesive tape, such as carpet tape, 2 in. wide, Belknap, Inc., Louisville, Ky.

12. Diamond grinding compound; 3 μm (violet code) and 1 μm (white code), heavy concentration, gold label, D-57 oil soluble. Penn Scientific Products Co., Inc., Abington, Pa. (Reportedly, diamond compounds of different companies have different properties.)

Table 2 continued

13. Lapping vehicle, for use with diamond compounds, #0S Glennel Corp., West Chester, Pa.

14. Polishing cloth for vibratory polisher, adhesive backed, Pan-W, T. C. Jarrett Company, Denver, Colorado.

Table 3

Major Parts of Microscope System

Microscope Stand for Vanox II
modified for analyzer and vertical illuminator

Circular rotating and centering stage

Polarizing condenser, flip out upper lens

Centering substage

Auxiliary substage lens system

Low voltage halogen light source

Turret objective mount

Objective 5 x /0.10 planachromat
Objective 10 x /0.25 planachromat
Objective 40 x /0.63 planachromat
Objective 60 x /0.80 achomat
Objective 100 x /1.3 Fluorite w/iris (oil)

Analyzing intermediate tube with Bertrand lens

Vertical illuminator for fluorescent light
altered to have "G" mirror and filter removed

Mercury burner 200-w

DC power supply for mercury burner

Exciter filter BG-12
Barrier filter Y-485
Barrier filter Y-495
Barrier filter O-515

Inclined binocular tube

Eyepiece 10 x wide field
Eyepiece 10 x wide field with cross hair
Eyepiece 10 x for 35 mm photography
Photo eyepiece 2.5 x
Photo eyepiece 6.7 x

Camera back 35 mm
Automatic exposure camera body
Automatic exposure control unit

Mica compensating plate 1/4 λ
Gypsum compensating plate 1.2 λ
Berek compensator I-III

Filar micrometer

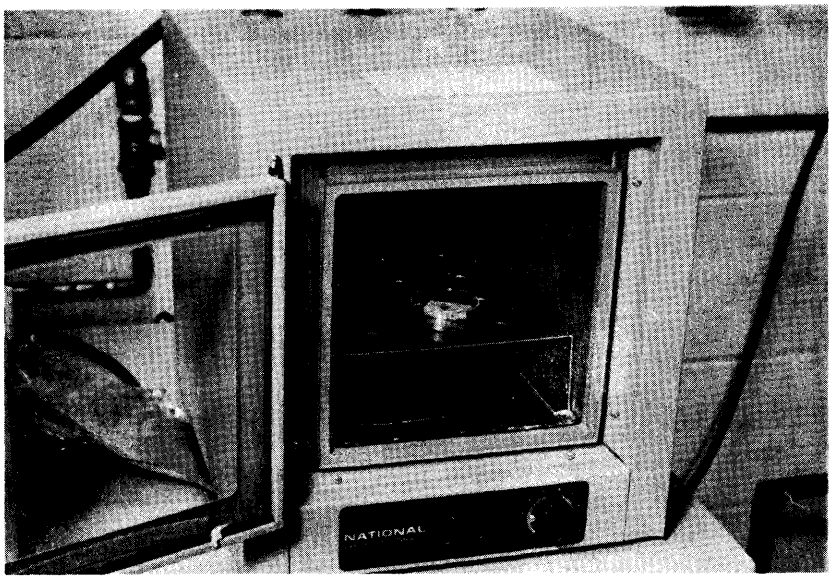

Figure 1. Vacuum oven with thin section slab in plastic petri dish.

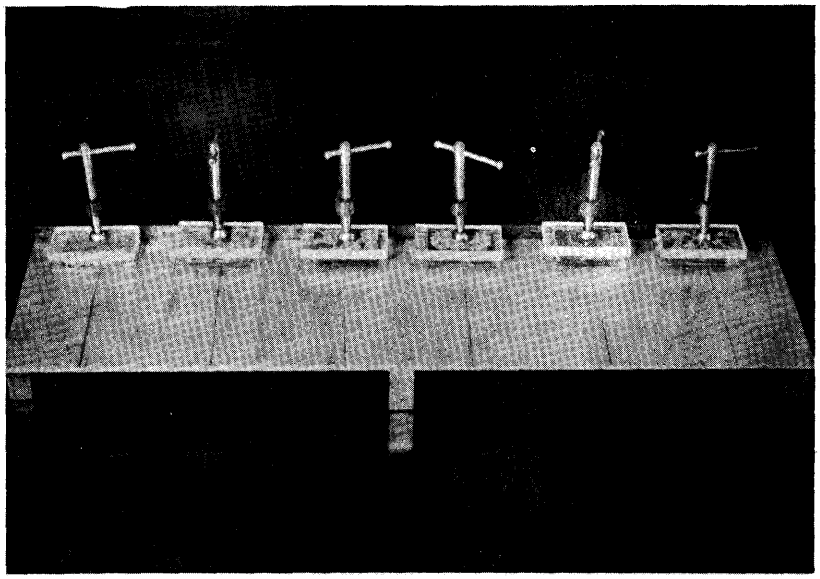

Figure 2. Clamp stand for bonding thin section slab to final "well" slide. Slabs of lucite distribute stress.

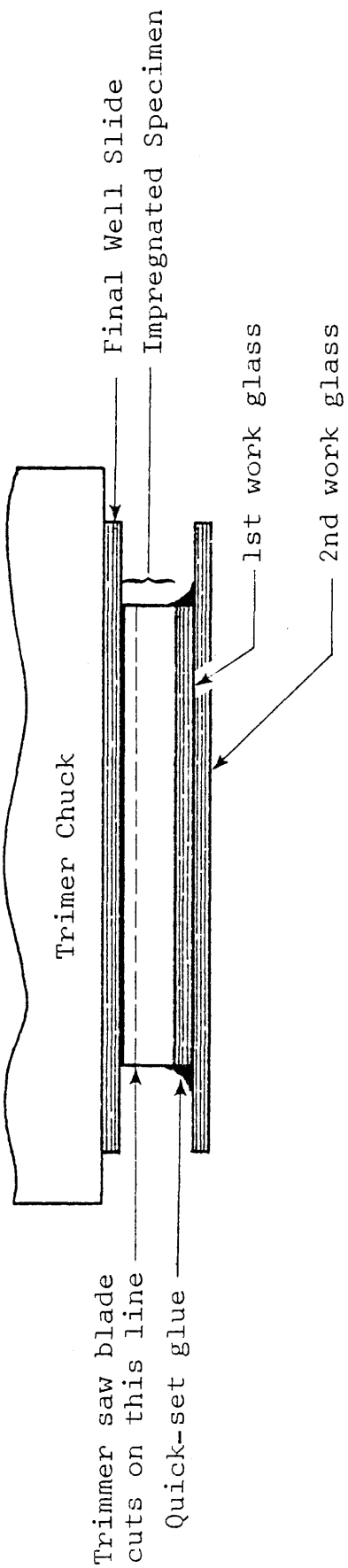

Figure 3. Impregnated thin section slab with work glasses mounted on final well slide ready for trimmer saw.

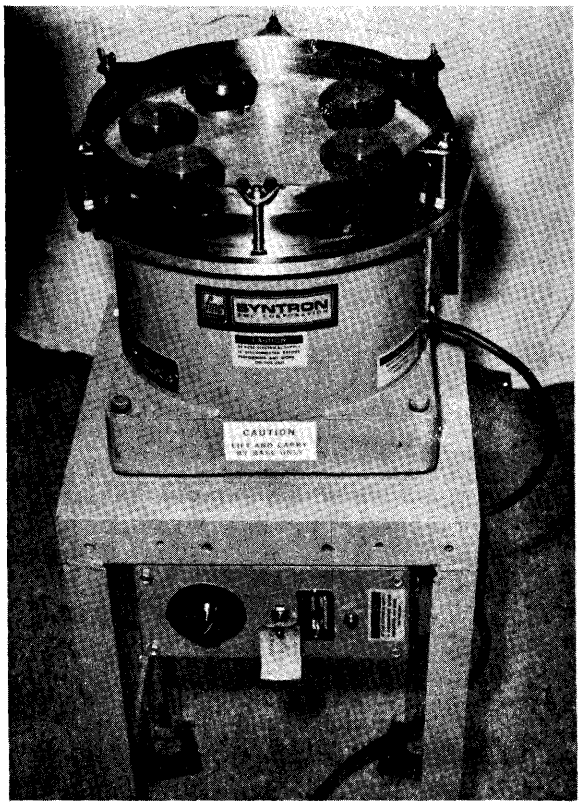

Figure 4. Vibratory polishing lap. Weights with "O" ring bumpers over thin sections.

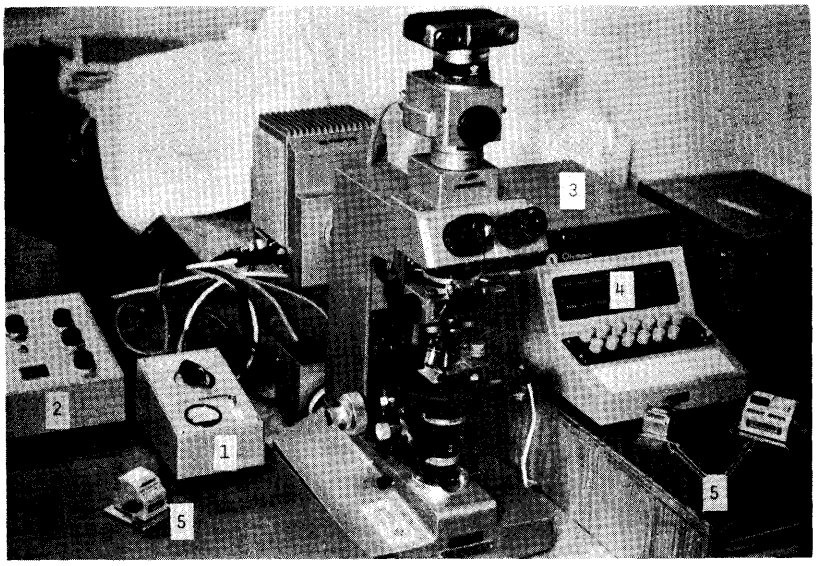

Figure 5. Microscope System.
1. Halogen lamp control
2. Photomicrographic control
3. D. C. power supply for Hg burner
4. Swift point count keyboard
5. Other counters

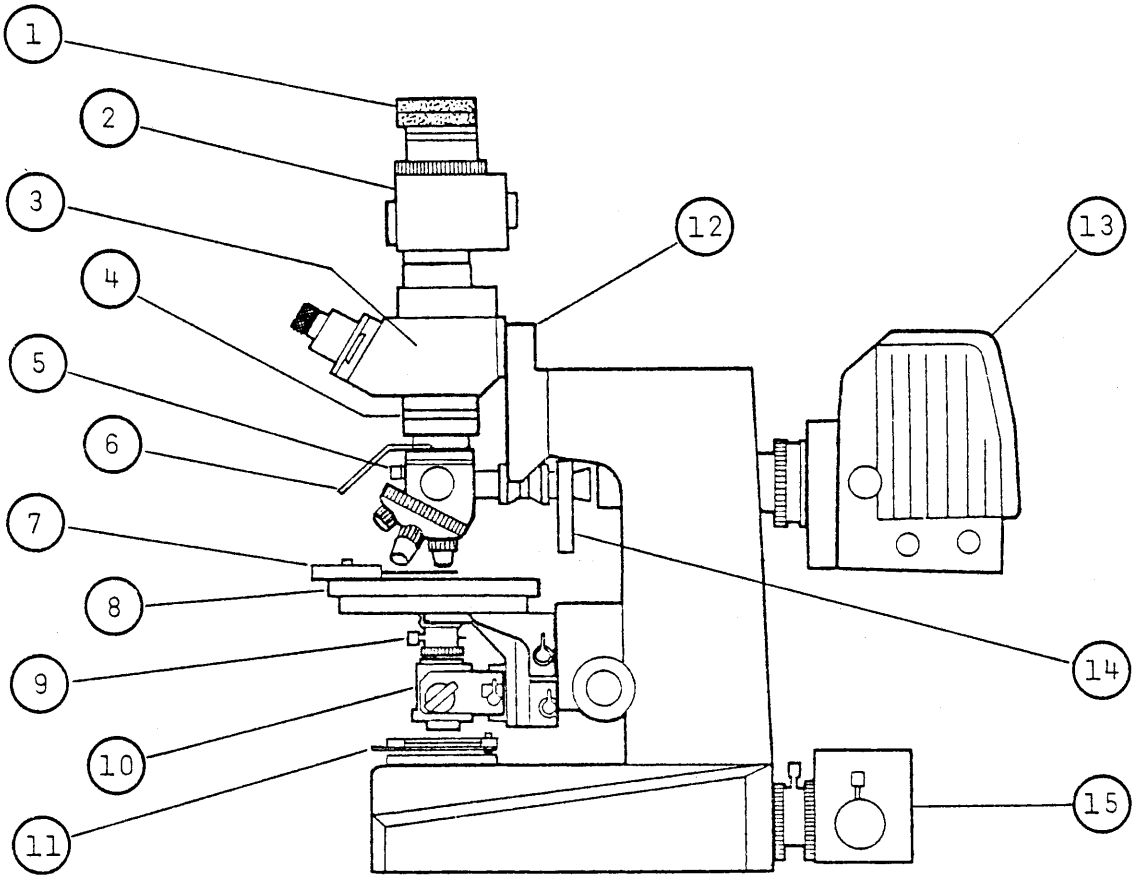

Figure 6. Major parts of microscope system.

1. Camera back, 35 mm
2. Automatic exposure meter
3. Binocular tube
4. Analyzer and Bertrand lens
5. Dichroic mirror and barrier filter selector
6. Light shield
7. Point count stage
8. Rotating centerable stage
9. Polarizing condenser
10. Auxiliary lens system
11. Swing out mount for BG-12
12. Stand modification
13. Mercury burner, 200 w, for incident illumination
14. Exciter filter turret
15. Halogen light for transmitted illumination

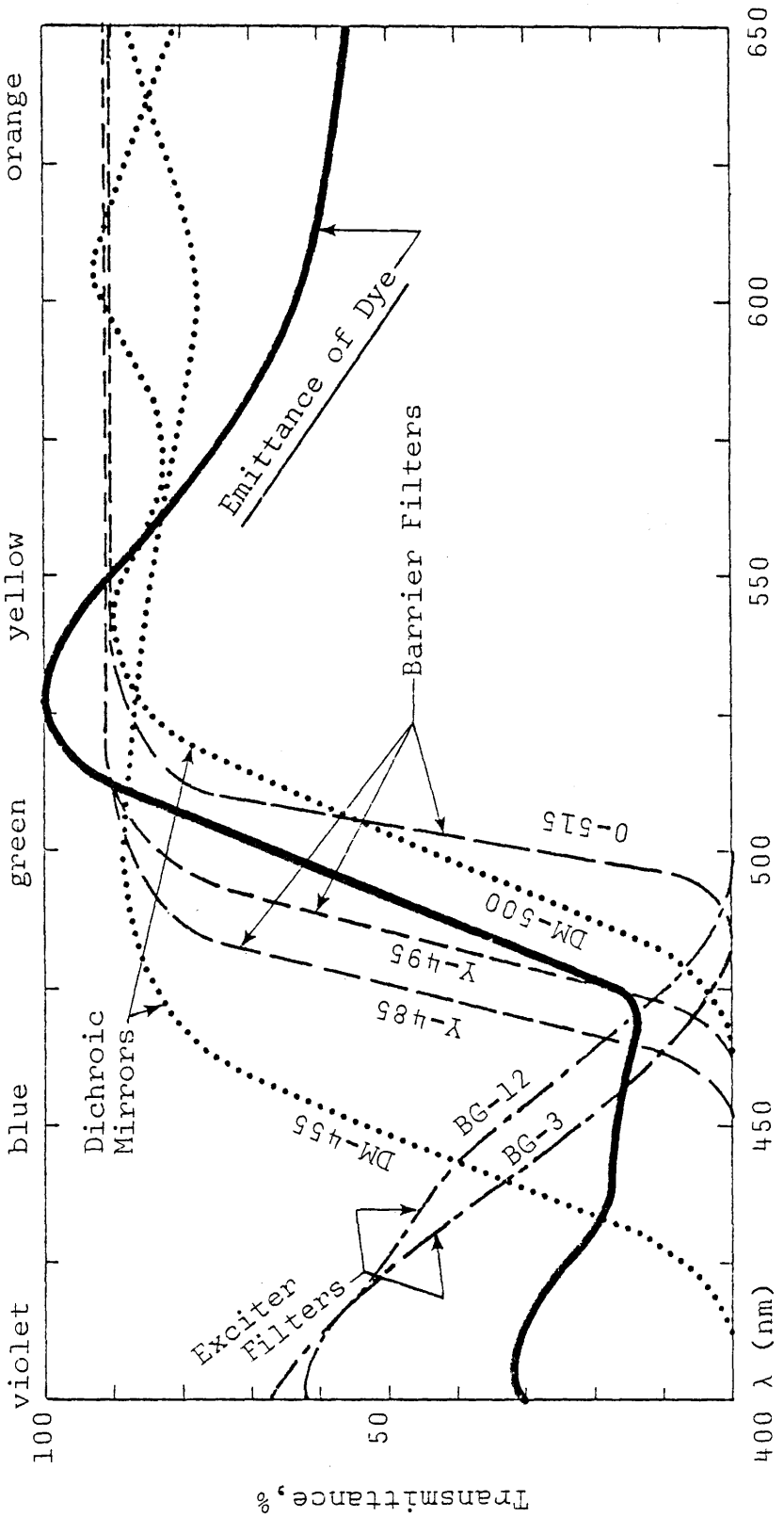

Figure 7. Percent transmittance of the exciter filters, the dichroic mirrors, and barrier filters compared with the excitation spectrum of the dye.

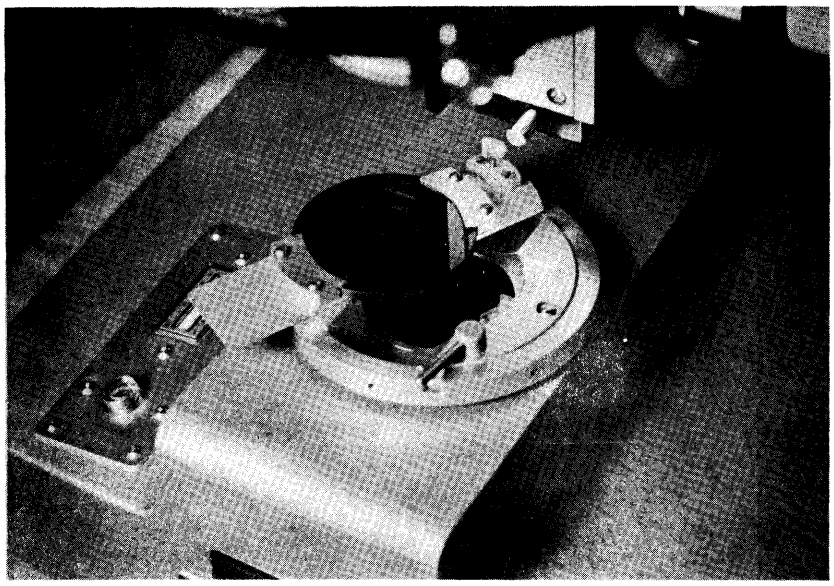

Figure 8. Swing-out mount for filter 3 mm thick, BG-12 over transmitted light port.

Figure 9. Dirty, angular sand particle in portland cement concrete. Polished ultrathin section (10 μm), transmitted plane polarized light.

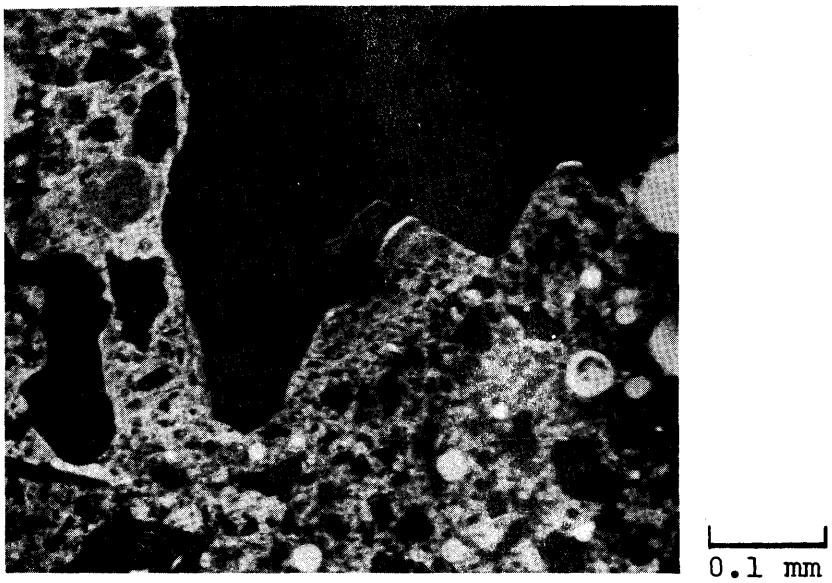

Figure 10. Same view as Figure 1. Incident violet light exciting fluorescent epoxy impregnation (barrier filter 0-515). The black areas are impermeable aggregate and unhydrated cement particles; the white areas are fluorescence indicating voids and cracks; the grey mix indicates the permeability and capillarity of the cement paste and the dirty clay coating on the aggregate.

Figure 11. Polished ultrathin section of 35-year-old portland cement concrete. Plane polarized light.

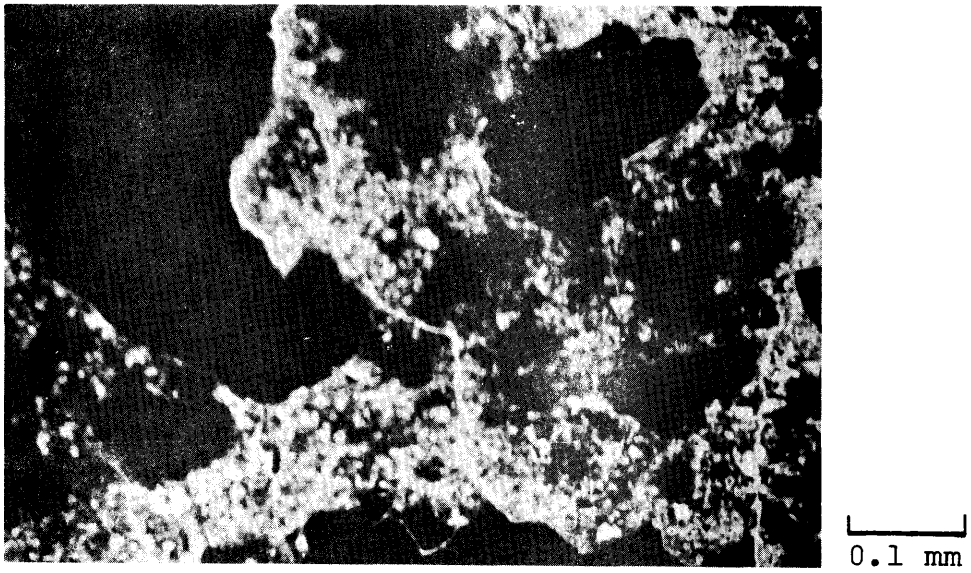

Figure 12. Same view as Figure 11. Incident violet light exciting the flourescence of the epoxy impregnation and showing the crack pattern, larger capillary structure, and voids within cement particles.

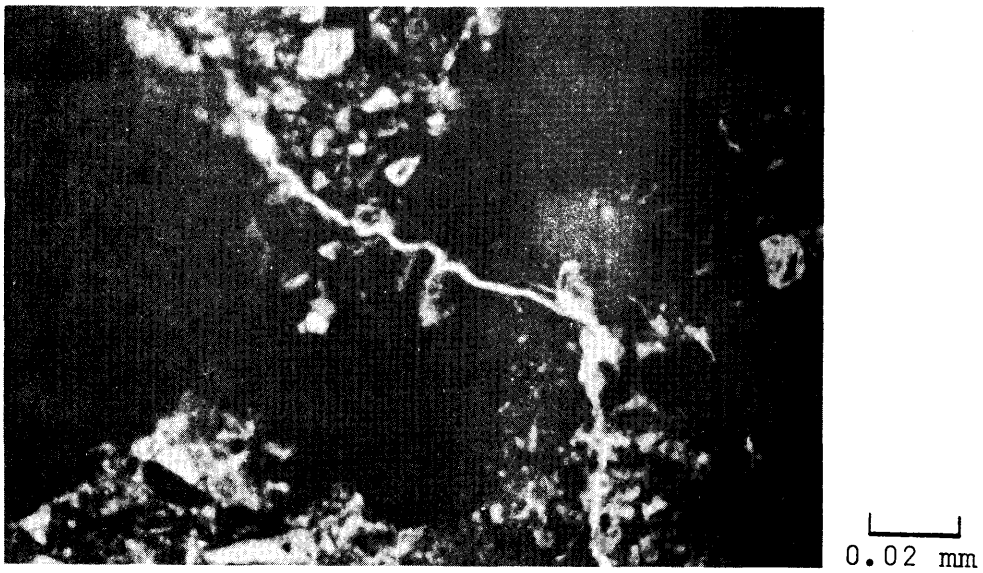

Figure 13. Detail of Figure 12 crack pattern.

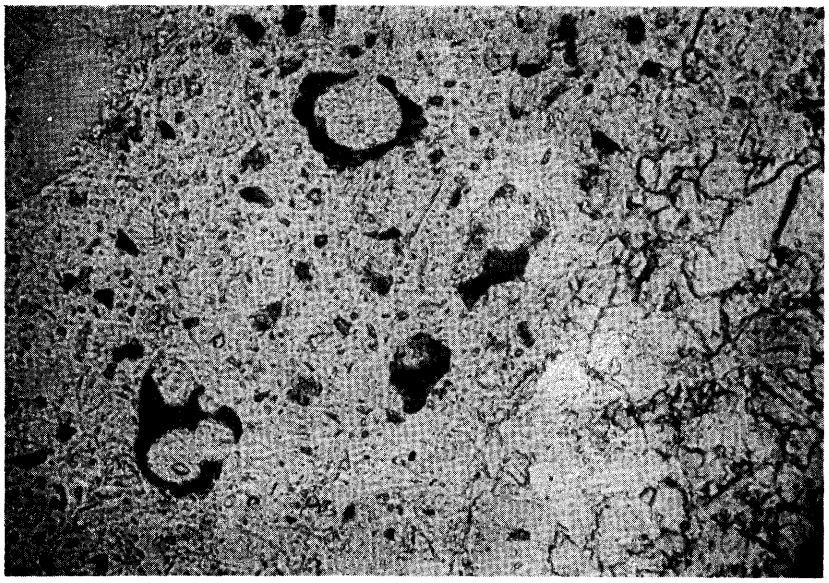

Figure 14. An area of paste of 35-year-old concrete, plane polarized light, quartz fine aggregate upper left, limestone coarse aggregate lower right. The dark ring structures are partially hydrated cement grains.

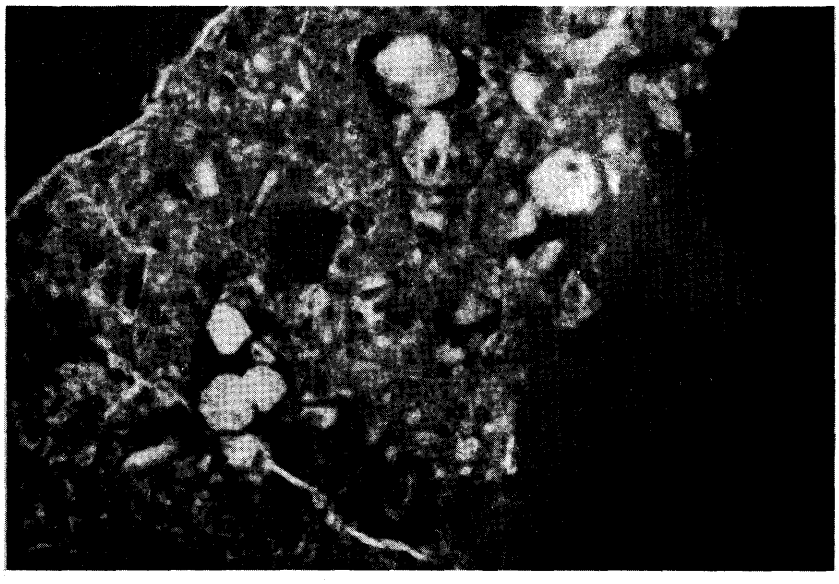

Figure 15. Same view as Figure 14. Incident violet light exciting the fluorescent epoxy impregnation and showing that the centers of the cement particles are nearly empty, as in Hadley's holes. The plate-shaped crystals run in these holes are probably a complex, solid solution of sulphur, aluminum, and silicon.(7)