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Raman Spectroscopic Investigation of Friedel's Salt

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Abstract

Friedel's salt (FS) forms upon chloride binding in monosulphoaluminate (AFm) phase. This removes chlorides from the pore solution, hence, delays the initiation of steel-bar corrosion. Apparently, characterising and, in particular, monitoring the formation and the status of FS facilitate the prediction of the service life of reinforced concrete structures. Raman spectroscopy offers a potential for investigating FS. The current work characterised FS, including the synthesised pure FS, and the FS formed in a Portland cement (PC) paste powder, using a bench-mounted Raman spectrometer. The results revealed the full Raman spectra of pure FS between 200 ~ 4000 cm^{-1} , including the featured Raman bands at 534/568 cm^{-1} and 783 cm^{-1} which correspond to the Al-OH stretching and bending vibration of FS respectively. Furthermore, similar Raman bands of FS were identified in PC paste sample subjected to accelerated chloride attack, further confirming the potential of Raman spectroscopy for distinguishing FS in cementitious materials.

Keywords: Cementitious materials, Chloride attack, Friedel's salt, Raman spectroscopy.

1. Introduction

Chlorides affect both the properties of concrete and steel embedded in it significantly. They can be introduced into concrete either internally or externally [1-4]. For the intermixed chlorides (usually from the mixing-water), they could react directly with the aluminium-bearing minerals in the cement, viz. tricalcium aluminate (C_3A) or tetracalcium aluminoferrite (C_4AF), and in presence of water, calcium chloroaluminate, i.e., the so-called Friedel's salt (FS) is formed [5]. In the case of hardened cementitious materials, the chloride ions from

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external environments diffuse into the concrete and propagate through the pore solution of concrete [6]. A part of the intruding chlorides is retained by the cement hydrates, through either chemical binding [e.g., formation of FS from monosulphoaluminate (AFm)] [7-9] or physical adsorption [e.g., calcium-silicate-hydrate (C-S-H)] [10], which are named as 'bound chlorides'. The residual chloride ions remain in the pore solution are 'free chlorides', which penetrate through the cover concrete, and when a sufficient amount of chlorides ('critical chloride concentration' or 'threshold value') reaches the reinforcement, a localised breakdown of its passivation film occurs [11]. This then causes the initiation of corrosion of the steel reinforcement. Undoubtedly, chloride induced corrosion is a major deterioration mechanism for reinforced concrete structures exposed to chloride-rich environments, such as marine, de-icing salts and brackish groundwater. However, chloride binding can remove the chloride ions from the pore solution and, thus, delay the initiation of corrosion process. Therefore, understanding the chloride binding, in particular, characterising and monitoring the status of the final binding product, viz. FS, is of great importance to the durability of reinforced concrete structures.

For mature concrete, AFm accommodates the external-chloride to form FS. AFm [7, 12-15] is a lamellar hydrated tetracalcium aluminate-ferrite family that has a representative formula of $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6] \cdot \text{X} \cdot n\text{H}_2\text{O}$, where X refers to a monovalent anion (e.g., OH^-) or half a divalent charged anion (e.g., SO_4^{2-}) and n represents the number of water molecules. They belong to Layered Double Hydroxides (LDH) consisting of ordered positively charged rigid main layers $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]^+$ formed by metal ions and hydroxide ions, and negatively charged interlayers $[\text{X} \cdot n\text{H}_2\text{O}]$ with anions and water molecules. The number of metal cations and hydroxides in the main layer is fixed, while the water and charge-balancing anions in the interlayer space are mobile and replaceable. This intrinsic nature of AFm, actually, defines its anion exchange capacity. In hardened Portland cement paste, AFm forms due to the reaction of ettringite, a product of aluminate minerals ($\text{C}_3\text{A}/\text{C}_4\text{AF}$) in Portland cement and sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), with C_3A . In commercial cement, very limited Fe(III) substitution of Al occurs in the above reaction and usually only the Al-bearing AFm phase is considered. Besides, the anions in the AFm phase formed within the unaffected cement matrix are originally dominated by SO_4^{2-} (sulphate) [7, 12-15]. Hence, for cement chemistry, AFm is represented as $(\text{Ca}_2\text{Al}(\text{OH})_6 \cdot \text{SO}_3)$ [16]. When concrete is in service condition, the anions accommodated at the inter-layer space are prone to be replaced by other anions. This includes the generally accepted mechanism associated with chemical binding of chlorides in concrete, i.e., Cl^- from external media displaces other anions in AFm to form the Cl-AFm phase, i.e., $\text{FS}(\text{Ca}_2\text{Al}(\text{OH})_6(\text{Cl,OH}) \cdot 2\text{H}_2\text{O})$ [17]. Due to this reason, AFm phase has been considered as a 'sink' for chloride ions [17].

Due to its importance, many analytical technologies have been employed to study the FS. The most popular and valuable tool is ^{27}Al Solid State Nuclear Magnetic Resonance (NMR) Spectroscopy [7, 18-20]. It detects and analyses only one nuclear-spin isotope (e.g. ^{27}Al) at a time by employing the nuclear-spin selectivity so that the aluminium chemistry associated with its chemical reaction, composition and local structure is well investigated. In particular, it has demonstrated its unique superiority in analysing Al-bearing phases, such as AFm and FS, as the high sensitivity for ^{27}Al nucleus (e.g. 100% natural abundance) allows to distinguish easily its tetrahedral and octahedral coordination. Furthermore, the recent development in Magic Angle Spinning (MAS) technique allows the use of MAS probe to obtain well-resolved NMR spectra. Unfortunately, a major disadvantage facing the ^{27}Al NMR is the effect of the non-spherical charge distribution around the ^{27}Al nucleus, which can make the spectra interpretation difficult [7, 18-20]. Whilst X-ray Diffraction (XRD) can qualitatively identify the various ionic-groups and the unit-cell parameters of FS [21-23], a high degree of disorder could be an issue for samples containing not perfectly ordered phases. Thermogravimetry (TG)/Differential thermogravimetry analysis (DTG) has been employed to study the mass loss of the FS as a function of increasing temperature, through which the thermo-stability and thermo-chemistry of FS can be illustrated [17, 23, 24]. However, a supplementary analysis is usually conducted jointly as TG cannot provide any fingerprint information for identifying the crystallographic features of FS.

In contrast, vibrational spectroscopy could be a valuable alternative for characterising FS by providing useful information on the molecular composition and symmetry of FS. For example, Fourier Transform Infrared Spectroscopy (FTIR) has been extensively and effectively employed to study the ionic structure of FS, and Table 1 below reports the absorption bands collected by FTIR [17, 25-32]. Evidently, FTIR has demonstrated its unique strength in characterising FS as manifested by its characteristic absorption bands primarily from the $\text{Al}(\text{OH})_6$ tetrahedral groups and OH bonds.

Table 1 Summary of the IR bands and assignments of Friedel's salt

Phase	FTIR bands / cm^{-1}	Assignments
FS	532, 577	Al-OH stretching vibration mode
	785	Al-OH bending vibration mode
	1621	Water bending vibration mode
	3480	OH stretching region
	3636	(e.g., water stretching vibration, M(metal)-OH stretching mode)

N.B.: Cl^- does not absorb in the range $400\text{-}4000\text{ cm}^{-1}$ due to the ionic nature of chloride bonding.

In addition to FTIR, another advanced vibrational spectroscopy, viz. Raman spectroscopy[33], can also provide 'fingerprint' information of molecular structures for solids, liquids and gases. It works on inelastic scattering that the scattered light occurs at wavelength (frequency) shifted up or down from the incident laser light. As this wavelength shift is specific to the chemical bonds and the symmetry of molecules, Raman scattered signal can thus be used to identify ionic groups in substances. Compared to FTIR, Raman spectroscopy is more appropriate for analysing non-polar molecules, inorganic materials as well as aqueous solutions, and no sample preparation is required. Application of Raman spectroscopy in cement and concrete was first demonstrated by Bensted in 1976 [34], after which various research data have been reported and the main application areas can be grouped as follows:

- i) identification of anhydrous cement/clinker minerals (C_3S , β - C_2S , C_3A and C_4AF) [35, 36], and their hydration phases (CH, C-S-H, AFt and AFm) [35, 37-41];
- ii) characterisation of concrete deterioration products, such as sulphate-bearing phases (i.e. AFt, gypsum and thaumasite) and calcium carbonate polymorphs (i.e. calcite, vaterite and aragonite) [39, 42-48];
- iii) some specific applications such as the study of the structural features of vaterite and C-S-H, characterisation of dehydration mechanism and properties of gypsum under high pressure as well as the phase transformation of C_2S under high-temperature [49, 50].

It may be noted that the AFm phase, the precursor of FS salt, has already been well studied by Raman spectroscopy in the literature. It has been reported that under Raman spectroscopy, all the internal vibrational modes [i.e. symmetric stretching (ν_1), symmetric bending (ν_2), asymmetric stretching (ν_3) and asymmetric bending (ν_4)] of SO_4^{2-} ionic groups, along with the Al-OH stretching vibration and other external modes, in AFm have been clearly identified [39, 41, 51]. Furthermore, although some research attempted to use Raman spectroscopy characterising LDH phases [15, 30, 31, 52, 53], unfortunately, to date, no comprehensive work has been reported on investigating pure FS and FS in cementitious materials with Raman spectroscopy.

Our current study, hence, seeks to characterise both pure FS (Section 3.1) and the FS formed in cementitious materials (Section 3.2) by using Raman spectroscopy. A FS sample was synthesised under laboratory condition and its phase composition and purity were first assessed by conducting XRD, TG/DTG and FTIR analyses. The FTIR resolved bands obtained were used as one reference for ascribing the Raman bands of FS. Following this, Raman spectroscopy was employed to characterise the pure FS sample and its fingerprint Raman bands were retrieved and assigned. The Raman fingerprint obtained from the pure FS was subsequently employed to recognise the FS formed in a PC paste powder after

being subjected to accelerated chloride attack. The results thus obtained are discussed to establish the potential of Raman spectroscopy for characterising the FS.

2. Experimental

2.1 Materials

The Portland cement (PC) used in this study was CEM I (in accordance with BS EN 197-1:2011) supplied by QUINN Cement. Its chemical composition is reported in Table 2, and its aluminate contents, i.e. tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF), are 11.31% and 8.98% respectively according to Bogue calculation. The cement pastes were manufactured at a water-to-cement ratio (W/C) of 0.35. After 24 hours' initial curing in plastic tubes, the specimens were removed from the tube and then covered with a water saturated hessian, which were then sealed in plastic sample bags and stored in a curing room at a constant temperature of $20(\pm 1)^\circ\text{C}$ for around 6 months. This rather long curing duration was purposely selected because in the real world, chloride induced durability issue is mainly occurred in mature concrete. At the end of the sixth month, selected pastes were ground into powder to a fineness of $63\ \mu\text{m}$. A 2.8M (165g/L) sodium chloride (NaCl) solution as specified in the NT BUILD 443 was employed in the chloride attack test. The quantity of the solution was determined in accordance with NT BUILD 443, and the solid (g) to liquid (dm^3) ratio was about 1:10. The powder was exposed to the NaCl solution for 14 days which was then filtered and dried in a vacuum chamber.

Table 2 Chemical composition of PC

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃
Content /w%	23.00	6.15	2.95	61.30	1.80	0.68	0.22	2.50

The FS was synthesised under controlled conditions in the laboratory by a coprecipitation method [25, 54]. The two chemicals used for synthesising FS, i.e., calcium chloride (CaCl_2) and sodium aluminate (NaAlO_2), were purchased from Sigma-Aldrich, UK. The CaCl_2 was anhydrous powder with assay of 99.99% trace metals basis, and the NaAlO_2 was anhydrous powder with impurities $\leq 0.05\%$. First, 300 mL CaCl_2 (0.5 M) solution was prepared and preheated to $50\ ^\circ\text{C}$. Then, 300mL NaAlO_2 (0.25 M) solution was added into the CaCl_2 solution at a rate of 5 mL/min, and the mixture was stirred continuously at 300 rpm. After reaction for 1 hour, the precipitate was collected by the filtration, washed three times with

deionised water to remove residual substances and dried in a vacuum chamber. The sample so obtained was ground and then stored in a desiccator for later analyses.

2.2 X-ray Diffraction (XRD)

The powder method of X-ray diffraction was adopted in the present study as a supplementary technique to verify the purity of the FS synthesised and the formation of FS in the PC paste sample. An XPERT-PRO diffractometer with a X-ray source of Co K α radiation ($\lambda=1.78901$ Å) was used. A scanning speed of 2°/min and step size of 0.017°2 θ were used to examine the samples in the range of 5° to 70° 2 θ . The X-ray tube voltage and current were fixed at 40 kV and 30 mA respectively.

2.3 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra were collected on a FTIR spectrometer in the range of 500-4000 cm⁻¹ with a resolution of 1 cm⁻¹ at ambient temperature under a transmission mode.

2.4 Thermogravimetry(TG)/Differential thermogravimetry(DTG) analysis

Thermogravimetric (TG) analysis was performed with a NETZSCH STA 449C instrument under N₂ environment. The DTG trace was recorded simultaneously. The tests were carried out between 25°C and 1000 °C with a heating rate of 20 K/min.

2.5 Raman spectroscopy

The Raman analysis was performed under back-scattering geometry on a Renishaw Invia micro-Raman spectrometer equipped with a Charged Coupled Device (CCD) detector. A 514.5nm single-line (Argon ions) laser with an output power of 25mW was employed as the excitation source. The laser beam was focused into a laser spot about 1.26 μ m diameter by means of a LEICA Plan N objective with 50X magnification, and then interrogated the sample. Measured power at the sampling level was around 4.1 mW. The Raman shift was calibrated before each experiment using the sharp peak of silicon at 520 cm⁻¹. Raman spectra were recorded with an exposure time of 10s and accumulations of 10 to improve the signal-to-noise ratio (SNR). The Raman data were analysed with the employment of the software OriginPro 8.6 (Origin, USA). To eliminate the troublesome background, baseline

correction using OriginPro 8.6 was conducted first to subtract the background (e.g. fluorescence). After removing the background, those Raman peaks obscured previously by the fluorescence could now be clearly observed. The Raman peaks were then fitted with Lorentz function in order to retrieve the peak wavenumber for differentiating the analytes.

3. Results and discussion

As aforementioned, the synthesised pure FS was characterised first in order to establish bench-mark Raman features for identifying the FS formed in cementitious materials. To obtain the genuine Raman spectrum of FS, the XRD and TG/DTG analyses were firstly conducted to verify the phase-composition and purity of the synthesised sample obtained. Besides, FTIR analysis was carried out in order to collect the IR-active vibrational information as a reference for assigning the Raman bands of FS later. The Raman features of the pure FS were first collected and attributed. Building upon this, the chloride attacked PC paste powder was investigated and the Raman fingerprint of the FS phase formed was then identified and assigned accordingly.

3.1 Pure Friedel's salt

3.1.1 Verification of synthesised FS

3.1.1.1 XRD analysis

The XRD pattern of the synthesised FS is presented in Fig. 1, which matches well with the standard JCPDS card No. 00-019-0201. As shown in the figure, the typical XRD peaks of FS (e.g. $2\theta = 13.2^\circ$, 26.5° , 27.3° and 36.5°) were identified in the synthesised phase, indicating the formation of the FS crystals in this sample. Furthermore, as those intense peaks dominate the XRD diffractogram, it could be concluded that the FS synthesised here under laboratory conditions has a high purity (to be further confirmed in the following section). At the same time, tiny amount of halite (NaCl) and gibbsite ($\text{Al}(\text{OH})_3$) have also been identified in this synthesised sample, which could be generated by the associated reactions between the raw chemicals (e.g. CaCl_2 and NaAlO_2) used during the synthesis processes.

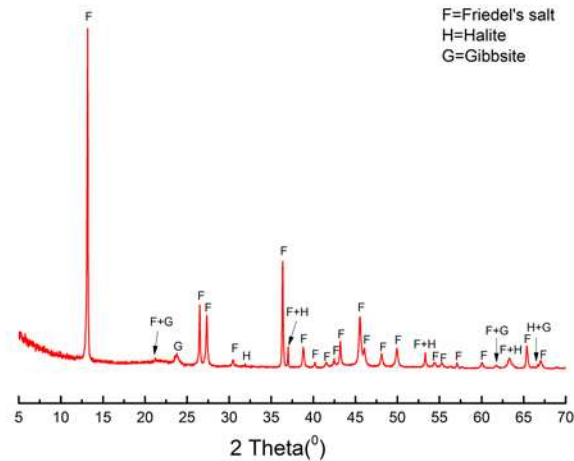


Fig.1 XRD pattern of synthesised Friedel's salt

3.1.1.2 TG/DTG analysis

Fig.2 reports the TG (weight loss) and DTG curves of the FS. Evidently, ordered crystalline structure of FS yielded a well-revolved TG curve with three weight-loss steps, which can be used to verify the composition of the synthesised FS, as described below [17, 23, 24]:

- (i) Weight loss between 25 - 200 °C: A peak at about 135 °C can be clearly observed, in DTG curve. This weight-loss is due to the removal of the water molecules in the interlayer space and this dehydration process may give rise to a product with reduced crystallinity, i.e. $3\text{Ca}(\text{OH})_2 \cdot 2\text{Al}(\text{OH})_3 \cdot \text{CaCl}_2$ [17].
- (ii) Weight loss between 200 – 400 °C: At this temperature range, there were two peaks seen at about 260 °C and 340 °C respectively, corresponding to the dehydroxylation of the main portlandite-like sheets, leading to the formation of a poorly structured phase.
- (iii) Weight loss between 400-1000 °C: This weak effect could be caused by various phase transformations, such as the recrystallisation of the amorphous phase (above ca 750 °C), yielding a mixture of CaO and mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) [23], or the release of water from recombination of hydroxyl groups or probably anion decomposition.

Based on the calculation, the weight loss in the abovementioned three steps are 11.5 %, 18.2 % and 8.0 % respectively, which is consistent with the findings obtained from typical FSs as reported in the literature [23]. Moreover, a total weight loss of about 38% can be obtained, and this result matches well with the theoretical water content of an idealised FS formula, i.e. around 32.1 %.

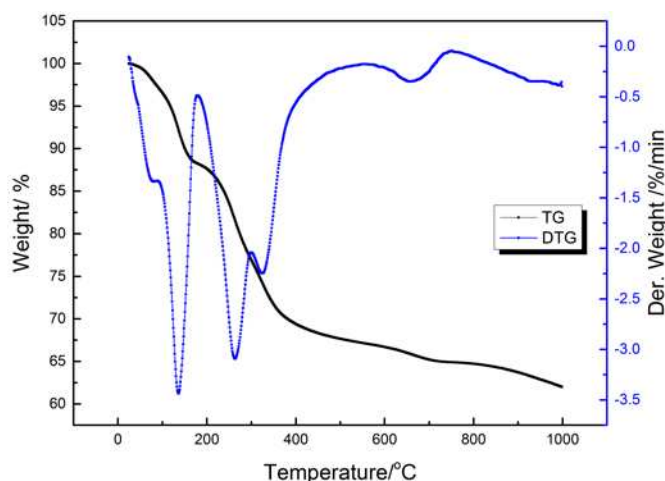


Fig.2 TG and DTG analysis of synthesised Friedel's salt

3.1.1.3 FTIR analysis

Fig. 3 depicts the IR spectrum of the synthesised FS sample and its various absorption bands can be assigned according to the information reported in literature [17, 25-31], as described next. The strong overlapping at the high frequency area, i.e. 3484 cm^{-1} and 3628 cm^{-1} , could be the OH stretching region associated with the water stretching vibration and the M(metal)-OH stretching mode of the hydroxide layer. The band at 1621 cm^{-1} is the H-O-H bending vibration of interlayer water. At the same time, the bands at low wavenumber area, i.e. 788 cm^{-1} and $530/585\text{ cm}^{-1}$, are characteristics of the bending vibration and stretching vibration modes of the Al-OH bonds of $\text{Al}(\text{OH})_6$ octahedra respectively. In addition, the band identified at 878 cm^{-1} and 1440 cm^{-1} are caused by the out-of-plane bending (ν_2) and asymmetric stretching (ν_3) vibration of CO_3^{2-} groups in carbonate phase in the sample [30, 32, 53], which could be formed during the sample preparation. There are some minor bands observed in the spectrum, which could be attributed to the impurities in the raw materials used to synthesise the FS. It should be noted that no vibrational bands of chloride ions in the range of $400 - 4000\text{ cm}^{-1}$ were identified due to the ionic nature of the chloride bonding [17].

Therefore, based on the FTIR, TG/DTG and XRD results, it could be concluded that FS phases with reasonable crystallographic compositions and dominant proportion have been formed in the synthesised FS product. This FS was then used in the following Raman spectroscopy analysis.

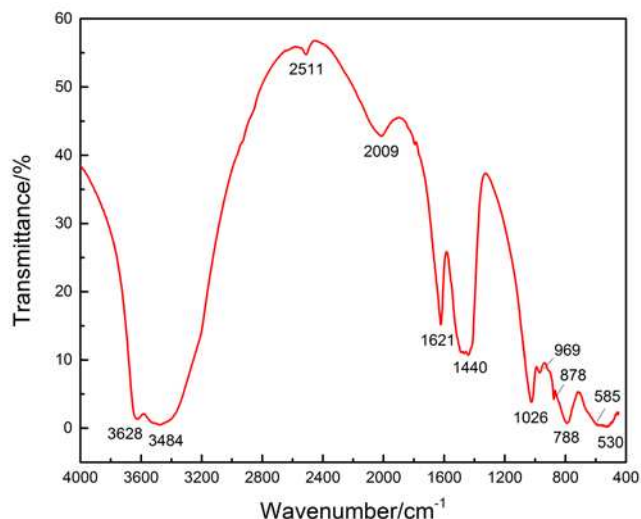


Fig.3 FTIR spectrum of synthesised Friedel's salt

3.1.2 Raman spectroscopy analysis

3.1.2.1 Raman spectra of FS and bands assignment

As mentioned above, until now no comprehensive research conducted on Raman spectroscopy study of either the pure FS or the FS formed in cement matrix. Hence, in the current study, the synthesised pure FS was analysed first so that the Raman bands retrieved and assigned can be used as bench-mark to analyse the FS formed in the PC paste sample later. In this study, in order to clearly identify all the possible molecular vibration modes in the synthesised FS, extended scan mode between 200 cm^{-1} and 4000 cm^{-1} was employed in an attempt to record all the detectable Raman bands. Fig. 4 represents the full Raman spectrum of the synthesised FS under extended scan mode. In the original spectrum Fig. 4(a), an unwanted sloping background was observed from 200 cm^{-1} onwards which may hamper the genuine Raman peaks. This background could be the troublesome fluorescence induced by the uncertain impurities in the raw materials used to synthesise the FS. Hence, baseline correction using OriginPro 8.6 was applied to eliminate the background effect and the resultant spectrum is presented in Fig. 4(b).

Obviously, as shown in Fig. 4(b), the Raman bands of FS were located mainly at two frequency regions, i.e. low frequency range ($200\text{-}1200\text{ cm}^{-1}$) and high frequency range ($3200\text{-}3800\text{ cm}^{-1}$). From FTIR bands assignment summarised in Table 1, the IR-active vibrations of the functional group $\text{Al}(\text{OH})_6$ octahedra is located at the low-wavenumber range, whilst the high frequency bands are mostly attributable to the water and hydrogen bond network. Hence, these two Raman frequency ranges are discussed separately below.

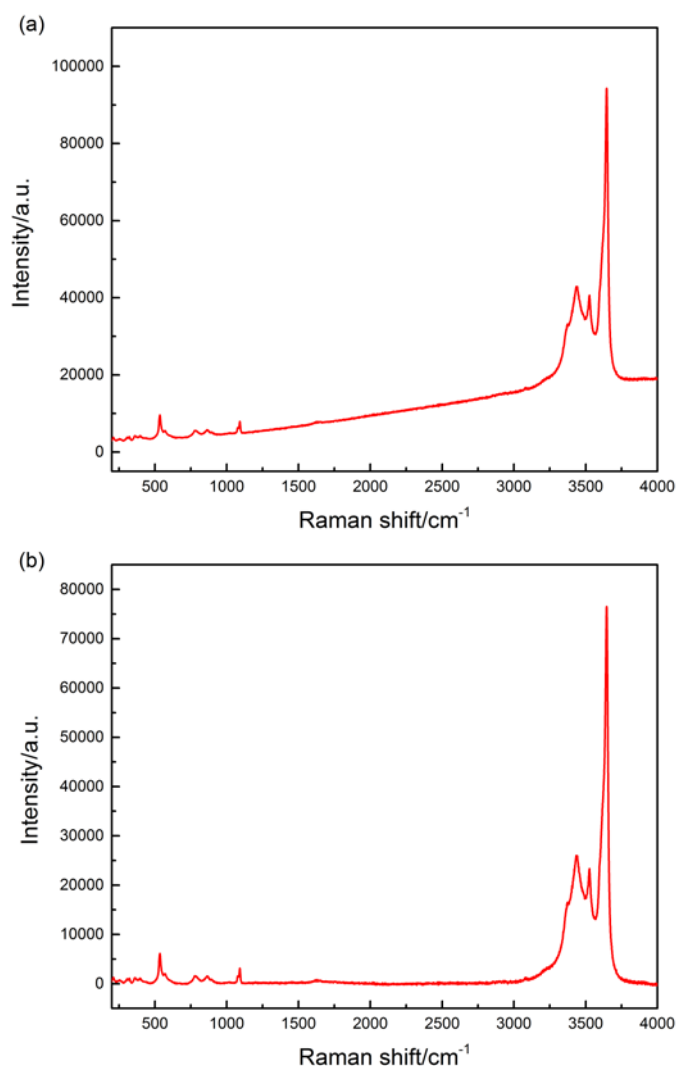


Fig.4 Raman spectra of synthesised Friedel's salt (200-4000 cm^{-1}). (a) Original spectrum. (b) Spectrum after subtracting background

a) Low frequency range (200-1800 cm^{-1})

The Raman spectrum (after subtracting background) of FS recorded between 200 cm^{-1} - 1800 cm^{-1} is presented in Fig. 5. Several Raman peaks can be clearly observed in this background-subtracted spectrum in this low wavenumber range.

In Fig. 5, the most intense and well-defined peak emerged at 534 cm^{-1} , as well as its shoulder at 568 cm^{-1} , are unique in FS representing the stretching vibration mode of Al-OH bonds in the $\text{Al}(\text{OH})_6$ octahedra. Furthermore, an adjacent band visible at 783 cm^{-1} could be attributed to the Al-OH bending vibration mode [17, 30]. Some minor bands at 200-500 cm^{-1} were also identified, i.e. the bands at 212 cm^{-1} and 255 cm^{-1} (external rotation and translation), and 362/397 cm^{-1} (Ca-O stretching vibration) [30]. Besides, the hump located at 1629 cm^{-1} could be assigned to

the H-O-H bending vibration of water molecules in the FS [17, 31, 55]. It is worthwhile to note that, instead of calcite the vaterite phase was identified in this sample as evidenced by its various Raman bands, i.e., the sharp peaks at 1077 cm^{-1} and 1092 cm^{-1} ($\nu_1\text{CO}_3$ symmetric stretching vibration), 868 cm^{-1} ($\nu_2\text{CO}_3$ out-of-plane bending) and $305/323\text{ cm}^{-1}$ (lattice vibration)[53, 56, 57].The formation of vaterite in the current sample could be due to the carbonation occurred during the sample preparation or storage under relatively dry environment, which is in good agreement with the literature [49, 57, 58].

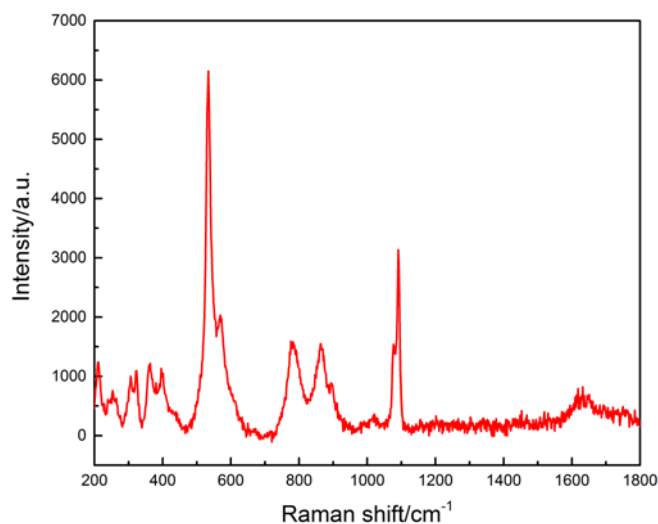


Fig.5 Raman spectrum of synthesised Friedel's salt in low frequency range (200-1800 cm^{-1})

b) High frequency range (1800-4000 cm^{-1})

The Raman spectrum (after subtracting background) of FS in the high wavenumber range is reported in Fig. 6. Obviously, contrary to the hydrogen bond in normal water which shows an extremely broad hump with strongly-overlapping bands at the wavenumber range of $3200\text{-}3800\text{ cm}^{-1}$, the hydrogen bond in the FS led to well-resolved peaks at high frequency range. More importantly, this spectrum range from $3200\text{-}3800\text{ cm}^{-1}$ represented two different hydrogen bond network in FS. The broad band on the left-side (at about $3200\text{-}3600\text{ cm}^{-1}$), with three well-resolved peaks at 3432 cm^{-1} , 3527 cm^{-1} and 3617 cm^{-1} , corresponds to the stretching of water molecules in the interlayer. On the other hand, the intense and sharp peak identified at 3646 cm^{-1} , was from the stretching of hydroxyl groups [30, 56, 59-61]. This phenomenon indicates the much ordered arrangement of the hydroxyls over the water molecules. Indeed in the FS, the hydroxyls in the main-layers are perfectly coordinated with bridge Cl^- ions and participated to the cohesion of the lamellar structure. However, there is a dynamic disorder in the interlayer part of the FS structure, and, hence, the water molecules have much high freedom.

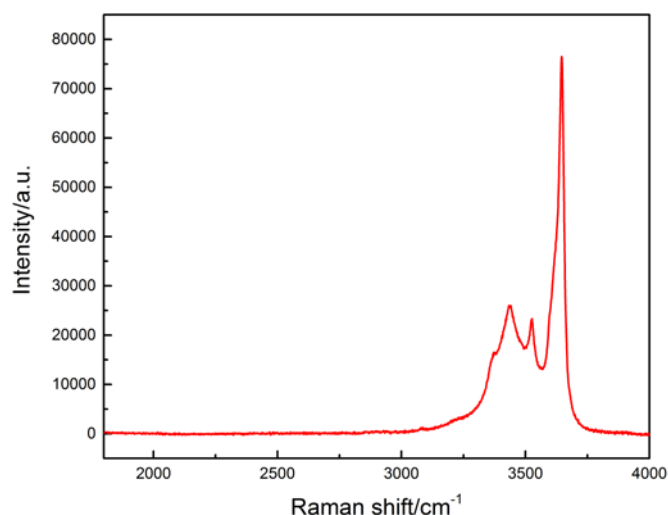


Fig.6 Raman spectrum of synthesised Friedel's salt in high frequency range (1800-4000 cm^{-1})

3.1.2.2 Discussion

In the above Section, the various Raman bands correspond to the functional groups of FS have been identified and assigned. In this section, attempts have been made to try to understand the possible relationship between the identified Raman vibrational information and the change incurred to the composition and structure of the interlayer when AFm was converted to FS in the presence of chloride ions. The structure of the FS, especially, the local structural information associated with the Cl^- ions is discussed in detail first. Building upon this, the Raman bands of FS are compared to those of AFm, in order to understand the effect that the incorporation of chloride ions might have on the structure and, consequently, the Raman bands, of FS.

a) Structure of FS and its Cl-site

FS [7, 18, 21, 60-63], also known as hydrocalumite or Cl-AFm, has a unique crystal structure amongst Layered Double Hydroxide (LDH) family and is the only member that a single crystal structure refinement is available. As introduced in Section 1, FS forms by replacing the anions (SO_4^{2-}) at the inter-layer space of AFm by Cl^- ions. Its crystallographic structure can be described by periodically stacking of the positively charged main layers $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ and negatively charged interlayers $[\text{Cl}^-, 2\text{H}_2\text{O}]$. The main layer demonstrates a portlandite-like structure, i.e. every third Ca^{2+} cations in the octahedral sites in principle hydroxide layer are replaced by Al^{3+} ions to form a permanent positive charge. This charge is neutralised by the compensating anions, Cl^- , in the interlayer space. Similar to AFm compounds, the Al^{3+} and Ca^{2+} cations are coordinated by six- and seven-oxygen (O) respectively. The chloride

anion, introduced into the middle-space of two adjacent main layers, is just suited in the centre of an octahedral cavity formed by O(w) atoms from water molecules. Fig.7 shows the environment of a chloride anion in the interlayer of the FS [62-65]. Apparently, a chloride ion is hydrogen-bonded to 10 neighbouring H-atoms, i.e. six from hydroxyl groups (three each from two adjacent main layers) and four from water molecules. The hydroxyls in the main-layers are coordinated with cations, e.g., Al is coordinated to six hydroxyl groups in the main layer [18]. The water molecules are on the other hand bonded to the Ca^{2+} cations in the main-layer viz. each Ca^{2+} is approached by the seventh O(w)-atom presents in the interlayer region. Hence, the so-formed hydrogen bond network bridges the Ca^{2+} ions, water molecules and Cl^- anions following: Ca (main layer)...O(w)-H(w) (interlayer)...Cl (interlayer)...H(w)-O(w) (interlayer)...Ca (main layer) ensuring the connection between main layers and interlayers. This symmetric hydrogen bond network keeps chloride ions virtually immobile even at temperature as high as 300°C . Furthermore, this H-bond arrangement around the Cl^- site affects the properties of FS significantly. It is reported that the phase transition of FS at temperature above 35°C , from a monoclinic (m) low-temperature (LT) polymorph (C2/c) to a rhombohedral (rh) high-temperature (HT) polymorph [R3C], is probably due to the altering of hydrogen bond network leading to a decrease of the unit cell volume [18, 21, 66].

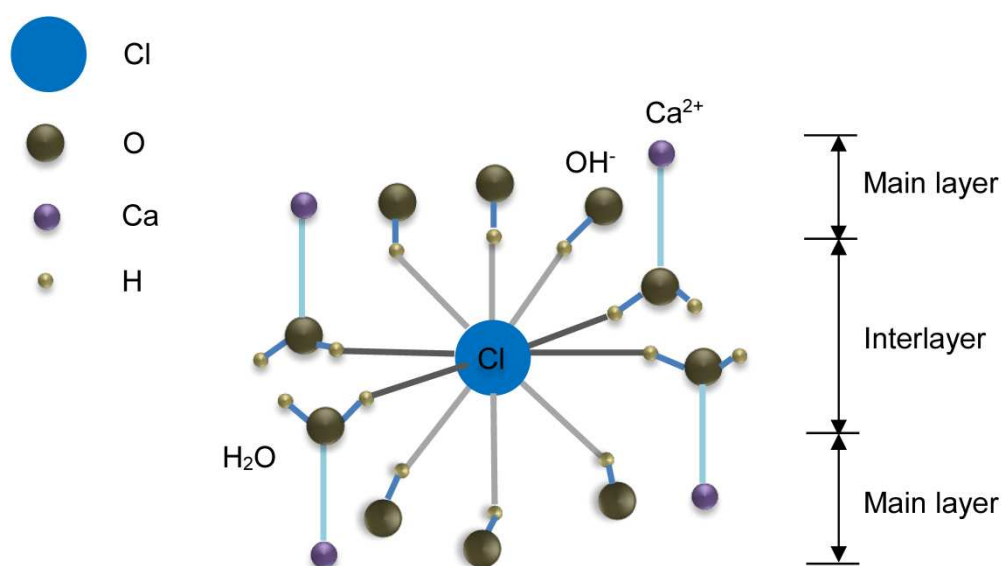


Fig.7 Schematic of the Cl-site in Friedel's salt

b) Featured Raman bands of FS

Table 3 presents the Raman bands recorded from FS, along with those of AFm phase reported [39] for comparison purpose. Apparently, by comparing the Raman bands of FS

here (first column) and its FTIR bands (Table 1), Raman spectroscopy provides much more vibrational information than FTIR, as evidenced by the vibration bands collected at low-frequency range, i.e. 212/255 cm^{-1} (the external rotation/translation band) and 362/397 cm^{-1} (Ca-O stretching).

Table 3 Raman bands of synthesised Friedel's salt and AFm phases

FS	Vibrational modes	AFm
Raman shift / cm^{-1}		Raman shift
212, 255	External rotation and translation	215
362, 397	Ca-O stretching vibration	360
534/568	Al-OH stretching vibration	531
783	Al-OH bending vibration	
305,323	Lattice vibration in vaterite	
868	Out-of-plane bending vibration ($\nu_2\text{CO}_3$) in vaterite	
1077, 1092	Symmetric stretching vibration ($\nu_1\text{CO}_3$) in vaterite	
1629	Water bending vibration mode	
3646	OH stretching of hydroxyl	3678
3432, 3527, 3617	OH stretching of water molecules	3416, 3221
	Symmetric stretching vibration ($\nu_1\text{SO}_4$)	983
	Asymmetric stretching vibration ($\nu_3\text{SO}_4$)	1114
	Symmetric bending vibration ($\nu_2\text{SO}_4$)	396,447
	Asymmetric bending vibration $\nu_4(\text{SO}_4)$	614

From Table 3, it can be seen that there are distinct differences in the Raman bands between FS and AFm, which could be possibly attributed to the following reasons:

- i) Disappearance of SO_4^{2-} ionic groups. The Raman features of SO_4 ionic-units in AFm were absent from the FS, which is fully consistent with the anion-exchange in FS viz. the SO_4^{2-} ions are replaced by Cl^- ;
- ii) Incorporation of chloride ions and subsequent modification to the local structure of $\text{Al}(\text{OH})_6$ octahedra. Evidently, at the Raman wavenumber range 500-800 cm^{-1} , corresponding to the vibration bands of $\text{Al}(\text{OH})_6$ octahedra, there were different Raman features in FS compared to AFm. Firstly, in FS a shoulder was observed at 568 cm^{-1} adjacent to the peak at 534 cm^{-1} (Al-OH stretching vibration), which is different from the AFm where only a single peak exhibited at 531 cm^{-1} . In addition, there was a new Al-OH vibration mode emerged at 783 cm^{-1} in FS over AFm. This Raman-active band, equivalent to the FTIR band observed at 788 cm^{-1} , represents the Al-OH bending vibration. The emergence of this Al-OH bending vibration band in the Raman spectrum of FS, as well as the shoulder of the Al-OH stretching vibration, could be caused by the alteration of the

local site of $\text{Al}(\text{OH})_6$ octahedral units due to the substitution of Cl^- for SO_4^{2-} ions. As aforementioned, Cl^- located at the interlayer is directly hydrogen-bonded to six hydroxyl groups in the main-layers. Meantime, these OH^- are coordinated to the cations, either Al^{3+} or Ca^{2+} , to form the rigid ionic units such as $\text{Al}(\text{OH})_6$ octahedra. Hence, for FS, the incorporation of Cl^- ions for replacing original SO_4^{2-} could change the bonding environment and subsequently the site structure of $\text{Al}(\text{OH})_6$ octahedra, leading to the emergency of the new vibrational features.

Besides, the high frequency Raman range gave an insight into the hydrogen bond network in the water molecules and hydroxyls. This feature is quite similar to that from FTIR.

3.2 Friedel's salt in cementitious materials

3.2.1 Verification of the formation of FS by XRD

The chloride attacked sample was first analysed by XRD in order to clarify the formation of the FS in the deteriorated PC sample. Fig.8 represents the XRD pattern of the chloride attacked PC paste sample.

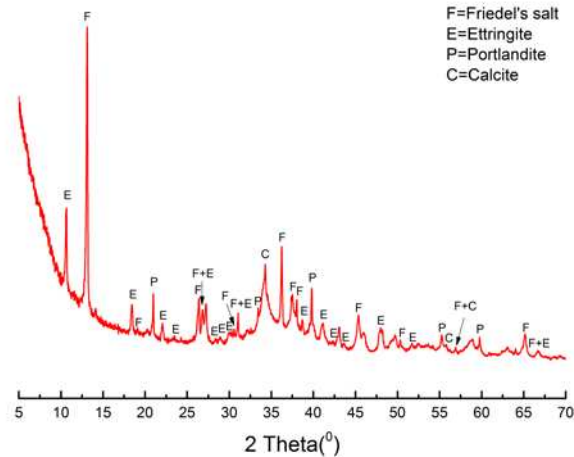


Fig.8 XRD pattern of chloride attacked PC paste sample

As shown in Fig. 8, FS has been formed in the cement paste exposed to chloride solution, as indicated by its XRD peaks located at $2\theta = 13.1, 26.4, 27.3$ and 36.2° . At the same time, various cement hydration products have also been identified, such as ettringite ($2\theta = 10.7, 18.5$ and 22.0°) and portlandite ($2\theta = 21.0, 33.4$ and 39.8°). Furthermore, there were some humps, such as those at about $2\theta = 46\sim 47$ and $48\sim 50^\circ$, cannot be assigned. These humps could be attributed to the calcium silicate hydrate (C-S-H) phases formed under the

hydration of Cement I - they could not give sharp XRD peak due to their poorly crystalline structures. Moreover, calcite is identified in the cement sample which could have been formed from the carbonation during sample preparation. Hence, it can be confirmed that FS crystals were formed in the chloride attacked PC paste samples.

3.2.2 Raman spectroscopy analysis

As discussed in Section 3.1, the synthesised pure FS can be readily identified under Raman spectroscopy. However, whilst the Raman bands of pure and white coloured FS salt can be easily identified, it could potentially be difficult to characterise FS salt in the chloride attacked cement paste due to the following reasons:

- i) the grey colour of PC paste sample. As Raman signal is basically occurred on the principle of scattering, grey colour could possibly reduce the signal because of its potential absorption effect to the excitation laser;
- ii) the heterogeneous nature of cementitious materials. Due to the fact that the laser-sampling spot of Raman spectroscopy is only at micron-scale, i.e. 1.26 μm diameter, it could be difficult to retrieve a holistic view of the samples;
- iii) the potential of strong fluorescence. The impurities existed in the cement (e.g. organic compound), the defects introduced during grinding and the inter-particle scattering could cause strong fluorescence background to the intrinsically weak Raman peaks [37], which can impose disturbance to or even totally hamper the weak Raman peaks.

Fig. 9(a) shows the Raman spectrum of the chloride attacked PC sample. As the Raman feature of FS is mainly located at the Raman shift of 500 – 800 cm^{-1} , only a Raman region between 200 and 1700 cm^{-1} is reported.

As illustrated in Fig. 9(a), strong sloping backgrounds, as expected, were emerged from 200 cm^{-1} onwards in the spectrum. These could be the unwanted fluorescence as aforementioned. Hence, the background was again subtracted and the resultant spectrum is presented in Fig. 9(b). The most intense doublet at 513/536 cm^{-1} could be attributed to the stretching vibration mode of Al-OH in the aluminite-bearing phases, such as the FS and AFm minerals. Besides, Al-OH bending mode was also recognised as manifested by the Raman band at 740 cm^{-1} . Additionally, there were two peaks identified at the low frequency region, i.e. 245 cm^{-1} and 356 cm^{-1} , which could be due to the external rotation/translation and Ca-O stretching vibration mode respectively. Furthermore, a vibration band was also observed at 673 cm^{-1} , which could be associated with the Si-O-Si symmetric bending vibration of C-S-H phase [67], whilst the peak at 988 cm^{-1} of the symmetric stretching

vibration of (ν_1 SO₄) could be attributed to calcium aluminate monosulphate (AFm) phases. The carbonate band emerged again at 1076 cm⁻¹ [ν_1 (CO₃)]. In addition, the hump located at 1607 cm⁻¹ represents the H-O-H bending vibration of water molecules in FS salt was also recognised. The above results indicate that the typical Raman bands of FS salt formed in the chloride attacked PC paste have been recognised by Raman spectroscopy, confirming fully the potential of Raman for distinguishing the FS formed in cementitious materials.

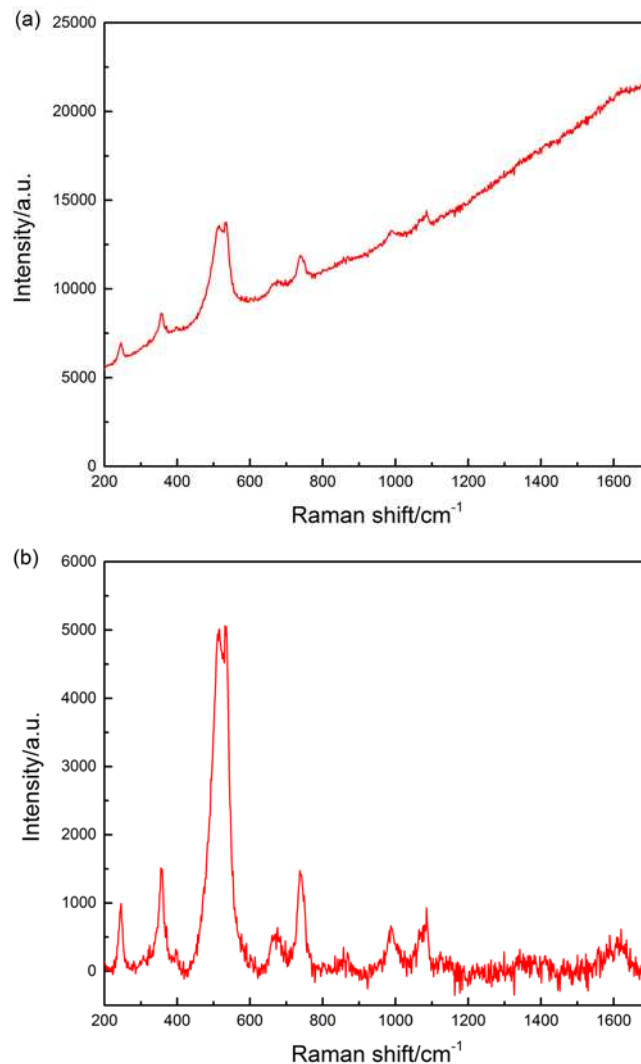


Fig.9 Raman spectra of chloride attacked PC paste sample. (a) Original spectrum. (b) Spectrum after subtracting background

Moreover, by comparing Fig. 5 and Fig. 9(b), it becomes evident that different Raman-band features were retrieved from the pure FS and the cement paste sample. Taking the Al-OH stretching band as an example, wavenumber-shift and band splitting were observed, and these bands were very strong. In pure FS, a sharp peak (534 cm⁻¹) and a shoulder (568 cm⁻¹) were identified. However, from the chloride attacked PC paste sample, an intense doublet

was recognised at 513/536 cm^{-1} . This could be due to the complex nature of the cementitious matrix. On the other hand, there could be more than one AFm phases existing in the current cement matrix which could also contribute to the Al-OH stretching vibration, resulting in enhanced Raman bands.

4. Conclusions

Friedel's salt (FS) forms upon chloride binding with monosulphoaluminate (AFm) phase. By characterising the FS formed under chloride attack, we can obtain useful information on the chloride binding capacity of concrete, which will eventually facilitate the prediction of service life of reinforced concrete structures. So far, there is no comprehensive research on the application of Raman spectroscopy for studying FS. In the current study, a full Raman spectrum of pure FS between 200 ~ 4000 cm^{-1} was successfully obtained, including the featured Raman bands at 534/568 cm^{-1} and 783 cm^{-1} which correspond to the Al-OH stretching and bending vibration of FS, respectively, as can be expected and inferred from the molecular structure of FS. Furthermore, similar Raman bands of FS were identified in a PC paste sample subjected to accelerated chloride attack, further confirming the potential of Raman spectroscopy for distinguishing FS in cementitious materials.

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