# DELAYED SETTING OF CONCRETE – A PETROGRAPHIC AND CHEMICAL INVESTIGATION

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## ABSTRACT

A comprehensive petrographic and chemical analysis was undertaken during the investigation of unusually delayed setting of a section of concrete placed during the repair of a bridge deck on a busy interstate highway. Reportedly, the final setting of concrete took more than 5 days and it was impossible to achieve the desired tyned surface finish within a reasonable period after the placement. Petrographic examinations determined a higher porosity, lower degree of portland cement hydration, and coarser size of calcium hydroxide component of portland cement hydration in the delayed set concrete compared to the normal set batch placed in the same day. The microstructural differences are consistent with the mechanism of delayed setting, which had kept many solution-filled pores empty for longer periods than the normal set concrete and allowed the development of relatively coarsely crystalline calcium hydroxide component of portland cement hydration in the open spaces. UV-VIS spectrophotometric analysis has determined approximately three times the dosage of the retarder in the delayed set concrete compared to that in the normal set. Concrete placed in hot weather usually contain a set-retarding chemical, whose dosage, if not controlled, can cause unusual retardation and associated early-age problems without necessarily affecting the design strength.

## INTRODUCTION

Concrete is no longer a simple three-component system of cement, aggregate, and water, but a complex multi-component salad including many solid additives such as pozzolans, cementitious materials, microfillers, fibers, and many liquid property-enhancing chemicals specially formulated to provide numerous benefits such as rapid strength gain, workability enhancement, set acceleration or retardation, water reduction, air entrainment, corrosion inhibition, alkali-aggregate reaction mitigation, shrinkage compensation, pigmentation, and eventually, strength and durability enhancements. Similar to adding spices to improve the taste of food, a carefully controlled addition of many of these solids and chemicals is sometimes mandatory to achieve the desired property in an otherwise unfavorable environment. Over-dosage of these chemicals, however, can introduce undesirable effects. Under-dosage can reduce the effect or the magnitude of development of the desired property. Sometimes one chemical provides multiple benefits (e.g., water reduction and set control); other times more than one chemical is needed to achieve multiple benefits. Uncontrolled addition of too many chemicals, however, can introduce problems due to incompatibility or adverse interactions between the chemicals, or between cementitious materials and chemicals with an adverse effect on the rate of cement hydration, setting, strength gain, and development of other properties.

There are several publications in literature on the issue of cement-admixture incompatibility and its effect on various concrete properties. There are also incidences of over-dosage of setaccelerating admixture creating the opposite effect of set retardation, or vice versa, or excessive dosage of a water-reducing chemical creating an undesirable effect of set retardation. Some chemicals act as retarders when used in small amounts (e.g., 0.3 percent by mass of cement) but in large dosage (e.g., 1 percent by mass of cement) they act as accelerators.

The present article provides a case study of over-dosage of a set-retarding chemical (Daratard 17, manufactured by W. R. Grace and Co.), which has caused severe delay (up to 5 days) in achieving the final set of a section of concrete placed in hot weather during the reconstruction of a busy bridge deck on an interstate highway. The study encompasses: (a) detailed microstructural investigation from comparative petrographic examinations of a delayed set and a normal set concrete for diagnosing the characteristic microstructural features of delayed set concrete; and (b) determination of the amount of retardar overdosage from chemical analysis. The study emphasizes the importance of quality control during proportioning and admixture dosage in the batch plant.

## BACKGROUND

The reported mix design of the concrete contains 520 pounds of Type II portland cement meeting the requirements of ASTM C 150, 124 pounds of ASTM C 618 Class F fly ash, 990 pounds of natural sand fine aggregate meeting the requirements of ASTM C 33, 1800 pounds of crushed gravel coarse aggregate, 21.4 fluid ounces per cubic yard of Daratard 17 set retarding chemical meeting the requirements of ASTM C 494 Type D retarder and water reducer, 7.7 ounces per yard of Darex II air entraining chemical conforming to ASTM C 260, 4 gallons per cubic yard (7 pounds per gallon of water) of DCI-S corrosion inhibitor, and 250 pounds of water (including the water from the corrosion inhibitor).

## MECHANISM OF SET RETARDATION IN A PORTLAND CEMENT-WATER SYSTEM

There are three ways a set retarding chemical can cause retardation – (a) a reduction in the dissolution rate of the rapidly dissolved anhydrous components of cement; (b) formation of insoluble and impermeable film around the hydrating cement particles; and (c) a delay in bond formation among the hydrates. Retarders impede the dissolution of calcium aluminate during early hydration. At low concentrations, some monovalent cations ($K^+$ or $Na^+$) reduce the solubility of $Ca^{2+}$ ions and some monovalent anions ($Cl^-$, $NO_3^-$) reduce the solubility of silicates and aluminates, and, thereby, they impart an overall retarding effect. At low concentrations (e.g., 0.1 to 0.3 percent by mass of cement), salts of weak bases and strong acids ($CaCl_2$), or strong bases and weak acids (e.g., $K_2CO_3$) cause set retardation. Surfactants, such as gluconates and lignosulfonates delay the bond formation among the hydration products. Calcium salts of phosphoric, boric, oxalic, and hydrofluoric acid are highly insoluble, which slow down cement hydration by forming dense and insoluble coatings around the hydrating cement particles.

Daratard 17 is an aqueous solution of hydroxylated organic compounds, which complies with ASTM C 494 Type D admixture; it has a recommended dosage that varies from 130 to 520 mL/100kg (2 to 8 fl oz/100 lb) of cement. Daratard 17 causes set retardation by forming a thick, dense impermeable film around the hydrating cement particles.

## SAMPLES

The following materials were received for detailed investigation:

(a) Two 6 × 12 in. size hardened concrete cylinders prepared in the field during the placement of normal set and delayed set concretes (Figures 1 and 2);

(b) A bag of Type I/II portland cement that was used in the concrete;

(c) A bag of fly ash that was used in the concrete mixture;

(d) A bottle of Daratard 17 liquid set-retarding chemical admixture.

The hardened concrete cylinders were used for petrographic examinations and chemical analysis. The cement, fly ash, and set-retarding chemical were mixed at the project-specified mix proportions to prepare reference samples for calibration purposes in chemical analysis.

## METHODOLOGY

Petrographic examination was done by using the procedures described in ASTM C 856: "Standard Practice for Petrographic Examination of Hardened Concrete". Briefly, the procedures include: (a) detailed visual examinations of normal-set and delayed-set concretes; (b) examinations of freshly fractured surfaces and lapped sections of concretes by using a stereomicroscope; and (c) examinations of oil immersion mounts and thin sections by using a petrographic microscope.

For chemical analysis, portland cement, fly ash, Daratard 17 admixture were mixed to prepare the reference samples for calibration for quantitative determination of the amount of retarder in the hardened concrete. The reference samples consist of pastes having water-cementitious materials ratios of 0.50, cementitious materials with 20 percent fly ash, and four different dosages of retarders to include 0, 3, 6, 9, and 18 fluid ounces of chemical per 100 pounds of cementitious material. The mixes were moist-cured for seven days, and subsequently chemically analyzed to establish the calibration curve. For hardened concrete samples, approximately 160 grams of paste-rich fractions of concrete was ground to pass through the No. 100 sieve. 120 ml. of deionized water was added. While stirring with a magnetic stir bar, the mixture was boiled for 20 minutes. During the last 2 minutes, carbon dioxide gas (high purity) was bubbled into the slurry; the mixture was vacuum filtered while hot through a highly retentive filter paper; the residue was washed with denatured ethanol; and the filtrate was dried on a hot plate in a 250 ml. glass beaker. The dried solids were dissolved in 25 ml. reagent grade sulfuric acid; a 5 ml. aliquot of this solution was added with 5 ml. of beta-napthol reagent in a 15 ml. glass test tube. The test tube was boiled for one hour. After cooling, the solution in the test tube was scanned in a UV-visible spectrophotometer in the region of 190 to 1100 nanometers (nm). The absorbance bands at 590 to 600 nm were used to determine the amounts of sugar and salts of hydroxylated carboxylic acid (referred as H.C.) in the sample. Sugar and H.C. are the common retarding agents present in set-retarding chemicals.

## PETROGRAPHIC EXAMINATIONS

Appearance – The normal set concrete cylinder is noticeably harder, denser and better consolidated than the delayed set concrete cylinder. A significant preferential loss of paste relative to the aggregates has occurred during sectioning and grinding of the delayed set concrete cylinder (Figure 3).

Aggregates – Coarse aggregate is crushed siliceous-calcareous gravel having a nominal maximum size of 1 in. Particles contain quartz-sandstone (quartz-arenite), calcitic sandstone, greywacke, microcrystalline and chalcedonic varieties of chert, limestone, and dolomite. Particles are angular to subangular, equidimensional to elongated, uncracked, uncoated and unaltered. Fine aggregate is natural siliceous-calcareous sand having a nominal maximum size of $^{3}/_{8}$ in. Particles contain strained and unstrained quartz and quartzite, feldspar, quartz-sandstone, greywacke, siltstone, chert, granite, limestone, dolomite, schist, and gneiss. Particles are subangular to well rounded, uncracked, unaltered and uncoated. There is a deficiency of finer and intermediate sizes of the coarse aggregate; thus, the total aggregate grading is poor (Figure 3). The fine aggregate is well graded. Both coarse and fine aggregates are well distributed and have been sound during their service in the concrete. Some coarse and fine aggregate particles are potentially alkali-silica reactive. There is, however, no evidence of such a reaction in the concrete.

Paste – Paste is medium grey, moderately hard to hard, and dense in the normal-set cylinder and porous in the delayed set cylinder (Figure 4). Freshly fractured surfaces have subtranslucent vitreous lusters and sub conchoidal fracture. Residual and relict portland cement particles are estimated to constitute 10 to 12 percent of the paste volume. The calcium hydroxide ($Ca(OH)_2$) component of cement hydration occurs as small, platy, and patchy units uniformly dispersed in the paste and is estimated to constitute 14 to 16 percent of the paste volume. Hydration of the cement is found to be normal in both cylinders (Figure 5). There is no evidence of any restricted cement hydration due to delayed setting. Distributed throughout the paste are fine, clear to dark brown, and black glassy spheres of fly ash (Figures 4 and 5) having the fineness of portland cement. The textural and compositional features of the pastes are indicative of cementitious materials contents estimated to be equivalent to 6 to $6^{1}/2$ bags of portland cement per cubic yard of which 15 to 20 percent is estimated to be fly ash and water-cementitious materials ratios estimated to be 0.45 to 0.50. Carbonation has extended to distances of $^{1}/_{4}$ in. from the ends and sides of the cylinders. There is no noticeable difference in the depth of carbonation between the normal set and delayed set concretes.

Air – Air occurs as: (a) numerous, very fine, discrete, spherical, and near-spherical voids having sizes up to 100 microns; (b) a relatively lesser amount of fine, discrete, spherical voids having sizes up to 1 mm; and (c) a few coarse, near-spherical, and irregularly shaped voids having sizes up to 3 mm. Items 'a' and 'b' are characteristic of entrained air, and item 'c' is characteristic of entrapped air. The concrete is air-entrained. The air content is estimated to be $6^{1}/_{2}$ to $7^{1}/_{2}$ percent. Circumscribing some coarse aggregate particles are excessive accumulations of entrained air voids that have given a frothy appearance to the paste in those aggregate sockets. Such frothy-textured paste in the aggregate sockets reduces the aggregate-paste bond and thereby reduces the compressive strength of the concrete. There is, however, no evidence of any excessive air entrainment in the delayed set concrete that is determined to have a retarder overdose.

## CHEMICAL ANALYSIS

Chemical analyses of the delayed set and normal set concrete cylinders were done to determine the dosage rate of the set retardar. The results indicate that the normal set concrete contains 2-3 fluid ounces of Daratard 17 liquid set retardar per 100 lbs. of cementitious materials, whereas the delayed set concrete has a three times higher dosage, which is equivalent to 6 to 9 fluid ounces per 100 lbs. of cementitious materials. The analysis has detected both sugar and salts of hydroxylated carboxylic acids, which are common retarding chemicals present in retarding chemical admixtures. Figure 5 shows the UV-visible spectrophotometer scans for the normal and delayed set concretes and a control paste (cement + fly ash + water at a *w/cm* of 0.50) with no admixture. Based on the above dosage rates and the reported mix design (containing 520 pounds of cement and 124 pounds of fly ash per cubic yard), the dosage rate of Daratard 17 retarder in the normal set concrete was determined to be 12.88 to 19.32 ounces per cubic yard, whereas in the delayed set concrete the dosage is found to be 38.64 to 57.96 ounces per cubic yard. The reported mix design indicates a dosage of 21.4 ounces per cubic yard. The delayed set has a significantly higher dosage of retardar than the amount recommended in the mix design.

## MICROSTRUCTURAL DIFFERENCE BETWEEN NORMAL-SET AND DELAYED-SET CONCRETES

There are three distinct characteristic differences in the microstructures of delayed-set and normal-set concretes:

Degree of portland cement hydration – The first difference is the degree of portland cement hydration in the two concretes, which is found to be higher in the normal set concrete than in the delayed set concrete. The lower degree of portland cement hydration in the delayed set concrete is judged to be due to the delay in initiation of the hydration of calcium silicates (which begins at the tail end of setting) at a later stage in the delayed-set concrete than in the normal set concrete. The difference in the degree of portland cement hydration is estimated from: (a) the relative amounts of calcium hydroxide component of cement hydration, (b) thickness of reaction rims around the residual portland cement particles, (c) the proportion of residual cement, and (d) the volume of capillary pores in the normal and delayed set concretes.

Size of calcium hydroxide component of cement hydration – The second difference is the size of the calcium hydroxide component of the cement hydration, which is found to be slightly larger in the delayed set concrete than in the normal set. The larger size of primary calcium hydroxide in the delayed set concrete is due to more space available for growth in the delayed concrete than in the normal set concrete. In spite of such a difference in size, however, the proportion of calcium hydroxide is similar in both concretes (due to the opposing effects of its higher degree of generation by the higher degree of portland cement hydration and the higher degree of its consumption by the pozzolanic reaction with fly ash in the normal set concrete than in the delayed set concrete).

Total porosity of paste – The third difference is the total porosity of the paste, which is found to be higher in the delayed set concrete than in the normal set concrete. The higher porosity is due to the lower degree of portland cement hydration in the delayed set concrete, and as a result, a lower degree of infilling of the capillary pores between the residual cement particles. It is important to note that despite higher capillary porosity of the delayed set concrete both delayed and normal set concretes have essentially identical water-cementitious materials ratio. Determination of water-cementitious materials ratio (*w/cm*) from florescence microscopy can give an erroneously high *w/cm* in the delayed set concrete due to its inherent high capillary porosity.

Degree of cement hydration, calcium hydroxide size, and capillary porosity of paste are all interrelated and hence, affected together by the delayed setting of the concrete. Due to the lower degree of cement hydration and higher capillary porosity, a delayed-set concrete usually provides a lower strength at a particular age compared to its normal-set companion. Delayed set concrete, however, should pick up the strength once the delay in setting ends and solidification starts; the late age strength of delayed set concrete should not differ significantly from the normal set concrete of the same mix proportions.

## CONCLUSION

Concrete placed in hot weather or in large structures commonly contain a retarder to delay the initial and final sets for the times needed for placement and finishing, respectively. Severe delay, however, is undesirable, which makes finishing difficult (and often prolonged). Top-down stiffening, or surface crusting (in a hot, dry, or windy weather condition) in a delayed set concrete can create a pseudo-solid (crusted) surface while the interior concrete is still in a plastic or semi-plastic state and may continue bleeding – this can increase the potential for surface delamination by accumulation of bleed water beneath the crusted surface.

In the present study, the proportions of three basic ingredients of concrete, i.e., aggregate, cement, and water (and water-cementitious materials ratio, aggregate-paste ratio, and air content) are found to be essentially identical in the normal and delayed-set concretes, which are also in conformance to the reported mix design. The difference in the setting behavior, however, is attributed to the clear difference in the dosage rate of the set-retarding chemical, which is three times higher in the delayed set concrete than in the normal set concrete. Such excessive dosage of the retarder in a couple of batches of the delayed set concrete (placed in the same day with the normal set concrete) indicates a probable malfunction of the admixture-dispensing unit. A delay in the addition of the retarder in the mix, however, can also cause a significant delay in achieving the final set, which should be investigated in laboratory trial mixes. Laboratory tests on Daratard 17 at the maximum recommended dosage by the South Dakota School of Mines and Technology [1] showed more than a 20-hour delay in the final set for a 2-minute delay in the admixture addition.

There is no evidence of excessive air entrainment due to retarder overdosage in the delayed set concrete, which, therefore, should have a compressive strength comparable to, or may even higher at a later age than the normal set concrete.

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[1] South Dakota School of Mines and Technology, Field Performance of Concrete Admixtures, Study SD97-09, June 1998.

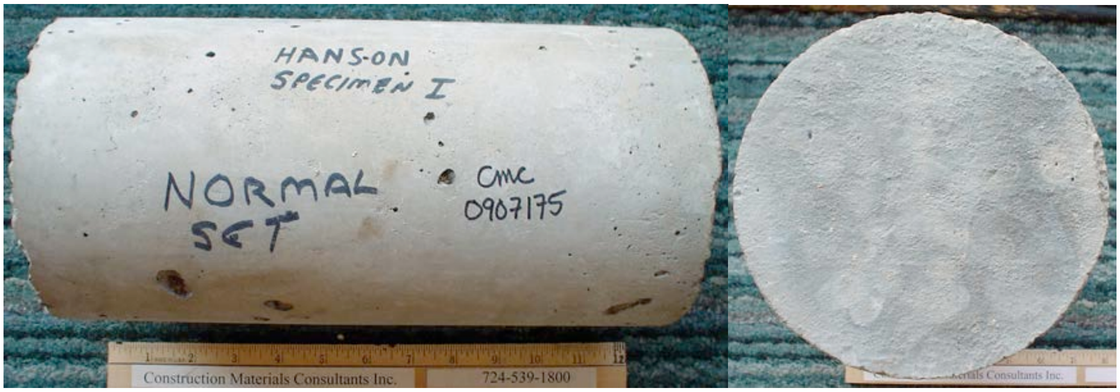


**Figure 1**: Shown are the side and top end of the cylinder for normal set concrete.

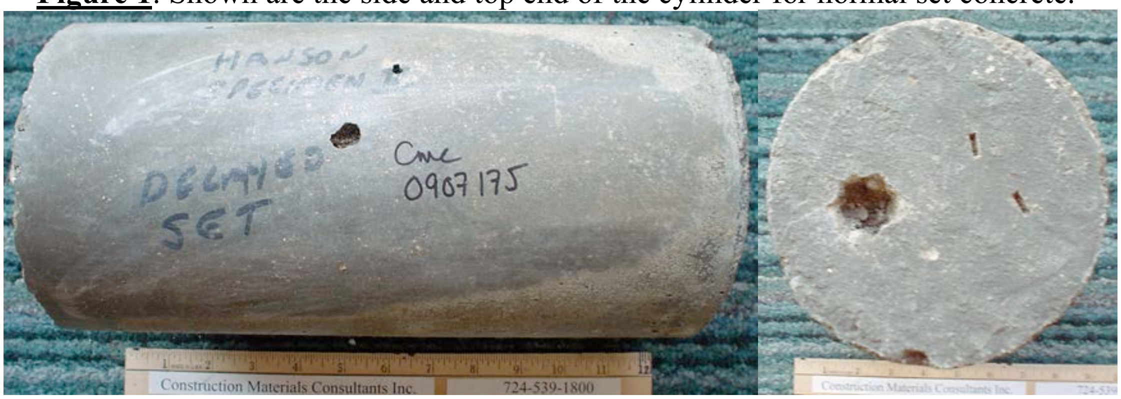


**Figure 2**: Shown are the side and top end of the cylinder for delayed set concrete.

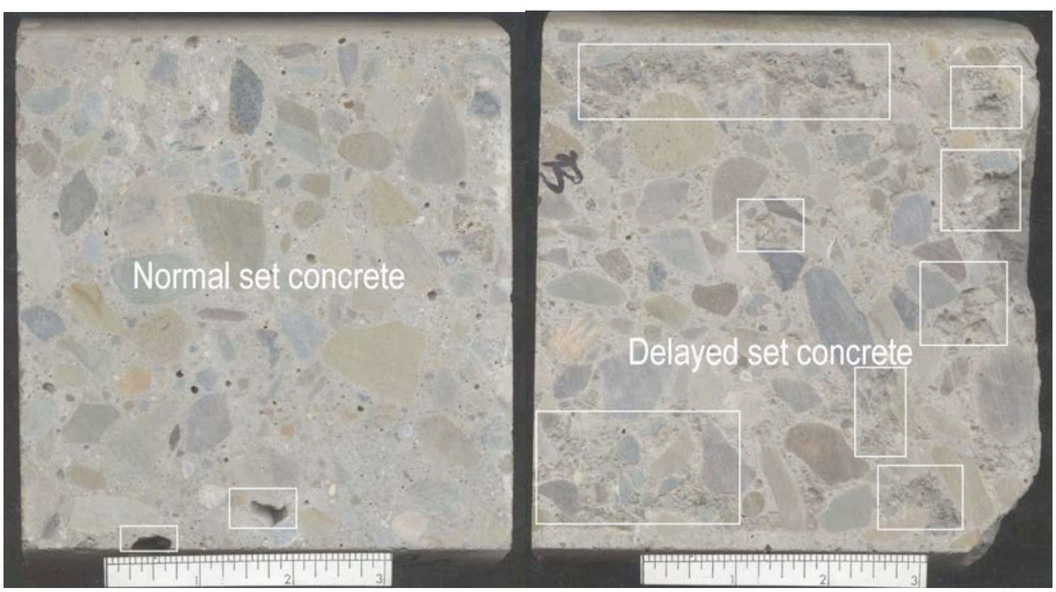


**Figure 3**: Cross-sections of portions of cylinders of normal and delayed set concretes showing: (a) crushed gravel coarse aggregates; (b) the distribution and overall poor grading of the aggregates; and (c) the loss of paste (boxed) during sectioning in the delayed set concrete. The scales are in 1-in. numerical increments.

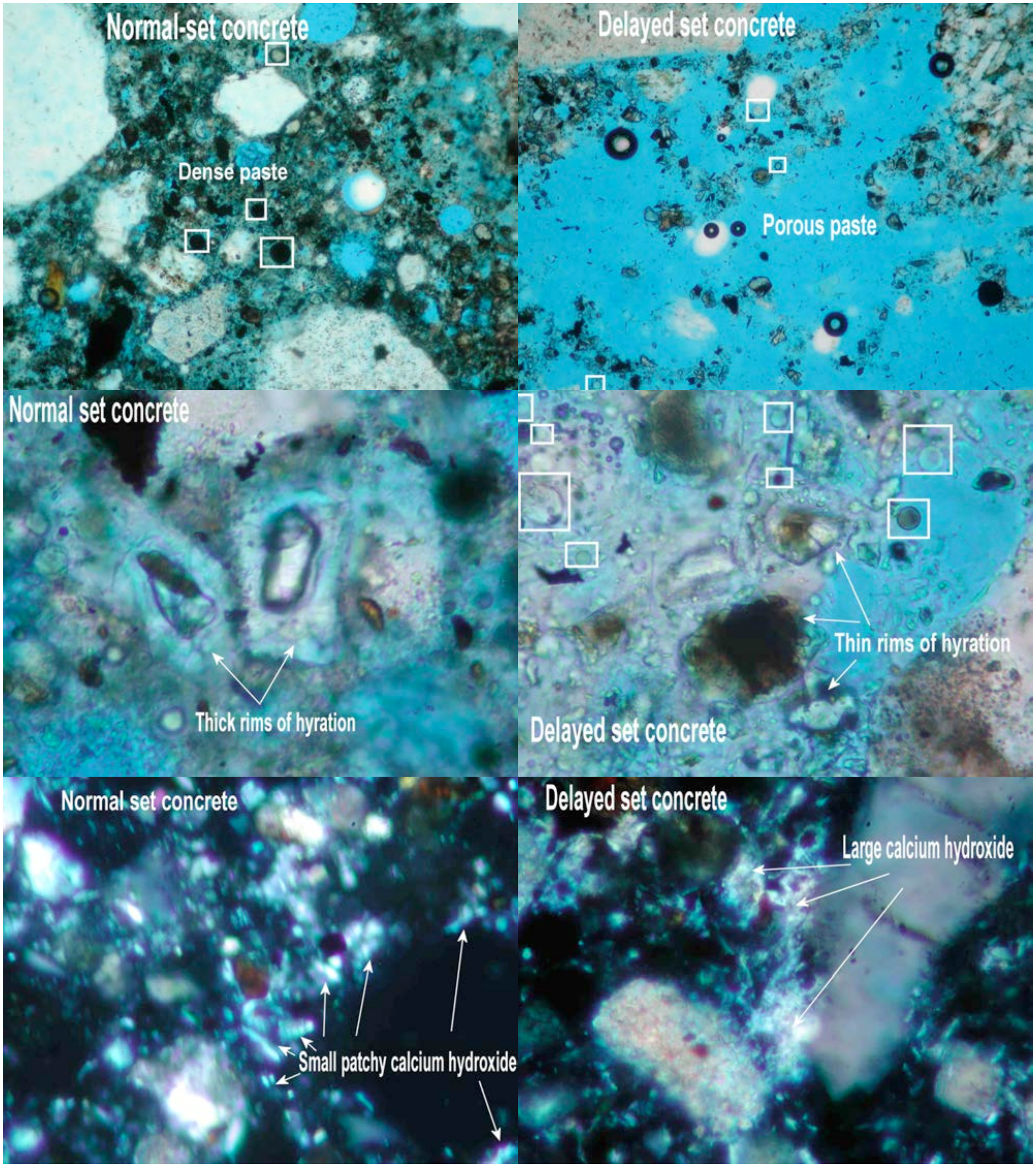


**Figure 4**: Microstructural differences between the normal and delayed set concretes: Top - Difference in porosities of the paste (fly ash particles are boxed; Middle – Difference in degrees of cement hydration; Bottom – Difference in sizes of calcium hydroxide component of portland cement hydration. Some fly ash particles in the paste are boxed. Field widths are 0.5 mm.

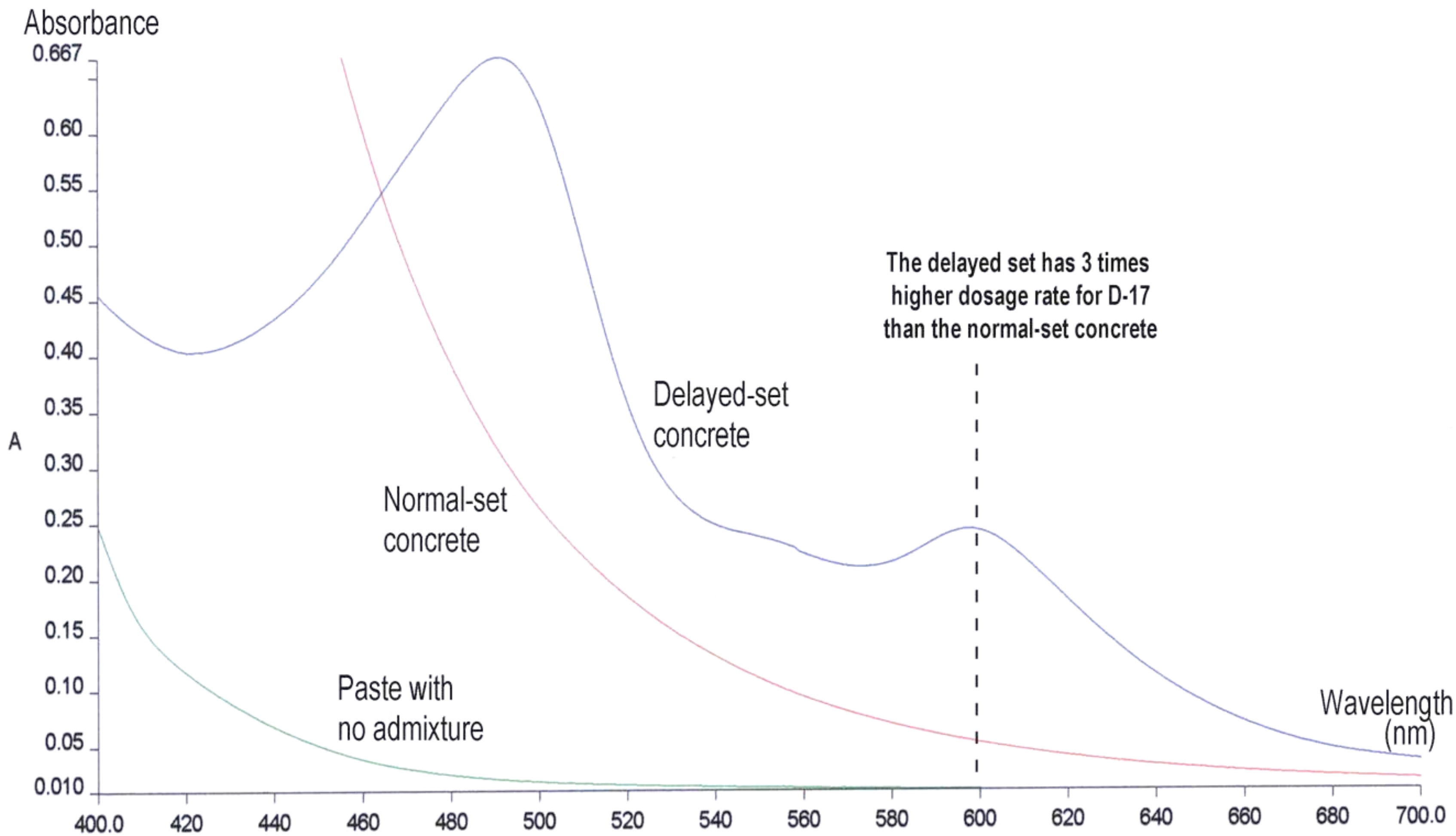


**Figure 5**: UV-Visible spectrophotometer scan of (a) a control paste sample (cement plus fly ash plus water at a 0.50 water-cementitious materials ratio) with no admixture (green); (b) the normal-set concrete sample (red line); and (c) the delayed set concrete sample (blue line). The delayed set concrete clearly shows a significantly higher dosage rate of set retarder (D-17) around the 595 nm region (shown in dashed line).