Nanostructure and Chemical Composition of Cement-Based Materials: Testing and Characterization Based on Solid State NMR and Electron Microscopy

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Abstract

With the research scale of materials science gradually changing from macro to micro, the research on the nanostructure and chemical composition of cement-based materials has become a hot research topic. Although the traditional research methods are very mature, and have also achieved good application results in the exploration of microscopic analysis, structural distribution, composition analysis, and morphology analysis, but for the specific cement hydration mechanism and the hydration of important constituent materials. The structure of Calcium Silicate Hydrate (CSH) gel is still not fully understood. Therefore, solid magnetic resonance and electron microscopy were used to test and characterize the nanostructure and chemical composition of cement-based materials. Firstly, the solid-state NMR technique was used to study the variation law of hydration products, and then the hydration degree was quantitatively described according to the research results. By comparing the analytical method of this paper with the traditional hydration degree characterization method, it is verified that the method has certain rationality and feasibility. Finally, the microscopic morphology of C-S-H was studied by electron microscopy. The C-S-H with C/S of 1.5 was found to be a fibrous amorphous material with a length of several tens of nanometers to several hundred nanometers. The experimental results show that the solid-state NMR and electron microscopy testing and characterization methods are of great significance for the study of the nanostructure and chemical composition of cement-based materials.

Key words: Cement-Based Materials, C-S-H, Solid State Nuclear Magnetic Resonance, Electron Microscope

1. Introduction

In recent years, the construction of infrastructure such as railways, roads and bridges, water conservancy and hydropower has been continuously promoted, and cement-based materials have been widely favored in the construction of transportation, agriculture, industry, and urban construction. And whether it is economic or technical, cement-based materials have shown certain advantages in replacing wood and steel. Therefore, the research on cement-based materials has very important theoretical and practical significance. At the same time, along with the development and progress of materials science, the testing and characterization techniques of nanostructures and chemical compositions of cement-based materials have become the current research hotspots. Regardless of the complexity of the system being studied, the performance of all aspects of the material is determined by its microstructure and composition. Compared with other materials such as wood and steel, the microstructure and composition of cement-based materials are more complicated, and there are various scales in the products after hydration reaction. Therefore, the research on the testing and characterization techniques of nanostructures and chemical compositions of cement-based materials is of great significance in the field of cement-based materials.

In cement-based materials, the composition of hydrated calcium silicate accounts for more than 60%. Calcium silicate hydrate plays a key role in the strength and durability of cement concrete. Therefore, more and more researchers at home and abroad have studied the microstructure of C-S-H. Fujii et al proposed a solid solution model and provided data on energy changes before and after C-S-H formation [1]. Taylor proposed that the structure of C-S-H is mostly similar to trans-base sillimanite [2], partially similar to the tobermorite model. Pollen et al proposed a molecular model of C-S-H gel and obtained data by using nuclear magnetic resonance [3], infrared spectroscopy, X-ray diffraction and other testing techniques. Studies have shown that the water molecules in the C-S-H gel can be adsorbed by the interlayer regions of the C-S-H gel and the pores in the

structural defects. After a certain period of equilibrium treatment, the composition of the resulting structure is almost identical to the experimental value obtained by neutron scattering measurement. However, whether it is the initial model or the post-relaxation model, their calculated density is slightly lower than the value measured by neutron scattering. Jennings constructed the CM-I model [4]. It is believed that CSH is composed of particles with a diameter of about 5.0-6.4 nm in nanometer size, and this small ball is composed of some elliptical basic structural units. The high-density (HD) CSH and low-density (LD) CSH formed after ball accumulation have a structure and water action to control the shrinkage, creep, strength and stiffness of the cement-based material. Bonnaud P.A. et al studied the thermodynamic behavior of water confined in the pores of CSH gels [5], and all Nano scale cement pores were filled with water according to the observed relative humidity above 20%, demonstrating that the surface of CSH has high hydrophilic. Marry et al studied the structure and kinetics of water molecules on the surface of hydration products by molecular simulation [6]. The results show that only 2-3 layers of water molecules are interfered by the hydration product layer and connected by hydrogen bonds. The diffusion coefficient is greatly reduced compared to capillary water. Wang et al studied the effect of crystal surface similar to cement hydration products on the molecular dynamics of water [7]. Studies have shown that the bulk density of water molecules is completely different on different silicate surfaces, with a hydrophilic surface. The formation of more hydrogen bonding with water molecules increases the bulk density of water molecules, while the bulk density of hydrophobic surface water molecules is much lower.

Throughout the research status at home and abroad, many studies have been made on the microstructure of hydrated calcium silicate, and it provides a reference for practical engineering in practice. However, the research on the hydration mechanism of cement-based materials and the nanostructure of the important constituent material C-S-H gel is not deep enough. At present, researchers at home and abroad are still exploring and investing more and more in the research of nanostructures and chemical compositions of cement-based materials. For example, Jennings has improved on the basis of the original CM-I model and proposed CM- In the model II [8], the particles in the model are no longer elliptical, but are similar to brick-shaped particles, which already have colloidal properties; Andrew et al tried on the basis of the Jennings model. Establish a structural model from the atomic scale to the nanometer scale. The basic structure of this new model is an irregularly shaped oval particle with a particle size of about 5 nm. There is relatively strong adsorption water around the particle, and a Nano void between the particles. Filled with free water, it has begun to involve the internal layered molecular structure of CSH, and there is also a distribution of combined interlayer water in the middle of the layered structure.

Solid-state nuclear magnetic resonance (NMR) technology can realize the manipulation of magnetization vectors in real space or spin space to eliminate, restore or separate certain interactions, thus providing information on the structure and properties of materials. Therefore, NMR has been widely used in the study of the structure and properties of materials. For example, H NMR was used to distinguish various hydroxyl groups on the surface, and Mo NMR was used to observe the change of Mo state in Mo/HZSM-5 molecular sieve reaction and C CP/MAS NMR found that the intermediate of methanol-based hydrocarbon process. Transmission electron microscopy (TEM), due to its high spatial resolution, is very suitable for the morphology analysis of nanomaterials. For example, Pollen et al used TEM to obtain a CSH test chart, which shows a clear layered structure of CSH; TMS is used to determine the degree of silicic acid anion polymerization of CSH, and the dehydration phase and dehydration phase rehydration are studied characteristics. From the above application results of NMR and TEM, solid-state NMR and electron microscopy can be applied to the testing and characterization of nanostructures and chemical compositions of cement-based materials.

In order to better characterize and analyze the nanostructure and chemical composition of cement-based materials, a method based on solid-state nuclear magnetic resonance and electron microscopy was proposed. In this paper, solid NMR technology is used to study the variation of hydration products, and then the hydration degree is quantitatively described according to the research results. By comparing the analytical method with the traditional hydration degree characterization method, the results show that the method is consistent with the experimental results obtained by the traditional acid selective dissolution method. The results show that solid nuclear magnetic resonance spectroscopy can quantitatively characterize the degree of hydration. In this paper, the microscopic morphology of C-S-H was studied by electron microscopy. The results show that C-S-H is composed of small spherical particles with a size of about 10 nm, and fiber flock particles with a size of about 100 nm are composed of these spherical small particles. When the magnification is relatively large, it is judged from the characteristics of the diffraction pattern that C-S-H is an amorphous gel. The experimental results show that the proposed method and characterization based on solid-state NMR and electron microscopy have good feasibility and rationality.

2. Proposed Method

Nanomaterials are special materials composed of nanometer-scale ultrafine particles. Test and characterization techniques are fundamental ways to understand nanostructures, identify nanomaterial, evaluate special properties and chemical properties, and are important technological means for continuous advancement

in the field of nanomaterial. There are many methods for testing and characterizing nanomaterial structures, and various new methods are emerging. The testing and characterization of nanomaterial structures can be divided into: component analysis, structure determination and morphology observation. Only the basic methods are introduced here.

2.1. Composition Analysis

In addition to traditional chemical analysis techniques, component analysis of nanomaterials includes mass spectrometry, ultraviolet, visible light, infrared spectroscopy, gas, liquid chromatography, nuclear magnetic resonance, X-ray fluorescence spectroscopy, electron spin resonance, Auger and X-ray photoelectrons. Spectroscopy, secondary ion mass spectrometry, electron probes, atom probes (in combination with fields, ion microscopes), laser probes, and the like. Among them, there are many applied research methods for some component analysis methods. For example, mass spectrometry is one of the basic means of identifying an unknown organic compound, which provides information on the molecular weight and elemental composition of the compound. The infrared spectroscopy test method is simple, and a large number of infrared spectra of known compounds and characteristic frequencies of various groups are accumulated, which makes the analysis of the test results more convenient. As a supplement to infrared spectroscopy, nuclear magnetic resonance spectroscopy has unique advantages for the identification of stereoisomers, analysis of polymer configuration and conformation, compositional quantification of copolymers and sequence structure determination. Therefore, the solidification NMR method is used to analyze the degree of hydration reaction of cement and fly ash. The following is a description of solid NMR related technologies:

(1)Magic angle rotation

The Magic-angle Spinning (MAS) technique was first proposed and put into use by Andrew and is now the most widely used technology in NMR. This technique is derived from the chemical shift interaction (HCS), the direct dipole interaction (HD) and the quadrupole interaction (HQ) of the Hamiltonian expression:

$$H_{CS} = \gamma B_0 I_Z \left(\delta_{iso} + \frac{1}{2} \delta_{CSA} (3\cos^2\theta - 1) \right) \qquad (1)$$

$$H_D = I \cdot D \cdot S = hb_{IS} (3\cos^2\theta - 1) \left(I_z S_z - \frac{1}{4} (I_+ S_- + I_- S_+) \right) \qquad (2)$$

$$H_Q = H_Q^{(1)} + H_Q^{(2)} \qquad (3)$$

$$H_Q^{(1)} = \frac{1}{12} h v_Q (3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\alpha) \qquad (4)$$

Among them, $H_Q^{(1)}$ and $H_Q^{(2)}$ is Hamiltonian of first-order and second-order quadrupole action, respectively. θ represents the angle between the axis of the electron cloud and the external magnetic field, when $(3\cos^2\theta - 1) = 0$ (i.e. = 54.736°): for H_{CS}, δ_{iso} (reflecting the magnitude of chemical displacement anisotropy) is 0, HCS only and δ_{iso} (isotropic chemical shift, which reflects The electronic structure averaged around the nucleus can be related to the chemical species), which greatly improves the resolution of the spectrum; for H_D, it is theoretically eliminated; for H_Q, the first-order quadrupole acts to a certain extent. The solid sample is placed in the sample tube and rotates at a high speed of 54.736° with the applied magnetic field. When the rotation speed is fast enough to exceed the anisotropic effect, only one resonance signal is observed in the spectrum; otherwise, peak splitting is observed, the center of the isotropic chemical shift peak and a series of spin-side peaks with a uniform frequency interval and rotor speed (sample speed).

(2)Cross polarization

In solid-state NMR, Cross Polarization (CP) generally increases the sensitivity of the dilute nucleus by transferring the magnetization vector of the nucleus I to the dilute nucleus S. The signal intensity can theoretically be enhanced to the original one Y1/y2 times. In addition, the waiting time of this experiment depends on the longitudinal relaxation time (T1) of the nucleus I, which is usually much smaller than the longitudinal relaxation time of the S nucleus. Therefore, in the cross-polarization experiment, the same time can be compared with the direct observation. The normal experiment of the S core collects more signals.

In the rotating coordinate system, a π/2 pulse in the Y direction is applied to the spin I to obtain a transverse magnetization vector in the x direction. An x-direction RF pulse is then applied to both spins I and S to lock the magnetization vector in the x-direction. This period of time is called contact time in a cross-polarization experiment, and the length is usually from tens of microseconds to hundreds of milliseconds. During this time, the intensity of the RF pulse field applied on spins I and S needs to match to satisfy the following equation:

$$v_{1I} = \gamma_I B_{1I} = \gamma_S B_{1S} = v_{1S} \tag{5}$$

During the contact time, since the x-direction pulse locks the magnetization vector, the spins I and S can be considered to be in the double-rotation coordinate system. In the new dual-rotation coordinate system, the RF field is independent of time, and the Zeeman split is also consistent for I and S, so polarization transfer between spins I and S can be performed. For the cross-polarization experiment involving the quadrupole nucleus S, the Hartmann-Hahn matching condition is related to the first-order quadrupole splitting, and the cross-polarization experiment can also be performed under the magic angle rotation condition, at which time the dipole action becomes time and time. Related, the best matching conditions are usually as follows:

$$v_{1I} = v_{1S} + nv_r, \qquad n = \pm \pm 1,2, \quad for \quad v_{1S} \gg v_Q' \tag{6}$$

$$v_{1I} = (S + \frac{1}{2})v_{1S} + nv_r, \qquad n = \pm \pm 1,2, \quad for \quad v_{1S} \ll v_Q' \tag{7}$$

Among them, v_r is the spin speed. In the experiment, some model compounds with high signal-to-noise ratio are often used to optimize the Hartmann-Hatm matching condition. In addition, when the activity of the molecule or group is strong, or the rotation speed of the magic angle is too high, it is not conducive to the smooth progress of the cross polarization, so the rotation speed should not be too high.

(3)Dipole coupling technology

The high-speed magic angle rotation eliminates chemical displacement anisotropy, dipole-dipole interaction and first-order quadrupole interaction in solid-state NMR, which greatly improves the resolution of the spectrum. But the dipole-dipole effect contains information about the distance between the cores

$$b_{IS} = -(\frac{\mu_o}{4\pi})\frac{\gamma_I \gamma_S \hbar}{r_{IS}^3} \tag{8}$$

B_{IS} is an item of H_D, and r_{IS} is the distance between I core and the S core. According to this principle, the dipole coupling can be reintroduced under the magic angle rotation condition. The information of the distance between the cores can be observed by observing the magnitude of the action, and the distance between the cores can be measured to obtain the structural information.

The REDOR (Rotational-Echo, Double-Resonance NMR) technique was designed and developed by Gulllon and Schaefer. The experiment consists of two separate experiments: the first is a control experiment, a normal echo experiment; the second is a double resonance experiment, which applies a spin on the S spin every half of the motor cycle. 180° pulse: if the spin S and the spin I space are close, the magnetic field of the spin S subjected to the spin I will be reversed with the occurrence of the 180° pulse, so the magnetization vector of I cannot be renormalized normally. Therefore, the weakening of the echo signal in the double resonance experiment can prove that the spins I and S are spatially close to each other, and the amount of signal attenuation is related to the magnitude of the dipole action.

$$S_r / S_0 = \frac{1}{2\pi}\int_0^\pi\int_0^\pi \cos(\theta)\sin\beta d\alpha d\beta \quad (\theta = 2ntD\sqrt{2}\sin 2\beta \sin\alpha) \tag{9}$$

Where S_0 is the peak intensity of the blank experimental spectrum and S_r is the peak intensity of the double resonance signal. N is the number of rotor cycles, and t is the time corresponding to one rotor cycle at the speed.

2.2. Structural Determination

The structure of nanomaterials is mainly determined by diffraction methods such as X-ray diffraction, neutron diffraction, electron emission, r-ray diffraction, and Mossberg spectrum. Among them, X-ray diffraction technology is the most widely used, including Debye powder photographic analysis, high temperature, normal temperature, low temperature diffractometer, back reflection and transmission Laue photography, quadrupole detector for measuring single crystal structure. In an X-ray diffractometer, a bundle of X-rays with a wavelength of $\lambda = 0.05$ to 0.2 nm is incident on the sample, and is diffracted by various crystal phases in the sample. The diffraction follows the Bragg formula as follows:

$$2d\sin\theta = \lambda \tag{10}$$

Where d is the interplanar spacing. A more specific method of structural determination is thermal analysis. Although thermal analysis technology is not in the category of diffraction method, it is an important means to study the structure of materials, especially the structure of polymer materials. The basis of thermal analysis

technology is that when the physical state and chemical state of a substance change (such as sublimation, oxidation, polymerization, solidification dehydration, crystallization, degradation, melting, lattice change, and chemical reaction), it is often accompanied by thermodynamic properties (such as Changes in enthalpy, specific heat capacity, thermal conductivity, etc., so the physical or chemical changes of the material can be understood by measuring changes in its thermodynamic properties. At present, thermal analysis has developed into a systematic analysis method, which is an extremely useful tool for polymer material research. It can not only obtain structural information, but also determine some physical properties.

2.3. Morphology Observation

The morphology of nanomaterials is mainly observed in microscopes, where optical microscopy is a common method for viewing materials on the micrometer scale [9]. Scanning electron microscopy and transmission electron microscopy advance the observed dimensions to sub-micron and sub-micron levels. Scanning electron microscopy is useful for the analysis of fracture morphology of materials [10]. Due to the improvement of the resolution of the scanning electron microscope in recent years, it is possible to directly observe the perfection degree of the spherulite size of the partially crystalline polymer, the size and distribution of the fractionation phase in the blend, and the mixed relationship between the continuous phase (parent) and the like. The field ion micro-defect (FIM) can directly display the grain boundary or the wrong head by using the difference of the electric field generated by the inert gas such as nitrogen and helium, using the difference of the electric field of the edge of the probe tip surface of the probe with a radius of 50 nm, the arrangement of atoms and the adsorption behavior of gas atoms on the surface. Transmission electron microscopy is a high-resolution, high-magnification microscope that provides information on the structure, crystal structure, and chemical composition of extremely fine materials [11]. It is an important means of materials science research. Although the preparation of samples by TEM is complicated, it is very useful in studying the defects of crystal materials and their interactions. Therefore, the main chemical component C-S-H in cement-based materials was observed by transmission electron microscopy.

3. Experiments

3.1. Experimental Raw Materials

The main raw materials for the experiment include Hubei Huangshi Portland cement and Zhenjiang Huayuan I grade fly ash. Among them, the main difference between the chemical composition of cement and fly ash is the Ca0 content; as an auxiliary cementing material [12], the main chemical components of fly ash are oxides of silicon and aluminum, and the Ca0 content of low calcium type fly ash is very high small. In the experiment, the acid selective dissolution method was used to test the degree of reaction of fly ash. The solution used was a hydrochloric acid having a density of 1.18-1.19 g/cm3 and a mass fraction of 36%-38%.

3.2. Testing and Characterization

Solid nuclear magnetic technology is an important means of structural analysis and property analysis of materials. NMR studies different local environments around various cores, and is particularly useful for studying the structure of solid materials and providing very rich and detailed structural information [13]. It can be used for structural analysis of homomorphic materials with high crystallinity, structural analysis of solid materials and amorphous materials with low crystallinity, and solid long-range monolithic structures with x-ray diffraction, neutron diffraction, and electron diffraction. The methods complement each other. This article uses the AVANCE III 400 WB solid-state nuclear magnetic resonance instrument produced by German Broker. It is a high-resolution instrument specially used for solid-state nuclear magnetic resonance. When measured with adamantane as a standard substance, the full width at half maximum of the peak is only 1.3 Hz. For a typical liquid nuclear magnetic resonance instrument, the full width at half maximum of the corresponding peak is at least 40 Hz. The resonance frequency of solid nuclear magnetic resonance (Si) during the test was 79.5 MHz. The test sample was mounted in a 7 mm rotor and tested under magic angle rotation with a rotation rate of 6000 rpm. The Si spectrum uses a single pulse sequence under high power to catastrophe, with a 90 degree pulse width of 5 microseconds and a cycle delay time of 5 seconds. The chemical shift of Si is determined by an external standard method, that is, the chemical shift of kaolin is -91.5 ppm.

Transmission electron microscopy is an effective tool for testing nanoscale materials [14]. It can not only observe the nano-scale particle contour and size, but also determine the atomic structure of the sample by the diffraction pattern of the sample. The transmission electron microscope used herein is a Japanese JEOL JEM-2100E transmission electron microscope with an operating voltage of 200 kV and an electron diffraction pattern (SAED) obtained by software Gatan Digital Micrograph3.9 conversion.

4. Results and Discussions

In this paper, the hydration degree obtained by deconvolution calculation of NMR spectrum is compared with the traditional acid selective dissolution method. It is verified that NMR spectroscopy can not only characterize the hydration degree of cement itself, but also fly ash. The degree of hydration is characterized. The degree of hydration reaction obtained by NMR spectrometry is shown in Table 1.

Table 1. Degree of hydration reaction by NMR profiling

| Degree of hydration reaction (%)	28d/20°C	28d/50°C	90d/20°C	90d/50°C
Cement	84.7	84.1	95.4	87.0
Fly ash	2.5	12.0	10.5	12.8

It can be seen from Table 1 that when the hydration is 28d, the degree of reaction of the cement itself is slightly lower than that of the normal temperature curing; compared with the normal temperature curing conditions, the high temperature curing does not promote the hydration process of the cement itself. When the fly ash is hydrated for 28 days, the degree of reaction of the fly ash cured at 50°C is about 5 times that of the normal temperature curing. The degree of hydration reaction measured by the acid selective dissolution method is shown in Table 2 below.

Table 2. Degree of hydration reaction determined by acid selective dissolution method

Degree of hydration reaction (%)	28d/20°C	28d/50°C	90d/20°C	90d/50°C
CH content	12.6	7.0	10.1	6.7
Combined water content	13.0	15.4	16.9	15.9
Fly ash reaction degree	3.1	12.1	10.5	13.4

It can be seen from Table 2 that the correlation between the results of the acid selective dissolution method and the NMR spectrum analysis results confirms the reliability of the NMR spectrum analysis method for the degree of hydration reaction. The degree of reaction of the fly ash measured by the acid selective dissolution method, and the result of the NMR spectrum deconvolution calculation is slightly higher. The results show that the deconvolution calculation results based on NMR Si spectra can accurately calculate the hydration progress of silicate minerals in cement. However, the traditional acid selective dissolution method still has some controversy on the selection and calculation methods of erosion solution types. Therefore, NMR profiling is a powerful means to accurately quantify the degree of reaction of cement silicate minerals and the degree of fly ash reaction.

A TEM study was performed on C-S-H with an initial C/S of 1.5. The ground C-S-H sample was first passed through a 200 mesh screen and uniformly mixed with absolute ethanol for 20 minutes to be sufficiently dispersed into the solution. The dispersed C-S-H particles were then adhered to a carbon film-coated ultrafine copper mesh. Finally, the copper mesh was taken out and dried until the absolute ethanol was completely evaporated, and the test was performed after the sample preparation was completed. The TEM test results of C-S-H at C/S = 1.5 are shown in Figure 1.

a) 200nm	b) 100nm	c) 50nm
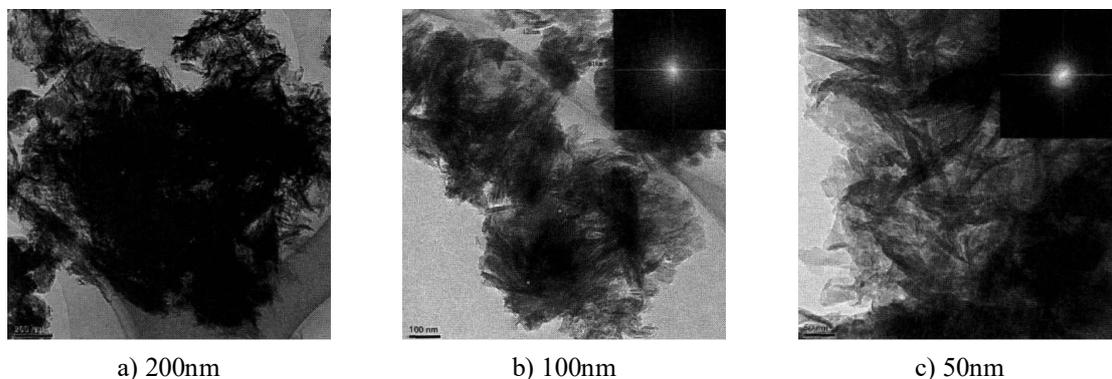
Figure 1. TEM test results of C-S-H at C/S=1.5

It can be seen from Figure 1 that Figure a) is a TEM test chart of CSH at 200 nm magnification when C/S=1.5, in which the leaf-like and fibrous substances agglomerated together can be observed, and the CSH large particles are composed of several The small fibrous particles are intertwined with each other to form large

particles. The partially agglomerated fiber particles with a heavier shadow in the middle are more than the edges of the large particles, so that the electron beam cannot pass through, so the degree of resolution is relatively low. The fibrous particles are clearly observed at the edge of the large particle; Figure b) is an enlarged view of the Figure a) with a magnification of 100 nm. The fibrous small particles are interlaced in a flocculent shape, and there is no clear between the particles boundary. The fiber particles have a width of about 10 nm, a length of different, ranging from 50 nm to several hundred nm and the direction is basically disordered, and there is not much rule. Observed from the topography, the ordered ness is less than that of the crystalline material [15]. It should belong to the amorphous material-gel; the magnification of the Figure c) is 50nm. In the figure, it can be observed that in addition to the fibrous flocculent particles, some CSH also accumulate. Irregular massive particles, which are intertwined with the fibrous flocculent particles to form the edge profile of the CSH large particles. In addition, the illustrations in the upper right corner of Figure b) and Figure c) are the respective diffraction patterns. The diffraction pattern of the CSH sample is a blur-like beam of the boundary, and does not have a regular circular diffraction pattern like the crystal [16], from which the diffraction pattern is characterized. It can be judged that CSH is an amorphous gel.

5. Conclusions

At present, cement-based materials, as the most used infrastructure construction materials in the world, have been widely used in transportation, agriculture, industry, urban construction and other engineering construction. Regardless of whether it is economic or technical, cement-based materials have shown certain advantages in replacing wood and steel. Therefore, the research on cement-based materials has very important theoretical and practical significance. In order to better characterize and analyze the nanostructure and chemical composition of cement-based materials, this paper firstly uses solid-state NMR technology to study the variation of hydration products, and compares it with the traditional hydration degree characterization method. The results show that solid-state NMR Atlas analysis can quantitatively characterize the degree of hydration. In this paper, the microscopic morphology of C-S-H was studied by electron microscopy. The results show that C-S-H with C/S of 1.5 is a fibrous amorphous material with a length of several tens of nanometers to several hundred nanometers. The experimental results show that the proposed method and characterization based on solid-state NMR and electron microscopy have good feasibility and rationality.

Acknowledgements

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