INDO SWISS JOINT RESEARCH PROGRAMME (ISJRP)

RESEARCH FELLOWSHIPS

EXCHANGE GRANT REPORT

Grant No.: RF04

Part 1 - General Information

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<th>Microstructural characterization of concrete with mineral admixtures, subjected to short term heat curing</th>
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Part 2 - Exchange Participant(s) Details

VISITING SCIENTIST

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Part 3 - Scientific & Technical Information

3.1 Purpose of visit

The purpose of visit was to undertake study on the microstructural characterisation of concrete with mineral admixtures, subjected to short term heat curing. The work at EPFL was aimed to help get trained on various techniques or tools used for understanding the concrete microstructure modified by admixtures. The student is currently working at IIT Madras on his Master’s project which is the understanding of concrete microstructure modified by admixtures. The study was a follow up to the work carried out previously by Dr. Manu Santhanam at EPFL in 2007.

3.2 Short description of work carried out during the visit

During the stay at EPFL the scholar was trained on Specimen preparation, Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Image analysis. The aim was to study the effect of short term heat curing on the microstructure and the composition of C-S-H of the concrete. Scanning electron microscopy and Energy dispersive spectroscopy were applied to study the microstructure, while Image analysis was used to determine the degree of hydration of the cement in the concrete.

**Specimen Preparation:** Specimen preparation is very important for Scanning electron Microscopy. The various stages of specimen preparation were first learnt. Specimen preparation involves selection of suitable chunks of concrete broken in the compressive strength test. Identification of suitable concrete for microscopic analysis is important due to the complex heterogeneity of concrete. Concrete surfaces with large areas of paste are better suited against those with a lot of aggregate because maximum information can be obtained. Then suitable sections of around 10mm are cut out using precision diamond saw and alcohol as lubricant. Hydration was stopped by solvent exchange using isopropanol. The specimens were then dried in desiccators for more than 3 days.

The dried specimens were then vacuum impregnated with a low viscosity epoxy resin and allowed to harden at room temperature for 12-16 hours. The impregnation of the specimens with epoxy resin was to protect the specimen and prevent its damage during subsequent stages of grinding and polishing. The impregnated specimens were then carefully ground and polished. The impregnated specimens are then coarse polished on #500 and #1200 grit paper to remove epoxy from the surface of the specimen. This surface was then subjected to fine polishing on automated polishing machine using series of successively finer grade of diamond paste: 9, 3, 1 and 0.25 µm. Petroleum was used as lubricant during polishing. After every stage of polishing the specimens were checked under an optical microscope for the quality of polishing achieved. Polishing is then advanced to the next stage and continued till desired level of polishing achieved. Normally each specimen was polished for 3-4 hours to obtain a good surface. The polished specimens were then cleaned in an ultrasonic bath and dried in vacuum to remove any remaining lubricant from the surface. The specimens were then coated with a thin layer of carbon to prevent charging during BSE imaging.

**Scanning Electron Microscopy:** Backscattered electron images of polished sections were obtained and quantitative X-ray analysis performed during the period. Scanning electron microscope consists of a beam of electrons which are scanned in a grid pattern over the specimen surface. When the incident electrons hit the sample surface, electrons are emitted. Backscattered electrons are higher energy electrons ejected by elastic collision of an incident electron; while secondary electrons are lower energy electrons formed from inelastic collisions. The electron vacancies resulting from a higher state
and a characteristic X-ray of element is emitted to balance the energy difference between the two electrons states. Therefore the elements in the material can be detected.

When operated in the backscatter mode the information about the phases present in the hydrated cement paste (C-S-H, calcium hydroxide, and sulphoaluminates) can be obtained due to the compositional contrast offered by them. Backscattered electron images of flat specimens reflect the backscattering coefficient of scattered regions. The backscattering coefficient is basically dependent on the atomic number of the elements present and their mass concentration. The higher the atomic number of the elements present in a phase and/or the higher their concentration the brighter the phase appears in the image. In the hydrated cement paste or concrete the unhydrated cement grains appear nearly white, calcium hydroxide light grey, other hydration products generally darker grey and pores nearly black. The grey level range of C-S-H phases will generally be much wider than that of other phases present because of its more variable composition and structure.

Energy Dispersive X-ray analysis was performed on specimens for determining the chemical composition of the inner and outer C-S-H products of the hydrated cement paste. Microanalyses were performed only in the bulk paste phase of the concrete and specimens hydrated for 90 days were only selected. This was because only the 90-day specimens formed inner C-S-H of sufficient thickness for the EDS spot analysis with reliable results to be performed. Analysis of outer product phase were made more arbitrarily but always at spots considered to be essentially of C-S-H. Of each specimen at least 200 analyses were performed in each of the inner and outer C-S-H. The composition of outer C-S-H was presented in the form of plots between S/Ca ratio and Al/Ca ratio to understand the nature of C-S-H, while the Ca/(Si+Al) ratio was determined for the inner C-S-H.

The SEM used for the study was equipped with stage control software, which enabled the stage to move to different positions within the selected user defined area so as to obtain photomicrographs of specimen at same magnification and light settings. The microscope used for the study was FEI Quanta 200 and was operated at an accelerating voltage of 15kV. For BSE imaging the spot size was chosen to have a good resolution of image; while for the EDS analysis spot size was a little higher to generate desired X-ray results. The count rate for EDS was about 20kcps and counting time was real time of 1s. Microanalyses were performed with ZAF corrections. Analyses were made for Na, Mg, Al, Si, S, K, Ca, and Fe. Oxygen was stoichiometrically calculated, to provide the analysis totals.

Image Analysis: The BSE images can be analysed quantitatively to get volume fractions of phases in concrete. BSE images contained 1024 x 768 pixels with 256 grey levels at a magnification of 800x and a scanning time of 8μs for each pixel. For each image, a histogram representing the frequency of pixels as a function of the grey level (0-255) was generated. The histogram exhibits peaks corresponding to the individual phases. Different images have different brightness and contrast, but the composition of aggregate (quartz) and alite is constant. Therefore grey values of the C-S-H products were calculated by interpolation between two phases with known and distinct backscatter coefficients; alite and quartz.

\[
\text{C-S-H relative brightness} = \frac{(I_{\text{C-S-H}} - I_{\text{quartz}})}{(I_{\text{alite}} - I_{\text{quartz}})}
\]

Where, \(I_{\text{C-S-H}}\), \(I_{\text{alite}}\), and \(I_{\text{quartz}}\) are the peak grey values of C-S-H, alite and quartz respectively in the grey level histogram of BSE images.

Separation of aggregates is much more complicated than that of C-S-H. It is a combination of image analysis techniques such as grey-level threshold, filtering, hole filling using a program developed at the lab.
Area fractions obtained from 2-D cross section are equal to volume fractions from the 3-D structure when the materials have a random and isotropic nature. The microstructure of cement paste can be considered to satisfy those conditions. Thus the imaging technique of BSE images is a method for quantitatively evaluating the 3-D microstructure by analysing the information on 2-D cross sections.

![Original concrete image](image1) ![Image segmentation](image2)

**Figure Segmentation of concrete**

This technique was used to study quantitatively the degree of hydration of cement and concrete. The area fractions of anhydrous cement and aggregates were calculated by comparing their pixels to total number of pixels of the image. According to stereological principles, this area fraction corresponds to the volume fraction. But since BSE images of concrete contain large fractions of aggregates which could lead to great variation in volume fraction of anhydrous cement in the concrete. Therefore the volume fraction of anhydrous phases relative to the cement paste in the concrete are calculated. The degree of hydration can be calculated as, $\alpha = 1 - \frac{A_{\text{paste}}}{A_{\text{total}}}$, where $A_\text{paste}$ is the initial volume fraction of the cement particles present in the fresh paste of concrete.

### 3.3 Outcomes

The exchange student was trained on tools for understanding concrete microstructure such as Scanning electron microscopy including specimen preparation for microscopy, Energy dispersive spectroscopy, and Image Analysis.

### 3.4 Future collaboration with host institution

The student would be interested on a visit to EPFL in near future for a period of 2 to 3 months for further studies on concrete microstructure modified by admixtures which would be helpful on the Master’s project at IIT Madras.

### 3.5 Various comments

The visit to LMC, EPFL was very much fruitful in the sense that the purpose of visit, to understand and learn on various techniques involving study of concrete microstructure, was achieved. While EPFL has
one of the best cement chemistry labs across world, Dr. Karen Scrivener is regarded as one of the best researchers worldwide in the field of cement chemistry and microstructure. The guidance of Dr. Karen Scrivener and Dr. Emmanuel Gallucci was helpful to gain considerable knowledge during the stay at EPFL. The interaction with doctoral students at the LMC was helpful in various ways.

3.6 Projected publications/articles resulting or to result from the exchange

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