International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.
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Vol. 45 No. 2 July 2024, pp. 01-21

FTIR Spectroscopic Studies on Hydration Propensities of the Preferentially Selected OPC Cements Manufactured in Nepal

Prof. Dr. Anant Babu Marahatta[1,*], Gaurab Baral[2], Karuna Dhital[2]

[1]Supervisor/Professor of Chemistry, Engineering Chemistry and Applied Science Research Unit, Department of Civil, Computer, and Electronics Engineering, Kathford Int'l College of Engineering and Management (Affiliated to Tribhuvan University), Kathford Int'l Education & Research Foundation, Kathmandu, Nepal
[2]Student, Department of Civil Engineering, Kathford Int'l College of Engineering and Management (Affiliated to Tribhuvan University), Kathford Int'l Education & Research Foundation, Kathmandu, Nepal
**Corresponding author: abmarahatta@gmail.com/anant.marahatta@kathford.edu.np*

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Abstract – In general, the performance and working efficiency of the cements, and cement made mortars & concretes are the direct consequences of the clinker phases and their wide ranged chemical constituents. But, the more specific and valuable descriptors vowed to rate their cementitious features genuinely are natures of the succeeding hydration reactions products and their contributions to enhance placing, adhering, setting, and hardening strength, types of the intergranular porosity and the capillary water retaining potentiality, and the overall kinetics of the temporal hydration reactions. In this work, all of these fundamental criteria are assessed via the FTIR spectroscopic technique employed in quantizing all type hydration reactions products produced by the variable technology manufactured Nepal based cements (CS1 and CS2) in their mortar mixtures cured with the sufficient amount of water time to time for 28 days. Based on the standard time regimes required by them to gain considerable porosity, denseness, and strengths plus their practical feasibilities, 1 day; 7 days; & 28 days long time periods are chosen here as the effective sampling intervals, and the different phases of the subsequent hydration reactions products & their explicit contributions towards the same are analyzed quantitatively. The same logical interpretations are taken here as actual bases by means of which superior performances of one cement brand over the other are evaluated. In the course of rating their potentialities at each individual timeframes, the quality and quantity of the silicate–, calcite–, portlandite– phases; SO_3^{2-}– & CO_3^{2-}– groups holding chemical compounds; and C–S–H nanosized gel released as predominant hydration reaction products, and the mass of water interlocked into the mortar matrices as evaporable (absorbed and capillary) water are examined precisely. The authors believe this article as a doctrine document explaining all the primary prerequisites needed to acquire good quality hydration reaction products which in turn illuminate the practical approaches of rating cements and cement based engineering materials.

Keywords – Cements/Mortars, Hydration reactions, Evaporable water, Performance evaluation.

1. INTRODUCTION

In the civil engineering construction sectors ranging from small scale renovation projects to the large scale mega constructions, cement serves as a standalone binding material. Being this engineering material a special fine blend mixture of limestone, clay, and many other assorted minerals offering an extraordinary cementitious ability, it's worldwide uses as an amalgamating material mainly in compositing the disparate ingredients of the concrete and mortar such as sand, gravel, water, etc. is highly impressive [1–5]. Amidst various promising physicochemical properties shown by the commercially available cements produced by the variable technologies equipped manufacturing industries, and their unique type chemical constituents required to meet intense public consumption demands, the notably strong propensities of them to solidify and set upon contact with water plus to undergo rapid yet consequent time–dependent hydration reactions by producing

various types of the chemical products bestowing marvelous cementitious features are few of their most significant attributes. In fact, these properties make themselves a discrete material employable to build the robust engineering structures capable of sustaining different type of loads acting on them, and of withstanding extreme environmental conditions [4,6]. Additionally, the unique hydration reactions of the cements and the most distinctive hydration products formed as a function of water-curing time further witness their promising properties indispensable to acquire notable multifaceted functions associated with the mortar, plastering, masonry, pointing/ shaping, concrete, joints, water impermeability, internal protective coatings, etc. Moreover, the same particularities distinctly mark themselves as an ideal engineering material for the unanimous applications in fixing drainage and piping systems, ensuring the water-tight integrity within the priory designed structures, architecting the basement floors and rooftops, designing the essential structural elements such as lintels, beams, stairs, pillars etc. [1, 7, 8]. The underlying facts behind all these critical roles of the cements are basically lied in their in-built chemical constituents comprising with the limestone ($CaCO_3$), clay (SiO_2 & Al_2O_3), gypsum ($CaSO_4 \cdot 2H_2O$), and their resulting chemical products of the clinker such as dicalcium silicate ($2CaO.\ SiO_2$; hereafter C_2S), tricalcium silicate ($3CaO.\ SiO_2$; hereafter C_3S), tricalcium aluminate ($3CaO.Al_2O_3$; hereafter C_3A), and tetracalcium aluminoferrite ($4CaO.\ Al_2O_3.\ Fe_2O_3$; hereafter C_4AF). The chemical reactions associated with them are: $CaCO_3 \rightarrow CaO + CO_2$; $SiO_2 + 2CaO \rightarrow 2C_2S$; $CaO + 2CaO.SiO_2 \rightarrow 3C_3S$; $Al_2O_3 + 3CaO \rightarrow 3C_3A$; and $4CaO + Al_2O_3.Fe_2O_3 \rightarrow 4C_4AF$ [1, 4, 5]. When the particular amount of cement is thoroughly mixed with water by maintaining water–cement ratio w/c = 0.3 –0.6 by mass, all these chemical components (C_2S, C_3S, C_3A, and C_4AF) undergo hydration chemical reactions as a function of time, and generate a nano sized calcium silicate hydrate (C–S–H) gel. The quantity and quality of this gelly matrix released as hydration products behave as the actual descriptor deterministic to the extent of which the cements and cement based materials glue the ingredients mixed to them, and make the entire structures hardened and durable, resistant towards wearing and tearing, and resilient against extreme environmental conditions [5]. According to the experimental tests and probing techniques reported elsewhere [1, 4, 5], the hydration reaction products obtained from the reactions of C_3S & C_2S with water offer early and late strengths to the cement made engineering structures respectively while the products obtained from the hydration reactions with the C_3A are responsible for rapid setting/hardening (fresh early paste). But, the hydration reaction products released from the chemical reactions with the C_4AF of the cement are vowed to contribute to very low strength, instead undertake the responsibility of its maximum heat of hydration ($H = H_1 - H_2 - 0.4(t_h - 25.0)$) [4, 5, 9]. The comprehensive meaning of this ideological fact is that there is an existence of the temporal dependencies to the complete hydration reactions of the C_2S, C_3S, C_3A, and C_4AF, and to the absolute release of their hydration products while intermixing cement thoroughly with water in presence of auxiliary ingredients. Even though the cement present in the water–cured mortars/concretes needs quite long time range (1 year or even longer) for the absolute completion of the hydration chemical reactions with water [5, 9–11], the continuous follow–up yet practically reasonable consecutive time periods recommended for inspecting the ongoing hydration reactions/products of the variable brand cements lie in the scale of 1 day to 28 days [9]: at 1st day of hydration, an incomplete hydration reaction takes place, and the resulting particle–matrix has a porous networks with very nominal hydrations; at 7th day of hydration, a slaked lime $Ca(OH)_2$ crystal is formed in a relatively more hydrated cement–water paste, and the resulting particle–matrix is quite dense; and by 28 days, the hydration reactions are progressively slower to the most extent, and the resulting paste acquires a very high degree of denseness with low degree of porosities [10, 11].

In general, the most responsible descriptor deterministic to the time dependent hydration reactions of the cements and the natures of the hydration products is none other than their particle morphologies, distribution ranges, and the crystallite/grain sizes: the faster hydration rates of the cements and the rapid hydration products are only achieved when the degree of fineness of the cement particles is higher, and the particle size/pore size distributions owing to the enlargement of the specific surface area are narrower [1, 4,5,9]. In other words, if the cements are comprising with the sufficient number density of the fine particles, they undergo quick hydration reactions with faster setting rates, but if they possess predominant number density of extra-fine particles (< 50 μm), the poor intermixing and placing abilities plus the slower hydration reactions are observed. Though the specific surface area, porosity of the cement materials, and the narrow range particles distributions don't stand for the responsible criteria of inspecting the precise degrees of fineness of the grains, the quality and quantity of the C–H–S based hydrated products formed as a function of reaction time, the compressive strength they gain after the complete hydration reactions with water, and the entire cementitious propensities of them, etc. are the direct functions of these morphological observables [9–11]. Towards unveiling these facts underlying with the variable brands Nepal made cement samples, and more importantly, towards characterizing them explicitly with the special emphasis on the grain sizes, present authors preferentially selected four publicly demandable yet commercially available ready–to–use Nepal made dry cement samples (named as CS1, CS2, CS3, and CS4), and analyzed their crystallite sizes with XRD techniques, and the type of the chemical constituents they possess with FTIR. As per the research report available herewith [1], the first two cement samples CS1 (L =15.71 nm) and CS2 (L =15.30 nm) have the crystallites size L half of the latter two CS3 (L=34.58 nm) and CS4 (L =32.44 nm), and hence, the former two specimens were concluded as the cement samples comprising with the relatively smaller particle or grain sizes because of which the net hydration reactions rates were speculated in the order CS2 > CS1 > CS4 > CS3. These dissimilar crystallite size L variations, and thus speculated unequal hydration rates of them were further strengthened by determining the number of parallel planes m stacked one over the others with the d gaps in their respective crystallite phases: m = 58 (CS1); m = 57 (CS2); m = 126 (CS3), and m =119 (CS4). Similarly, the FTIR confirmations of the functional groups and the chemical constituents present in them were also in accordance with the requirements for undergoing efficient chemical hydrations and heat of hydrations of the cements. However, the granular size dependent hydration reaction products can only be materialized if we could probe the types of the hydration products deposited around the spherical particles of the cements as a function of hydration reaction time, and their major chemical constituents with precise instrumentation techniques. Owing to the same, present authors preferentially selected the first two relatively more finely grained cement samples CS1 and CS2, and cured their mortar pastes with the sufficient water/moistures consecutively. The standard timeframe selected for curing each of these two cement sample made mortars, and the sampling times of them are exactly similar to those standardized in the literatures [9–11], viz.; 1 day (fresh stage), 7 days (early stage), and 28 days (moderate stage). It means, we cured both CS1– and CS2– mortars with water by maintaining the standard w/c (w/c = 0.3–0.6 by mass) ratio continuously for 28 days, and investigated the natures of the hydrated products, types of the chemical compounds they bear, and the quantity of them responsible for showing variable cementitious propensities at 1–day, 7–days, & 28–days of hydrations. Despite the presence of considerable roles of (a) morphology of the consecutive mortar pastes, and their porosity, (b) natures of the particle size distributions of the powdered cements, (c) size dependencies of the cement particles as a function of reaction time, (d) temporal dependencies on the total specific surface

area of the entire paste matrix, etc., present authors are unable to search out them explicitly in the current investigations as they lie beyond the scope of the currently employed FTIR spectroscopy based instrumentation techniques. The entire article is structured as: in section 2, Materials and Methods, in section 3, Results and Discussions, and in section 4, Summary and Conclusions.

2. MATERIALS AND METHODS

2.1 Collection of the Preferentially Selected Cement Samples

As mentioned in the Introduction section, the preferential selection of the two cement brands named as CS1 and CS2 was just because of their fine crystallite and grain sizes due to which the hydration propensities of them were peculated as CS2 > CS1 [1]. The Nepal based manufacturers that produced these cement samples in large scale, and supplied in the commercial markets as per the needs of the consumers are Sarbottam Cement Ltd., and Hongsi–Shivam Cement Pvt. Ltd. In order to maintain their confidentialities including R&D features revealed to the public and the overall industrial cement manufacturing guidelines implemented by



Figure 1. The 50 kg sacs of Hongshi and Sarbottan cements packed in High–Density Polyethylene (HDPE). The dry ready–to–use powdered cement samples were collected directly from them prior to mixing with the sand and water.

Government of Nepal [12], the samples CS1 and CS2 were named, and handled without any prior orders. Before mixing with water, and its consecutive applications in treating/curing the resulting mortar matrices, the specific amount of ready–to–use powdered dry cement samples were collected directly from their respective High–Density Polyethylene (HDPE) 50 kg sacs (Figure 1) stored in the designated depos constructed in the elevated areas where the degrees of humidity, dampness, and the scales of temperature required for protecting the distinctive characters of the cements are well maintained, and the cement bags stacked one over the others remain fully partitioned with the waterproof plastic sheets. Immediately after samplings, they were kept in the polythene bags, and zipped properly in order to ensure the null exposures of

them to the humid weathers and for the fine preservabilities of their characteristic physicochemical properties. While preparing the mortar samples, the required amount of water–washed sand collected from the designated supplier was mixed with the definite quantity of CS1 and CS2 cements separately. The quality of the sand mixing to them is as similar as that prevailed earlier in the commercial markets of Nepal. Therefore, no separate instrumental analysis of the sand was carried out (blank tests). And, the IR active bands appeared due to the chemical constituents of the sand were excluded while interpreting the spectral patterns of the CS1– and CS2– mortars.

2.2 Preparation and Curing of the Mortars

The cement–sand mortar pastes of the CS1 and CS2 cement brands were prepared by mixing them with the exactly same type sand thoroughly in which the ratio was maintained as cement: sand = 1:3 (a standard mortar mix ratio) by mass. And, the quantity of water was fixed to the ratio water– cement (w/c) = 0.5 (the standard w/c = 0.3–0.6) by mass [4, 5]. The digital electronic weighing machine was used to measure the accurate weights of the cements and sands, and a glass jar of 1 liter capacity was used to measure the volume of water. Prior to pouring the definite amount of water in the cement–sand blends, the perfectly dry cement powders of CS1 & CS2, and the water– washed almost dry sand particles were mixed thoroughly in a separate mortar–tray. The resulting water–cement–sand composite slurry was then poured into a steel mould of inner dimensions 70 mm × 70 mm × 70 mm (Figure 2). The internal linings of each moulding structure were made lubricated with the Mobil motor oil so as to take out the developed shapes of the water–cement– sand composites easily without disrupting the structural entities. As soon as the CS1– and CS2– mortars get 24 hours of hydration reactions time, the steel–mould frame was dismantled, and the required amount of them was taken for the FTIR measurements (time lapse between sampling and measurement = 1 hour), and accordingly are for the 7 days– and 28 days– old mortar samples. At the intermittent timings wherein the cements CS1 and CS2 present in their respective mortar–blocks undergo smooth hydration reactions, the low water/moisture content in their porous matrices was completely avoided either by curing each individual block with water time–to–time or by wrapping them with the wet cotton fabrics, or sometime by submerging them into the water for specific time periods.

2.3 Fourier Transform Infrared (FTIR) Spectroscopic Measurements

Since the institution where the authors are affiliated with is not equipped with the Fourier Transform Infrared



Figure 2. The 1 day, 7 days, and 28 days old mortar blocks of the CS1 and CS2 cement brands set in the steel mould frame of 70×70×70 internal dimensions.

(FTIR) Spectroscopy facility, the specific amount of 1 day–, 7 days–, and 28 days– old hydrated CS1– and

CS2– mortar samples was submitted to Nepal Academy of Science and Technology (NAST) for the spectral measurements. The FTIR spectrophotometer used for the specific measurements was 'Shimadzu IR Tracer–100'; a high–precision equipment offering an outstanding measurement speed, sample sensitivity, and the spectral resolution with easy–to–use analytical software [13]. Prior to measuring the IR spectra of each of these mortar sample specimens, the spectrophotometer was calibrated at ambient air conditions, and its in–built functions were standardized. As soon as the instrument reached to the fully–functional states, a trace amount of every mortar samples in a pellet form was injected into its sample compartment, and the concerned interferograms (intensity of IR over time) were recorded. In every measurements, the IR frequency radiations of the range 4000–400 cm^{-1} was used for scanning the samples, and the spectra was recorded at 4 cm^{-1} resolution with an average scan rate of 50 per sample. The Fourier transformation facility was used while converting the concerned interferograms into the human readable infrared (IR) spectra.

3. RESULTS AND DISCUSSIONS

3.1 XRD and FTIR Spectral Summary of the Non–hydrated CS_1 and CS_2 Cement Powders

As per the previous research works published by the present authors elsewhere [1], the four variable manufactured ready–to–use dry OPC type cements available in the commercial markets of Nepal were mostly found to possess almost all the requirements essential for exhibiting time dependent hydration reactions and exceptional setting/placing attributes, but each one of them was speculated to dispense variable propensities towards the same. In particular, if the cement sample specific to the brands was varied, the grain/particle sizes & their porosity plus the moderate or narrow range particle distributions, types of the crystallite phases & their interlayer packing fractions, chemical compositions & the proportions of the constituent chemical compounds etc., were noted as quite distinctive. Based on all these potential descriptors, present authors predicted the two cement brands namely CS1 and CS2 as relatively better in terms of exhibiting faster hydration reactions kinetics, and the overall cementitious abilities. According to that research report, the XRD and FTIR based instrumentation techniques probed analyses of their powdered forms identified those type of the crystallite phases and wide range functional groups holding chemical compounds that exhibit very crucial roles towards facile hydration reactions and promising hydration products responsible for gluing the ingredients of the mortar in the greatest extent. The key crystallite phases associated with such type hydration affinities and the majorly contributed chemical constituents are shortly summarized herewith as they lie in the principal objective of this study set to examine the hydration propensities of these variable manufactured cement brands without which no detailed interpretations can be presented practically. The XRD based spectral analyses revealed their closely packed interatomic layers of various type crystallite phases such as $CaCO_3$, $Ca(OH)_2$, and As^{5+}–based oxyanions (AsO_4^{3-}) unit bearing $CaHAsO_4$. $2H_2O$, $CaH_4(AsO_4)_2.2H_2O$, and $Ca_3(AsO_4)_2$, which in fact act as the founding constituents of their stabilization/solidification (S/S) matrices. Additionally, the explicit and average crystallite sizes *L* and thickness based quantitative analyses of them depicted the excessive presence of nanosized particles with low range granular distributions along with the traces of SiO_2, CaO, and MgO compounds modified boehmite crystallite phases made up of stacked sheets of AlO(OH) and the boehmite derived alumina Al_2O_3 system. And, the Fourier Transform Infrared (FTIR) investigations and the functional group identification tests disclosed Si–O, SiO_4^{4-}, SO_4^{2-}, OH^-, CO_3^{2-}, Al_2O_3, MgO (Magnesia), SO_3, SO_3^{2-}, etc., based chemical moieties as their pivotal constituents. For example, the different yet unique IR vibration modes confirmed the absolute presence of C_2S, C_3S, SiO_4^{2-} tetrahedral and

SiO_4^{2-} holding chemical compounds, Al_2O_3 and Al_2O_3 made hardening constituents, SO_4^{2-} & CO_3^{2-} radicals bearing phases, AsO_4^{3-} containing compounds, SO_3 & SO_3^{2-} functionalized chemical moieties, etc. And, the similar spectral interpretations also ensured us that none of the cement samples contain pseudoboehmite ($AlOOH.xH_2O$) type aluminum compounds, magnesia (MgO) & MgO based chemical compounds, Mn and Fe holding chemical moieties, and heavy & active $CaCO_3$ with high content of aragonite & the traces of organic compounds respectively. All these dissimilarly constituted chemical compounds with different types of the functional groups available in the CS1 and CS2 cements actually make the latter outstanding in terms of rendering unique hardening products as a function of hydration reactions time with water. The same nonequivalent quantitative proportions of the chemical species contribute differently to the release of different ratios by mass of the nano sized C–S–H gel matrices when the concerned mortars are allowed for complete hydration reactions. The most interesting facts underlying with this is that the extent to which the hydration products of the cements glue potential ingredients of the mortars/concretes, enhance the placing abilities of the cement–sand–water pastes and increase their rapid setting rates, exhibit variable hardening strengths, etc., is a direct function of their reaction times with water. Therefore, the precise investigation of the hydration products formed from an early fresh stage to the late hardening stage of the mortar paste is very much essential in order to understand the dissimilar cementitious trends of the variable brand cements, and to rate their working efficiencies as a function of time at ambient temperature range. Herewith, the different range hydration reaction times of the CS1 and CS2 cements: 1 day is taken as 'too early–stage', 7 days are taken as 'early– stage', and 28 days are taken as 'moderate–stage', are assessed separately, and the FTIR spectroscopic interpretations are carried out to every consecutive samples (subsection 3.2).

3.2 FTIR Spectral Interpretations of the Hydrated CS_1– and CS_2– Mortars

As mentioned in the subsection 3.1, the FTIR spectroscopy technique is one of the most potential instrumentation methods that enables the chemists to probe varieties of the chemical constituents present in all type dry ready–to–use powder cements and their wet mortars hosting wide range hydration products formed as a result of hydration reactions. In principle, every chemical moieties possess almost non–identical type chemical bonds due to the special binding forces between the variable electronegative heteroatomic nuclei, and the FTIR technique offers an ability to recognize each of them based on the intensity of the IR radiations absorbed for particular type bonds' vibrational transitions. In the same arena, its additional skills related to the instrumental rejections of all type IR inactive chemical bonds associated with the homoatomic nuclei and their untraceable IR regions stand as indispensable applications. In the material science domains, more especially in characterizing the cements and cement based products, the net matrix or modulus forms of them developed in the course of preparing the clinker balls, and more importantly, the hydrated mixtures (mortars, concretes, etc.) and the distinctive hydration products, the trends of employing this quantitative technique are extensively increasing day by day [1, 14─17]. These massive uses and applications of the FTIR based analyses in cements are majorly supported by their in–built multi–atomic yet uniquely bonded raw materials such as limestone/chalk ($CaCO_3$), silica (SiO_2) and alumina (Al_2O_3) of the clay and shale, etc., and their most distinguishable IR active vibration modes at distinctive wavenumber frequency. Amidst the same, present study set its principal objective underlying with the FTIR instrumental characterizations of the cement–sand–water made mortar pastes of the two publicly demandable yet variable technology produced cement brands CS1 and CS2 at different consecutive hydration reactions time periods of duration; 1 day (too

early–stage), 7 days (early–stage), and 28 days (moderate–stage), and the types of the hydration reactions products produced as a function of reaction time in quantitative scales. The concerned FTIR spectra measured for their respective mortars cured with the water time to time from the very early stage to the moderate stage of hydrations are shown in Figure 3, wherein the most intense yet typical IR bands of the 7 days old mortar samples appeared at the wavenumber frequencies ~1000 cm^{-1}, ~1420 cm^{-1}, ~2350 cm^{-1}, and ~3440 cm^{-1} are encircled as they are preferably taken here as representative bands while interpreting them in respect to the net specific areas (A) under them. For the comparative purposes, the FTIR spectral bands obtained for the 1 day–, 7 days–, and 28 days– old mortar samples prepared with the cement brands CS1 and CS2 are plotted separately in Figure 4 and Figure 5. And, for enabling the readers to approximate the total areas lying under each of these intense spectral bands manually, the carefully cropped spectral parts of the same frequency regions (7 days old mortar samples) are enlarged in Figure 6 and Figure 7. Actually, the same are the spectral bands whose specific peak heights (h), and the full– width at half maximum (FWHM) values (β) are measured explicitly, and incorporated them to determine their underneath area into the mathematical formula: $A = \left[\frac{\beta \times h}{0.3989 \times 2.35}\right]$ mm^2; a standard relation used to approximate the area under the typical *Gaussian* peak [18].

As shown in Figure 3, the sharp spectral peaks are appeared in the wavenumber frequency ~ 460 cm^{-1} for the 7 days old and 28 days old mortar samples prepared with the cement CS1, but the same peak is completely absent in an 1 day old mortar sample. As per the standard databases, this specific frequency can be assigned to the Si–O bending vibrations of the SiO_4^{4-} tetrahedra, and it is in support of the anhydrous Calcium Silicates – Ca_3SiO_5/Ca_2SiO_4 compound; signifying that such type silicate compounds are one the predominant hydration products formed mainly by 7 days of hydration, and remain in the same moiety form even after 28 days long hydration period, but is completely absent at the very early stage of hydration. And, the natures of the same spectral bands, their intensities, and the shifting magnitudes in IR radiation frequency are found as slightly changed when the mortar sample gets 28 days old; confirming that the SiO_4^{4-} unit is absolutely involved in polymerizations reactions, and generates more varieties of the silicate products when the hydration reaction time goes on increasing as reported elsewhere [9, 19]. Another intense IR band appeared at ~800 cm^{-1} region signifies the presence of CO_3^{2-} unit and the CO_3^{2-} group holding chemical compounds as next major hydration reaction products. This region is specifically intense when the CS1–mortar sample gets 7 days old and 28 days old, but relatively negligible at the very early stage of hydration (1 day). It means the significant quantity of the CO_3^{2-} based chemical compounds are released gradually into the resulting mortars when the hydration reaction time increases. The relatively low intense peaks observed at ~860 cm^{-1} in all time long mortar samples indicate the presence of traces of As^{5+}–bearing oxyanions unit (AsO_4^{3-}) and AsO_4^{3-} group holding chemical compounds (such as $CaHAsO_4.2H_2O$, $CaH_4(AsO_4)_2.2H_2O$, and $Ca_3(AsO_4)_2$) as the next type hydrated products; a quite essential observation underscoring the retentive the next type hydrated products; a quite essential observation underscoring the retentive features of the chemical moieties present originally in a perfectly dry ready–to–use cement powders as reported by the present authors elsewhere [1].

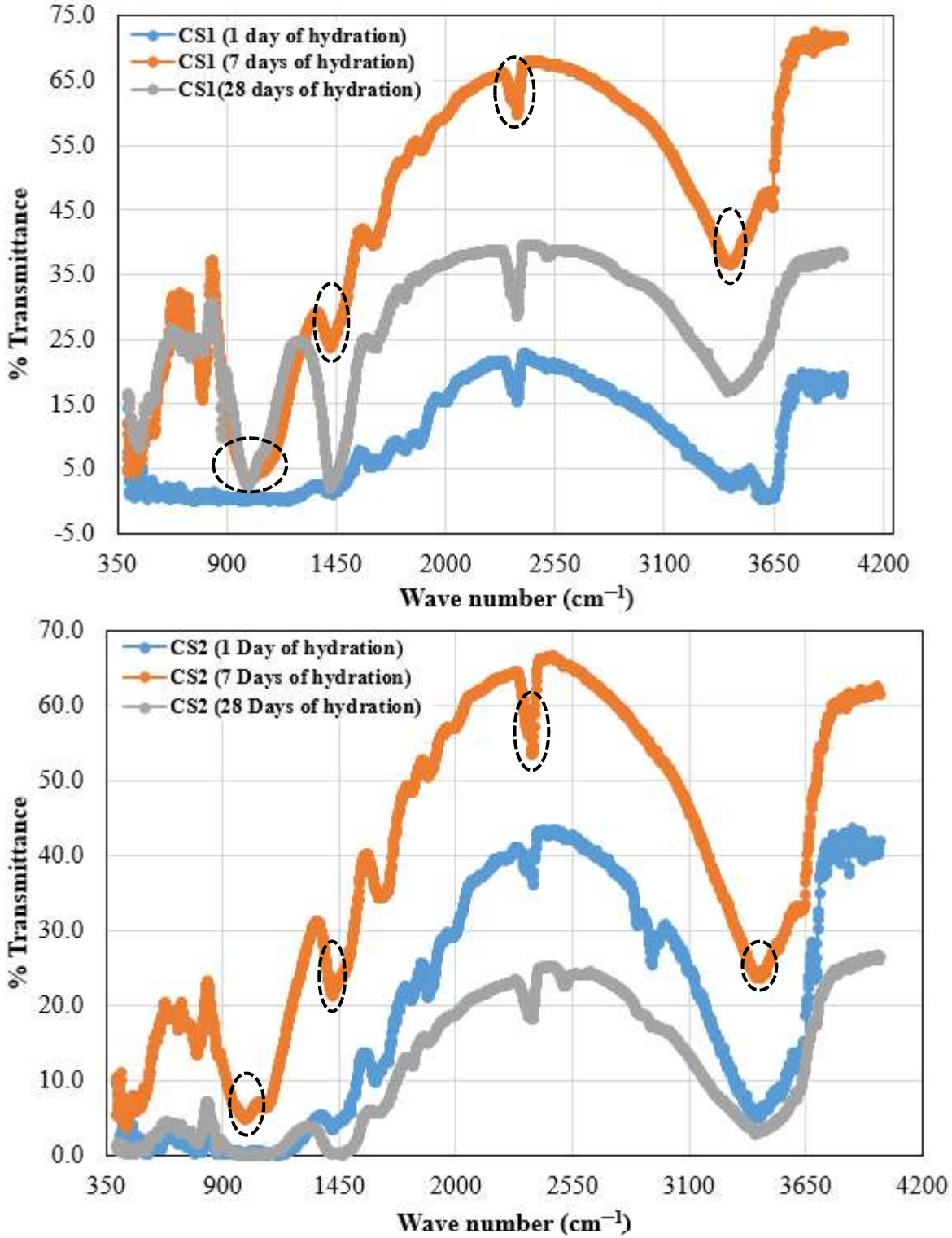


Figure 3. The FTIR spectra of the mortars prepared with the cement sample CS1, and CS2 as a function of hydration reaction time (too early–stage: 1 day; moderate–stage: 7 days; and late–stage: 28 days). The most intense IR peaks of the 7 days old samples of the both type mortars appeared at wave numbers ~1000 cm^{-1}, ~1420 cm^{-1}, ~2350 cm^{-1}, and 3440 cm^{-1} are encircled. These spectral regions are enlarged in Figure 6 and Figure 7, and are used as representative bands for calculating specific areas under them explicitly.

The progressively increasing hydration trends of the calcium silicate and the polymerizations propensities of the SiO_4^{4-} unit as a function of hydration reactions time are furthermore ensured by the IR spectral band located at ~1000 cm^{-1}. The unequal intensity depth (spectra broadening at ~1000 cm^{-1}) of the spectra of the mortar samples when they get older and older from 7 days to 28 days unveils the gradual occurrence of the hydration reactions and the consecutive release of the hydration products as the hydration reaction time goes on passing, and ultimately attains higher rate at 28 days [9, 19]. Interestingly, none of the early to late stage hydrated CS1–mortar samples show IR active bands at ~1120 cm^{-1} wavenumber region; assuring the complete absence of the Ettringite – $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$ phases and the associated chemical compounds in their hydration products. This type of the compound was even found to be completely absent in the dry CS1 and CS2 powder cements [1]. The next intense IR band at ~1430 cm^{-1} confirms the presence of $CaCO_3$ phases and the associated hydration reaction products. The same band is observed as the most intense (broadened) for the 28 days–, more intense for the 7 days–, and almost flattened for the 1 day– old mortar samples; illuminating the excessive relative abundance of the $CaCO_3$ (calcite phases) compound in the former period followed by the traces of it in the middle, and almost negligible in the latter. It underscores herewith that the dense $CaCO_3$ based hardening matrix with extremely low porosity is started to be formed by 7 days of hydration reactions, and its amount is progressively increased when the mortar gets 28 days old. The same is the explanation why the mortars and concretes gain higher hardening strengths by 28 days of consecutive water curing as the calcite phases in them provide exceptional nucleation sites and promote the water to cement (w/c) ratio effectively [20]. This finding is well justified by the sharp spectral bands at ~2360 cm^{-1} assigned to the CO_3^{2-} radical vibrations; whose intensity proportions are observed in the samples as 28 days– >7 days– >1 day– old. In between ~1500 to ~1750 cm^{-1} wave number regions, the very fundamental yet common bands are appeared: all the minor bands lying in between 1650–1750 cm^{-1} are usually allocated to the IR active bending vibration modes of the H_2O. The presence of the sufficient wet condition and the absence of the shortage of H_2O molecules (reactants of the consecutive hydration reactions) sieved into the granular porous network matrix of the temporal mortar pastes are confirmed by the stretching vibration modes of the OH^- part of the H_2O appeared at ~3500 cm^{-1}. The IR peaks at ~3650 cm^{-1} wavenumber region intensive maximally for the 1 day– and minimally for the 7 days– old mortar samples pinpoint the presence of Portlandite – $Ca(OH)_2$ phases and the associated compounds as the hydration products. These are the actual chemical compounds released differently in quantities in respect to hydration reactions time, and are responsible for dispensing high porosity & low density features to the fresh mortar sample, and relatively less porosity & more degree of denseness to the early stage mortar pastes. Based on the current spectral frameworks and the standard instrumental IR frequency radiation gauge (400 to 4000 cm^{-1}) used herewith to scan every hydrated mortar samples, none of them contains even the traces of CaO (absence of peak at ~ 420 cm^{-1}), magnesia (MgO) and MgO based chemical compounds (absence of Mg–O stretching vibration mode at ~548 cm^{-1}), Al–O/Al–OH made molecular constituents (absence of peaks at ~540 cm^{-1}, and ~615 cm^{-1}), heavy $CaCO_3$ (absence of peak at 855 cm^{-1}), divalent SO_4^{2-} radicals holding crystallite phases (absence of peaks at ~1120cm^{-1} – ~1140 cm^{-1}), active $CaCO_3$ with the traces of the organic compounds (absence of peaks at ~2800 cm^{-1} – ~2900 cm^{-1}), etc., upon their treatment with water at regular time intervals for the period of 28 days. This result is as consistent as the research work conducted to the hydrated OPC cements collected from the Texas Industries, Inc., USA [19].

While comparing all the above spectral bands, the specific IR frequency wavenumbers of the 1 day–, 7 days–, and 28 days– old CS1–mortar samples, and the overall spectral frameworks with that measured for the CS2–mortar samples of same day/s old, the more distinguishable IR active bands specific to the former and latter time periods are observed at ~1180 cm^{-1}, and 2925 cm^{-1} regions (Figure 3(b)). The first typical region can be assigned to the C–H stretching modes (traces of active $CaCO_3$), which is however, progressively disappeared when the hydration reaction time reaches to 7 days and 28 days long. It means neither the early–stage nor the moderate–stage hydrated products of the CS2–mortars are found to comprise with the traces of C–H type skeleton units (the quality of the hydration reactions products is not worsen by the traces of active $CaCO_3$). Instead, the clearly observed C–H stretching mode in fresh mortar paste (too early stage) signifies the minimal involvement of the active $CaCO_3$ in providing prompt strength; a typical feature of the mortars required for constructing easily removable supportive structures and the verities of 3D printing sculptures [21]. Towards creating these temporary yet valuable engineering motifs, the CS2–mortar paste may offer better benefits than the CS1. And, the second typical band (υ = 2925 cm^{-1}) is assigned to the symmetric SO_3^{2-} stretching modes, which is completely absent in 7 days old mortar samples, but intensely present in 1 day old and minimally in 28 days old. This observation is also in accordance with the fact that the SO_3^{2-} unit always adds an immediate strength to the freshly released hydration products, and its variation in quantities by mass often makes the setting propensities of the mortar pastes different [9]. Therefore, the actual involvement of the SO_3^{2-} unit in cement paste is mostly for generating such type products that offer quick setting and placing features at the very fresh stage, but minimally for increasing hardening strength at the

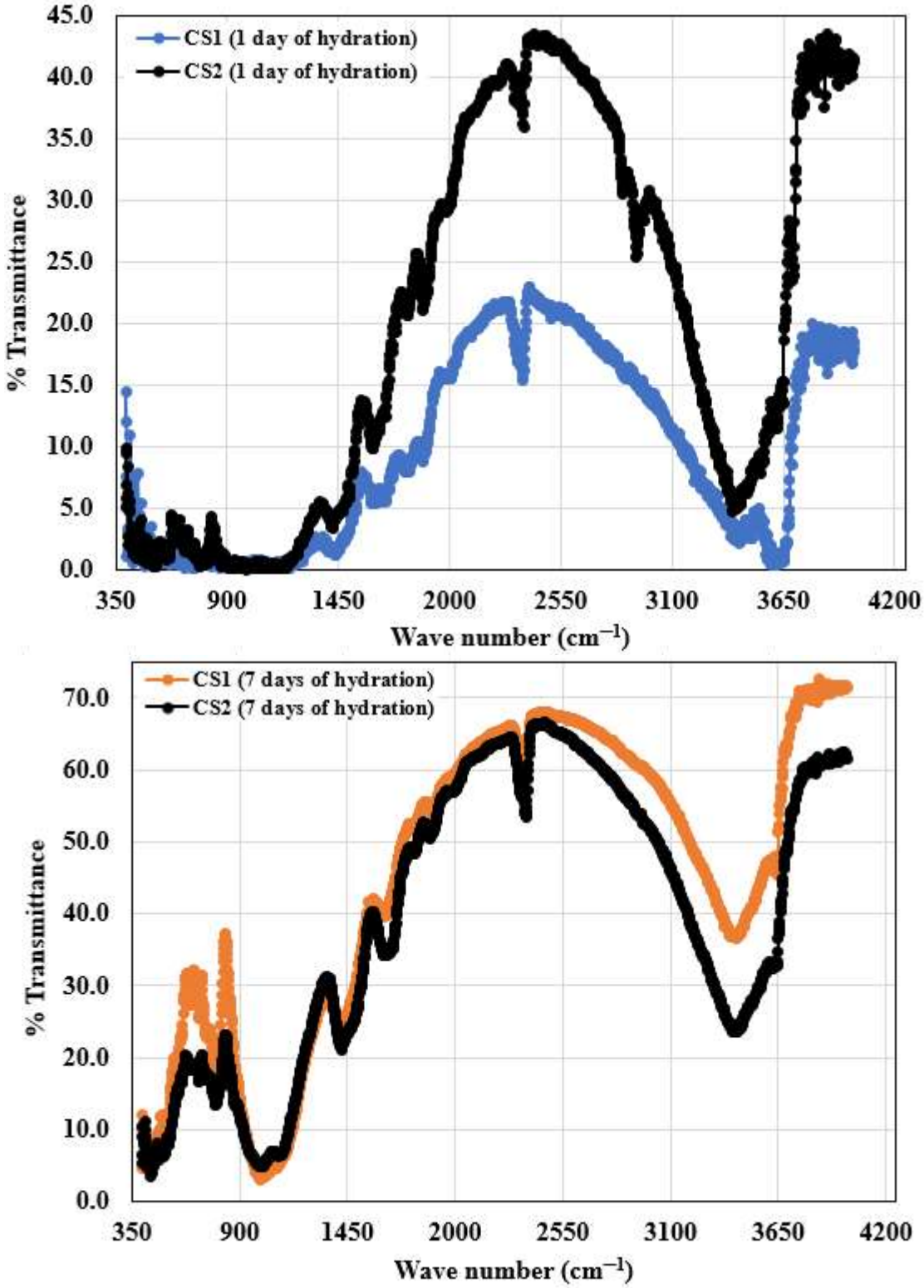


Figure 4. The FTIR spectra of the mortars prepared with the cement samples CS1, and CS2 as a function of hydration reactions time: (a) 1 day old samples, (b) 7 days old samples.

late stage. However, the proper optimizations of the SO_3^{2-} type chemical compounds are very needful in the production phase of the cement as its deviation by 1% can reduce the strength of the mortars and concretes by about 5MPa or more by 28 days of hydration [9]. In the support of the same, the more concrete explanations applicable to assess the superior performance of the one cement brand mortar over the other are discussed in the following paragraphs.

As shown in Figure 4(a), the slight IR spectral deviations, intensities, and the shifting of the active vibration modes are observed while comparing their patterns measured for the 1 day old CS1– and CS2–mortar samples. The IR band appeared at ~800 cm^{-1} region (the active vibration modes assigned to CO_3^{2-} unit) is observed as relatively more intense for the latter type sample. It suggests that the CS2–mortar contains more amount of calcite phases than the CS1, and so is the amount of the CO_3^{2-} based hydration reaction products even at the very early stage of hydration. The relatively more distinguishable, acute yet minor IR active bands that lie in between 1650–1750 cm^{-1} frequency region (vibration modes of the H_2O) of the latter type sample elucidate its higher water absorption and retaining capacity (capillary action). So, in terms of the porosity (high specific surface area, more capillary action), and the early strength dispensing ability, the CS2–mortar matrix is better than the CS1. The same analogy is strongly supported by the presence of next relatively very sharp IR band of the CS2–mortar at ~3500 cm^{-1} (stretching vibration modes of the OH^- of H_2O). This better water holding capacity of the CS2–mortar stands in favor of the smaller crystallite (L =15.30 nm), grain, & particle sizes, and the low range particle distributions of the dry CS2 cement powder [1]. In fact, the smaller range particle distributions and the low granular sizes facilitates the execution of the nucleation sites of the hydration chemical reactions, and the related time dependent polymerization processes so that the rate of the net uses of the sieved H_2O as reactants is accelerated. Interestingly, the next very pronounced band typical to the symmetric SO_3^{2-} stretching modes (ν = 2925 cm^{-1}) is only observed in 1 day old CS2–mortar sample. It means the extents of the immediate strength and the placing capacities contributed by the SO_3^{2-} type chemical constituents in the fresh paste is remarkably high in CS2–mortar. Instead, the next IR active band in the wavenumber frequency region ~3650 cm^{-1} (assigned to the Portlandite – $Ca(OH)_2$ phases) appeared only for the CS1–mortar paste attributes to the facts that the quality of the fresh stage CS1–mortar paste is better than that of the CS2 in terms of the contributions offered by the $Ca(OH)_2$, viz.; denseness, thickness, and plastering. The similar type comparative interpretations and the efficiency ratings of these two type cement mortars can further be assessed by referring the IR spectral patterns shown in Figure 4(b). Except the intensity depth ratio of the almost all the designated spectral bands owing to the presence of higher percentage compositions of the concerned chemical constituents, the overall spectral patterns and the IR active wavenumber frequencies are very much reproduced to each other. In general, it ensures us that no significant variations in setting abilities and the early–period hardening strength dispensing capacities are observed in two different mortar pastes. However, the critical analysis of the peak broadening and the net area underneath to the pronouncedly observed spectral bands unveils their dissimilar working efficiencies and performance ratings. For example, the relatively more intense and higher depth peaks at 660 cm^{-1}, and 825 cm^{-1} assigned to the different type vibration modes of the SiO_4^{4-} unit and its polymerized chemical compounds speculate us the more quantity of them as hydration reaction products in a 7 days old CS1–mortar paste. It is a strong evidence to explain relatively more gluing ability of C–S–H nanosized gel developed in the CS1–mortar than that in the CS2. In contrast to this, few deeper depth IR active bands observed at 1450 cm^{-1}, 1670 cm^{-1}, 2360 cm^{-1}, and 3450

cm^{-1} wavenumber frequencies specifically to the CS2–mortar paste disclose its more potentiality in maintaining the calcite phases based hydration products and the exceptional water retention intensities, and emphasizes the progressive occurrence of the time dependent hydration reactions at more smooth rates. It further elucidates that the rate of releasing calcite based hydration products in the CS2–mortar paste goes on increasing (than in CS1–mortar) upon the increment of the hydration reactions time, and is found considerably higher in 7 days old sample. In addition to this, the approximate area (A) underneath to the few representative peaks at the wavenumber frequencies ~1000 cm^{-1}, ~1420 cm^{-1}, ~2350 cm^{-1}, and 3440 cm^{-1} (enlarged in Figures 6 and Figure 7) calculated herewith (Table 1) further theorizes the unequal cementitious efficiencies of the CS1– and CS2– 7 days old mortars. The respective calculated areas under them are: (a) $A = 4503.65$ mm^2 (CS1–mortar) and 3745.30 mm^2 (CS2–mortar), (b) $A = 352.47$ mm^2 (CS1–mortar) and 766.88 mm^2 (CS2–mortar), (c) $A = 30.38$ mm^2 (CS1–mortar) and 68.28 mm^2 (CS2–mortar), (d) $A = 2149.44$ mm^2 (CS1–mortar) and 2831.03 mm^2 (CS2–mortar). In principle, the net specific peak area always provides the exact percentage compositions by mass of the specific chemical constituents. Therefore, the respective area-wise quantitative approximations of the types of the hydration products formed in the both type 7–days old mortar pastes reveal that amount of (a) calcium silicate $Ca_2(SiO_4)$ and SiO_4^{4-} polymerized hydration products are slightly higher in CS1–mortar; but that of the (b) $CaCO_3$ phases and the CO_3^{2-} radical holding hydration products, and (c) water held and retained by the porous matrix of the paste from where the slow release of the H_2O as a reactant of the further hydration reactions occurs are significantly greater in CS2–mortar. So, in terms of the effective roles associated with the setting, adhering, and hardening strength of these most potential chemical constituents, the CS2–mortar paste can be rated as higher in rank than the CS1–mortar paste at 7 days of consecutive hydrations. Moreover, the explanations underlying with the 28 days old CS1– and CS2–mortar samples are presented by referring their IR spectra plotted in Figure 5, wherein the remarkable change in spectral broadening

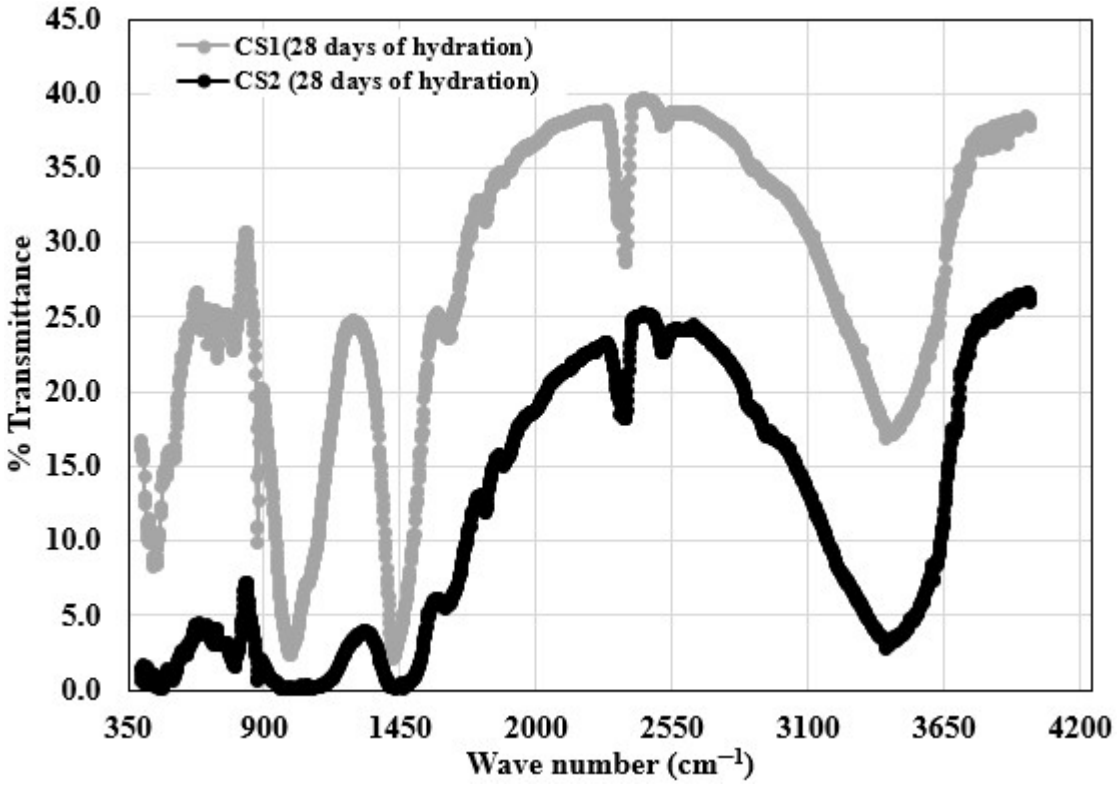


Figure 5. The FTIR spectra of the 28 days old mortar samples prepared with the cement CS1, and CS2.

Table 1: Approximate area (*A*) (*calc.*) under the FTIR peaks of CS1 – and CS2 – mortars (7 days old) intense at wave numbers 1000, 1420, 2350, 3440 cm^{-1}.

Wave number (cm^{-1})	Area (A) under the peaks (7 days old samples) (mm^2)	
	Mortar–CS1	Mortar–CS2
1000	4503.65	3745.30
1420	352.47	766.88
2350	30.38	68.28
3440	2149.44	2831.03

and intensity depth plus the abrupt spectral shifting by about 10–20 cm^{-1} are speculated while changing the cement brands. If the total specific surface areas (*A*) under every intense bands located at ~1010 cm^{-1}, ~1460 cm^{-1}, ~2360 cm^{-1}, and ~3450 cm^{-1} wave number frequencies are considered manually (the areas *A* are not calculated here as the bands are very much contrasting and broadened widely), the CS1–mortar paste presents itself as a relatively better than the CS2 at

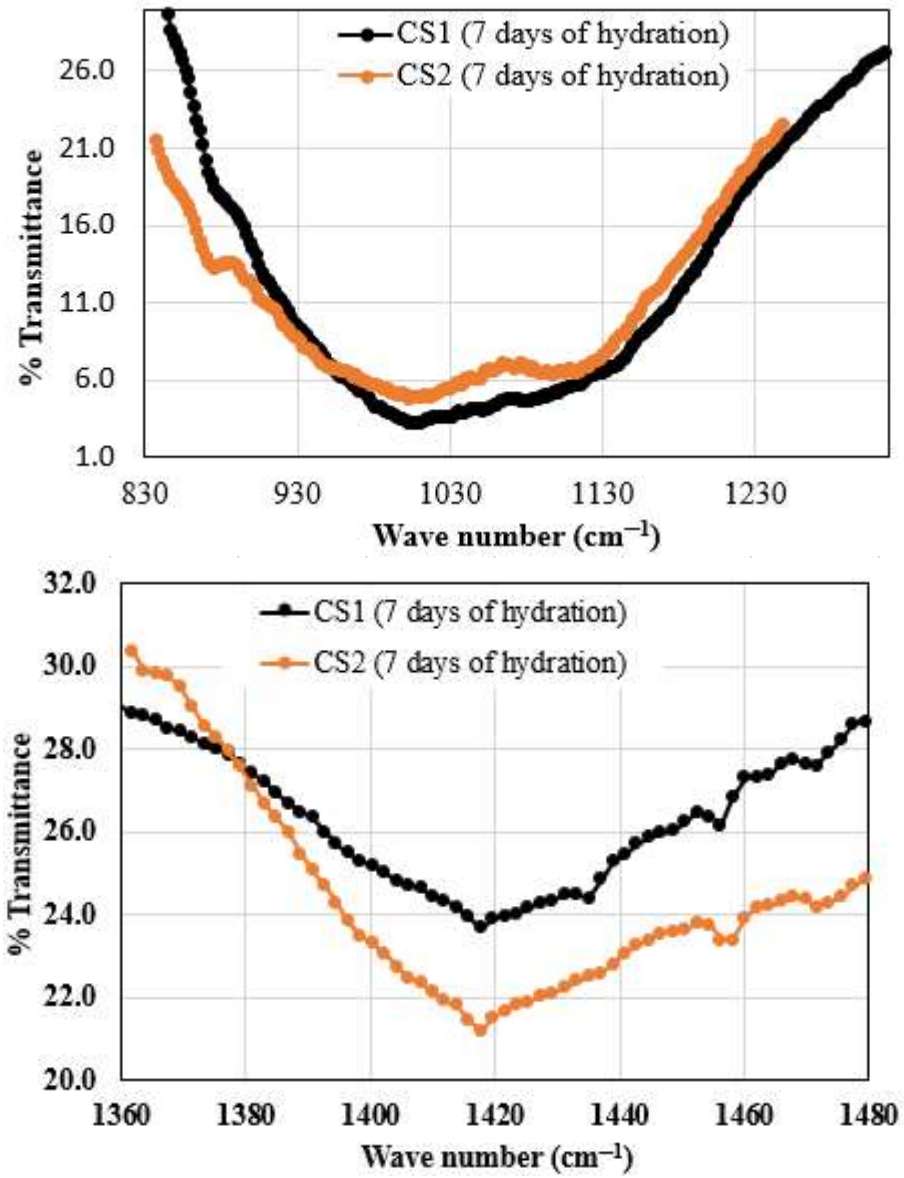


Figure 6. A part of the FTIR spectral regions of the 7 days old mortar samples prepared with the cement CS1, and CS2 intense at wavenumber (a) ~1000 cm^{-1}, (b) ~1420 cm^{-1}. They are enlarged here for approximating the area under them (Table 1).

28 days of continuous hydration. But, in terms of the water holding ability and the capillary action of thus developed 28 days old hardened matrix, the CS2–mortar still demands higher rank; ensuring that the hydration reactions are not fully terminated by 28 days of consecutive hydrations, and the more variety hydration products are going to be released progressively when the same

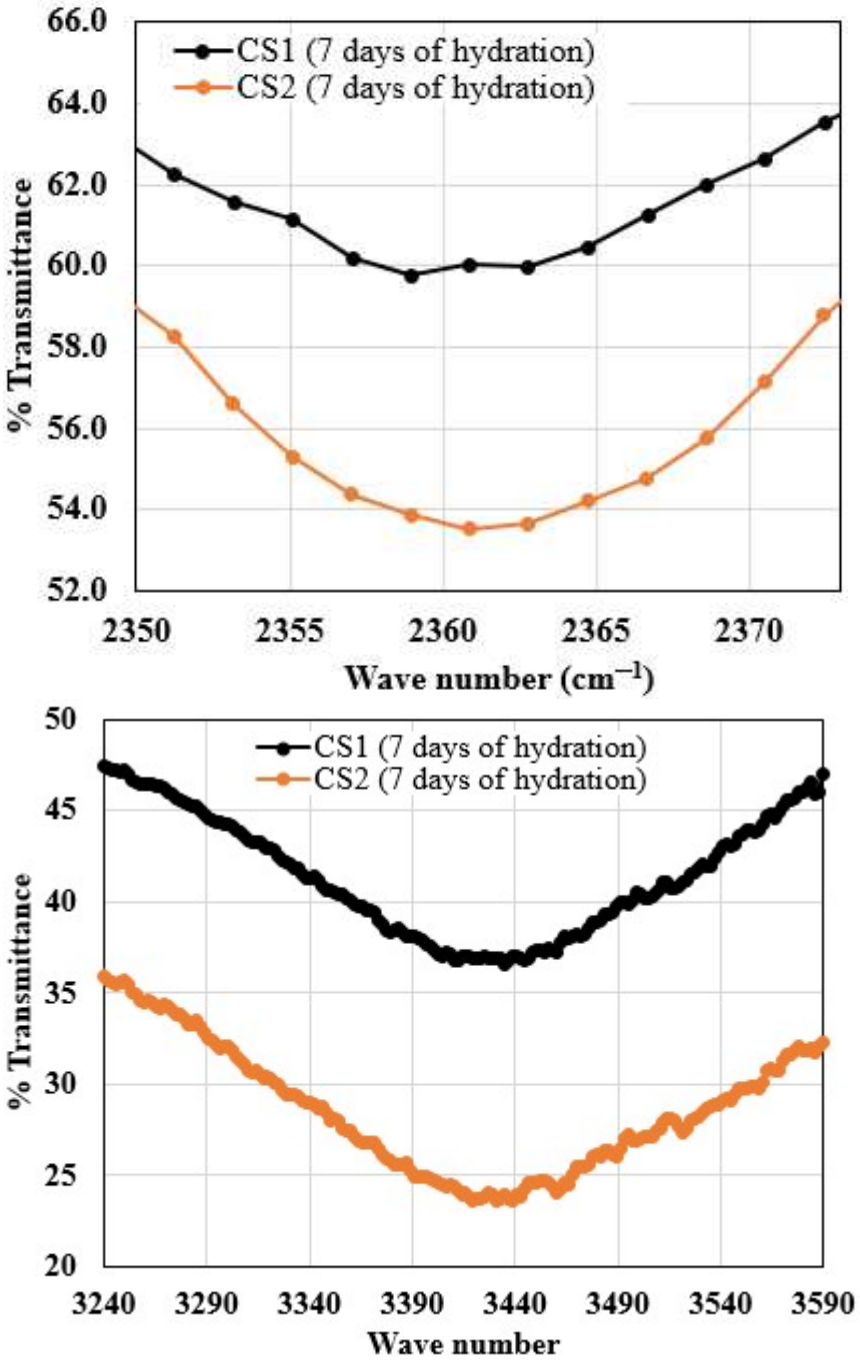


Figure 7. A part of the FTIR spectral regions of the 7 days old mortar samples prepared with the cements CS1, and CS2 intense at wavenumber (a) ~2350 cm^{-1}, (b) ~3440 cm^{-1}. They are enlarged here for approximating the area under them (Table 1).

matrices are prolonged for longer time period. This is applicable to the CS1–mortar as well, but the expected time frame is relatively shorter. According to the literature surveys [9, 14, 15, 17], the continuous hydration reactions of the cement based mortars and the associated concretes take place even after a month long time period but with the slower rates. This is in favor of the present FTIR predictions related to the extraordinary

water retaining features of the either type 28 days old mortar matrices. More specifically, if the quantity of the H_2O molecules interlocked into the hard matrix of the concerned mortars and concretes is larger in amount, the rate of the hydration chemical reactions as a function of reaction time would be faster, and the additional hydration reactions remain prolonged in a greater extent. The same is the conclusion of the article reported by Mollah MYA et al. herewith [14, 15, 17], where the Texas Industries, Inc., USA produced OPC type cement pastes of 10-day–, 1-month–, and 10-years– old are instrumentally characterized, and the progressive reactions in them as a function of time are seriously recorded. Therewith, they identified As^{5+}–bearing chemical compounds in the 10 years old sample alike to the fresh early stage paste but the completely new $NaCaAsO_4.7.5H_2O$ and $Ca_5(AsO_4)_3OH$ phases only in the former period unlike in 1 day–, 10-day–, and even 1 month– old mortars, and no ettringite $[Ca_6(Al_2O_6)(SO_4)_3.32H_2O]$ phases at all in the 10 years old sample despite its predominant presence in the fresh mortar pastes. In the support of the same, few other potential research papers [21, 22] explain the water retention abilities of the 1 year old mortars and concretes by measuring the amount of evaporable water (absorbed and capillary water) sieved into them quantitatively. Therewith, the concerned authors concluded that the optimum hardening and hydration reaction completion timeframes of the cement made mortars and concretes at ambient temperature regimes is longer than 1 year, and the granular water interlaced firmly into them act as the potential reactant for proceeding the remaining successive hydration reactions. Towards these perspectives, the presently prepared and properly water–cured CS1– and CS2– mortars, the minimum and maximum timeframes given to them for the consecutive hydration reactions, the distinguished FTIR spectral bands based interpretations, the ratings of their working performance in respect to placing/ adhering/setting/hardening propensities, etc. are finely tuned.

4. CONCLUSION

This research article was mainly aimed at investigating the hydration propensities of the two dissimilar cement brands CS1 and CS2 having contrasting crystallite, grain & particle sizes, and characterizing their hydration chemical reactions products produced as a function of reaction time when they separately intermix with the standard ratio by mass of the sand, and water, and firmly attain the respective mortar matrices of dissimilar characteristic features. The net hydration reaction time periods given to the both type wet mortar samples (CS1– and CS2– mortar) and their sampling intervals chosen for the in–depth FTIR instrumental inspections/characterizations of all the successive reactions products were 1 day, 7 days, and 28 days; the reasonable yet practically affordable timeframe in which relatively more vigorous hydration reactions and optimum heat of hydrations take place with significant release of the products offering multidimensional features to the mortar pastes. Based on the critical analyses and the precise quantitative interpretations of all the IR active vibration bands specific to the particular type hydration reaction products produced as a function of all those standard reaction times periods, the working efficiencies of the fresh–, early–, and moderate–stage mortar pastes of the CS1 and CS2 cement brands were rated explicitly in terms of the placing/adhering/setting/hardening propensities and the overall quality of the hydration products towards dispensing variable range yet time dependent porous networks, material denseness, cementitious strengths, and the capillary water retaining attributes.

As per the IR spectral intensities, relatively more contrasting spectral bands, and the approximate depth area investigations of the specific peaks appeared at (a) ~800 cm^{-1} assigned to the active vibration modes of CO_3^{2-} unit; (b) 1650–1750 cm^{-1}, and ~3500 cm^{-1} assigned to the vibration modes of the H_2O and the stretching

mode of its OH^- part respectively; (c) 2925 cm^{-1} assigned to the symmetric SO_3^{2-} stretching modes, the 1 day old (fresh paste) wet CS2–mortar was found to bear more amount of the calcite phases and CO_3^{2-} based chemical compounds as the predominant hydration reactions products, relatively higher water absorption and retention capacity (capillary action), and the better immediate strength gaining & placing potentialities. However, the unique IR active band of the CS1–mortar paste inspected at ~3650 cm^{-1} (characteristic wavenumber frequency for the Portlandite – $Ca(OH)_2$ phases) was attributed to its superior ranking than the CS2 – mortar in terms of the denseness, thickness, and adhering features offered more specifically by the $Ca(OH)_2$ compounds. When the consecutive hydration reactions of the both type mortars reached to 7 days old, the CS1–mortar was identified as relatively better (in respect to the gluing ability of thus formed C–S–H nanosized gel) than the CS2–mortar because of possessing more intense and broadened peaks at 660 cm^{-1}, and 825 cm^{-1} wavenumber frequency regions designated to the multiple vibrational modes of the SiO_4^{4-} tetrahedral and SiO_4^{4-} bearing silicate compounds plus their polymerized chemical composites. However, if the propensities of the mortar pastes in maintaining early staged $CaCO_3$ phases and the CO_3^{2-} radical holding hydration products, in creating exceptional water holding and retention capillaries, and in proceeding the every successive time dependent hydration reactions with smooth kinetics were considered, the performance rating of the CS2–mortar was still observed to be better. Again, when the hydration reaction time period was progressively increased and reached to 28 days long, the CS1–mortar paste was found to occupy relatively better position than the CS2 as the concerned peaks located at ~1010 cm^{-1} (SiO_4^{4-} tetrahedral and its polymerized products), ~1460 cm^{-1} ($CaCO_3$ phases and the associates), and ~2360 cm^{-1} (CO_3^{2-} and CO_3^{2-} holding constituents) deterministic to the quantity of same type chemical compounds were inspected with more broadened and larger specific depth areas. But, the pronouncedly wide yet intensive peak standing at ~3450 cm^{-1} (stretching vibration modes of the OH^- part of the H_2O) wave number frequency of the 28 days old CS2–mortar and its absolute indications of higher water holding and capillary water retaining potentialities made this mortar relatively superior than the CS1. The same observations implicated us to conclude that the cement based mortars and concretes require longer than 28 days for the absolute completions of the hydration reactions with more progressive yet successive trends, and when the same hardened matrices are prolonged to the longer time regimes, the additional hydration products are subjected to form gradually. In the views of the same, the net time required for utilizing granular level water (capillary water) molecules of the CS2–mortar matrix in the form of potential reactants of the remaining subsequent hydration reactions would be relatively longer, and the extent to which more varieties hydration products are gained by it as a function of reaction time could be more than that by the CS1–mortar. After all, if the above presented dissimilar quantitative proportions of the distinctive yet temporal hydration reactions products, and their explicit key–roles underlying with the quality assurance of the fresh to late staged CS1– and CS2– mortars are referred, the CS2–mortar deserves superior ranking with promising features applicable to rating its working efficiency genuinely. Nevertheless, all these predictions and the performance ratings of the CS2–mortar stand firmly in favor of the smaller crystallite (L = 15.30 nm), grain, & particle sizes, and the low range particle distributions of its CS2 cement powder. In conclusion, the dimensions of the descriptors and their key attributes underscored throughout this article in rating performance efficiencies of the two different variable technology produced Nepal made cement brands in their wet mortar mixtures definitely serve as the effective guidelines towards improvising the chemical compositions of the clinker and raw materials, optimizing the chemistry and chemical constituents of the cement, and standardizing the entire production technologies.

5. ACKNOWLEDGEMENT

The authors are indebted to Nepal Academy of Science and Technology (NAST) for providing the FTIR spectroscopic measurement facility. They are thankful to Mr. Santosh Thapa (Laboratory coordinator), and Dr. Rajendra Kumar Pokhrel (Principal, & Assoc. Prof.) of Kathford International College of Engineering and Management for the kind cooperation and assistance throughout this work. The Engineering Chemistry and Applied Science Research Unit of the same institution is acknowledged for bearing the publication cost of this article.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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