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TRAN NGO QUAN[1,2,3,4], BUI THI THAO NGUYEN[1,2], PHAM TRUNG KIEN[1,2,3,4*]

DEVELOPMENT OF CALCIUM SILICATE HYDRATE (CSH) MINERALS FROM WASTED POLYISOCCYANUCRATE (PIR) AND ROCKWOOL – THE EFFECT OF MIXING RATIO BETWEEN PIR AND ROCKWOOL

Calcium Silicate Hydrate (CSH) mineral has long been highlighted as a material with many potential applications, especially in the fields of construction and environmental protection, thanks to its special physical and mechanical properties such as durability, high surface area, low cost. In this study, synthesizing CSH by taking advantage of available waste from Industrial products and Rockwool household appliances, acting as the main raw material to form CSH minerals in the hydrothermal environment. Polyisocyanurate (PIR) has a construction application as a stable layer of fireproof insulation. PIR and Rockwool affect the environment when out of service, this study takes advantage of PIR to make the filler in CSH material synthesized from Rockwool to solve the environmental problems. In this research, the effect of mixing ratio (wt.%) of PIR to Rockwool with different ratio such as 100/0; 66/34; 34/66 and 0/100 on the forming of CSH were investigated. The microstructure of obtained CSH were studied to understand the chemical forming of CSH. Conduct an analysis of FT-IR to determine the chemical bonds in CSH and XRD menthods to determine the phase and crystal components. In addition, the SEM and EDX methods are conducted to determine the surface micro structure as well as the elemental composition of CSH material. This research also summarizes the ability to synthesize industrial and civil waste sources containing silicon and calcium and suggest the aggregate potential from various waste sources.

Keyword: Calcium Silicate Hydrate; PIR; rockwool; hydrothermal

1. Introduction

Currently, environmental issues are increasingly of concern in the world in general and each country in particular. Waste management is being considered an urgently important issue because it affects the living environment of living beings. surrounding creatures as well as humans. In the outstanding issue that is industrial and household waste, in this study, rockwool and polyisocyanucrate (PIR) waste will be processed to produce multifunctional material Calcium Silicate Hydrate (CSH).

Polyisocyanurate (PIR) is a thermoset plastic with excellent thermal insulation properties, derived from the reaction of polyols and diisocyanates. Its unique chemical structure provides enhanced thermal stability, fire resistance, and mechanical strength, making it a popular choice in industrial and construction applications. However, its production and disposal pose environmental challenges due to the use of petrochemical-based raw materials, hazardous by-products, and non-biodegradable waste [1]. Innovative approaches to recycling and repurposing PIR waste are needed to address these issues. Recent research has focused on developing sustainable methods for recovering and reusing PIR materials, such as using PIR waste in the synthesis of CSH material for many applications .Rockwool, also known as stone wool or mineral wool, is an insulation material made from volcanic rocks like basalt, diabase, and dolomite. It is highly valued for its thermal, acoustic, and fire-resistant properties, making it popular in construction, industrial, and manufacturing sectors. Rockwool enhances energy efficiency, safety, and comfort in buildings and industrial installations. However, producing and disposing of Rockwool presents environmental challenges. Its manufacturing process is energy-intensive and generates greenhouse gas emissions, and the material is non-biodegradable, contributing to landfill waste [2]. Innovative recycling and repurposing methods are being developed to address these issues. One promising approach is using Rockwool waste to synthesize CSH for construction materials. Utilizing PIR and rockwool will help mitigate environmental impacts also support circular economies.

1 HO CHI MINH CITY UNIVERSITY OF TECHNOLOGY (HCMUT), 268 LY THUONG KIET STREET, DISTRICT 10, HO CHI MINH CITY, VIETNAM
2 VIETNAM NATIONAL UNIVERSITY HO CHI MINH CITY, LINH TRUNG WARD, THU DUC DISTRICT, HO CHI MINH CITY, VIETNAM
3 POLYMER RESEARCH CENTER, HO CHI MINH CITY UNIVERSITY OF TECHNOLOGY (HCMUT), 268 LY THUONG KIET STREET, DISTRICT 10, HO CHI MINH CITY, VIETNAM
4 VNU-HCM KEY LABORATORY FOR MATERIAL TECHNOLOGIES, HO CHI MINH CITY UNIVERSITY OF TECHNOLOGY (HCMUT), 268 LY THUONG KIET STREET, DISTRICT 10, HO CHI MINH CITY, VIETNAM

* Corresponding author: phamtrungkien@hcmut.edu.vn

CSH is a crucial compound in materials science, particularly in the construction industry. It is the primary hydration product of Portland cement and is responsible for the development of mechanical strength and durability in concrete. CSH's formation and properties are integral to understanding cement chemistry and the behavior of concrete over time. It is a complex, amorphous material with a variable composition, characterized by a disordered, layered arrangement of calcium and silicon atoms, linked together by oxygen atoms and interspersed with water molecules. This structure results in a high surface area and a porous nature, contributing to the material's ability to bind other components within cement and enhance the overall cohesion and strength of concrete [3]. CSH is predominantly found in cement and concrete, playing a vital role in various applications such as building and construction, repair and restoration, and specialty concretes. There is a growing interest in developing sustainable alternatives and supplementary cementitious materials (SCMs) that can reduce the carbon footprint of cement production. One approach is the synthesis of CSH from industrial by-products and waste materials, such as fly ash, slag and silica fume [4,5]. This process involves selecting and characterization of raw materials, optimizing synthesis conditions, and evaluating the properties of synthesized CSH. The use of PIR and Rockwool waste in CSH synthesis addresses both waste management and sustainability challenges, reducing landfill burden and promoting the circular economy. To obtained the CSH, other researchs already use source of Ca and Si such as wasted glass [6-7], rice hush [8] and using polymer fiber [9-10] as and reinforce fiber. However, there is still lack of research attention on the development of CSH by using PIR and Rockwool as starting materials. PIR provide the whisker fiber to enhance the interlocking of matrix by the present of Calcium. In addition, Rockwool can provide both Ca and Si, the main element to form CSH. Thus, our research aim to find the effect of mixing ratio between PIR and Rockwool follow by hydrothermal treatment at 180°C for 96 hour and investigate the microstructure changed of obtained CSH. This research aim at the initial step to recycle the wasted PIR and wasted rockwool in industry, thus contributing the circular economy.

2. Materials and methods

2.1. Preparation of green pellet

The wasted PIR was supplied by Phuong Nam panel manufacture, Vietnam. Rockwool was collected as thermal insulator in high temperature furnace, provided by Khai Hoan rockwool, Vietnam. First, rockwool and wasted PIR are grinded and sieved to a particle size of <0.45 mm. Rockwool and PIR material samples are analyzed by XRD, FT-IR and SEM to evaluate the structure and properties. The grinded materials are mixed according to the given ratio of PIR and rockwool which are 100/0; 66/34; 34/66; 0/100 and named P/R 100; P/R 66; P/R 34; P/R 0 respectively. A small amount of water is added to increase adhesion to support the ability to shape CSH minerals before hydrothermal treatment. The mixture of PIR and rockwool is compressed into pellets at pressure of 1 MPa using an 8 mm diameter stainless steel mold with the present of moisture water 5 wt.% to enhance the forming of green pellet, follow by hydrothermal treatment at 180°C for 96 hours.

2.2. Synthesis of CSH from green pellet using Hyrothermal reaction

The resulting tablet sample is then placed on a shelf for hydrothermal synthesis in a KOH 8M environment at 180°C for 96 hours. Following hydrothermal autoclaving, the sample is dried at 90°C for 24 hours to ensure complete water removal from the CSH sample. After synthesis, the CSH sample undergoes analysis methods to evaluate its microstructure, phase composition, and mineral composition before and after the hydrothermal treatment. The flowchart process to synthesis CSH was schown in Fig. 1(a) and hydrothermal synthesis experiment in Fig. 1(b).

2.3. Materials characterization

Fourier-transform infrared spectroscopy (FT-IR) method by Thermo Scientific Nicolet 6700 FTIR is used to analyze the chemical bonds in CSH materials scanning wavenumber in range 400-4000 cm^{-1}.

X-Ray diffraction analysis (XRD) is used to analyze the phase composition of CSH before and after synthesizing by Bruker D8 Advance scanning from 5 to 80°, operation at 40 kV and 4 mA.

The surface microstructure and chemical composition analysis methods used are Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX) on Hitachi S-4800 at 10 kV. In brief, the pellet sample were put on the copper stage adhesived by conductive carbon tape, and irradiatin using electronic beam at 10 kV.

3. Results and discussions

The chemical composition of CSH and PIR/rockwool ratios have been proven through EDX analysis in TABLE 1. The mass ratio between Ca and Si is equivalent in rockwool and gradually increases in samples P/R 100, P/R 66, P/R 34, P/R 0, while the carbon ratio gradually decreases for PIR materials. EDX has proven that the synthesis process is stable without loss. The mass ratio Ca/Si ~ 1 also proves the possibility of forming specific CSH minerals by hydrothermal synthesis such as Xonotlite, Tobermorite [11]. Basically the The trace element such as Na, Mg, Al as crystal seed and accelerator the forming of CSH in alkaline medium since it increase the alkaline concentration of medium. Infact, the amount of Si and Ca increase with the increaing of P/R mixirng ratio. When the amount of Rockwool is 100%, the amount of Si and Ca is 17.23 and 17.07 wt.%, respectively,

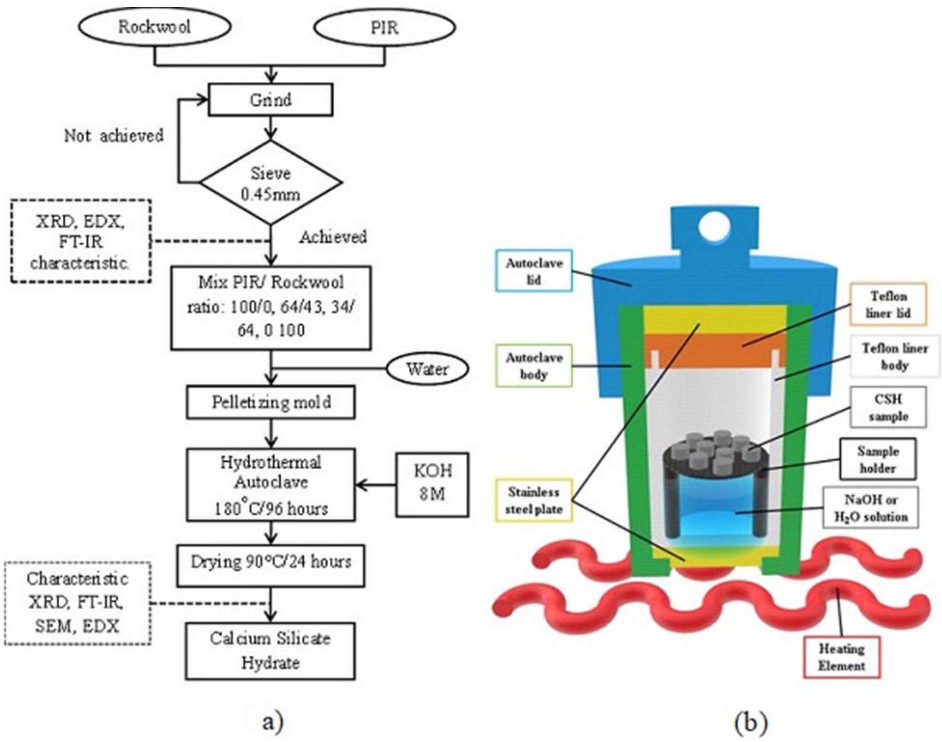

Fig. 1. (a) Flowchart of CSH synthesis process, (b) Model describing the CSH hydrothermal synthesis experiment

In fact the hydrothermal treatment does not change the chemical compostion of mixture, but change the surface morphology of rockwool and PIR as show in the SEM analysis. In comparions of starting materials PIR and P/R 100 after hydrothermal treatment, the C in PR-100 lower than in raw materials PIR due to the release of C by hydrothermal treatment. Also in P/R-100, there is no trace of Ca, since PIR compose of polyisocyanurate C3H8N2O, and they use SiO_2 as reinforment ceramic filler. Thus the amount of Ca in PR-100 is lower than P/R-0

The FT-IR spectrum analysis results shown in Fig. 2, this method analyze the characteristic spectral peaks of the bonds that exist in CSH synthesized from rockwool and PIR. The elas-

TABLE 1

Element composition of rock wool, PIR mixture ratio of P/R 100; P/R 66; P/R 34 amd P/R0 analyzed by EDX

Materials	Percentage by weight (%wt)					
	C	Si	Ca	Na	Mg	Al
Rock wool	17.17	17.03	21.56	1.22	3.75	4.68
PIR	80.71	0.52	—	—	—	—
P/R 100	74.67	0.47	—	—	—	—
P/R 66	64.73	4.73	4.12	0.59	0.84	1.27
P/R 34	61.26	6.20	5.66	1.38	—	1.69
P/R 0	20.12	17.23	17.07	1.84	3.62	4.18

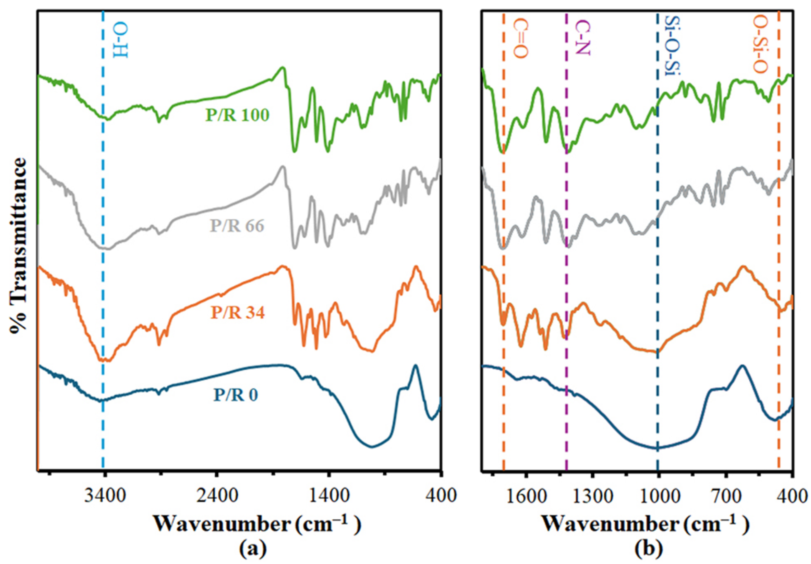

Fig. 2. FT-IR results with wavenumbers (a) 400-4000 cm^{-1}, (b) 400-1600 cm^{-1} of CSH mineral at different ratios

ticity vibration of –OH is in the peak around 3500-3200 cm^{-1}, representing water molecules in the CSH mineral structure when exposed to air [14]. The C=O bond stretching vibration in the CSH structure is detected through the absorption peak at about ~1700 cm^{-1} and the magnitude of the peak changes gradually when increasing the PIR ratio in CSH. Furthermore, the absorption peak at about ~1400 cm^{-1}, which is characteristic of the stretching vibration of the C-N bond of the isocyanurate ring in CSH mineral and similar to the C=O bond, gradually increases with increasing PIR ratio in CSH [13-14]. The absorption peak at ~1000 cm^{-1}, characterizes the symmetric stretching vibration of the Si-O-Si bonds of rockwool and shows a peak change when increasing the ratio of rockwool in CSH. O-Si-O deformation bonds are characterized at a peak at ~490 cm^{-1} and are proportional to the ratio of rockwool present in CSH. Based on the characteristic bonds analyzed in the FT-IR spectrum of CSH minerals synthesized at different rockwool and PIR ratios, can be concluded that CSH can be formed after hydrothermal treatment [15-16].

Based on the analysis of the surface microstructure of CSH mineral by SEM method in Fig. 3, Rockwool raw material shows the characteristics of mineral fibers with fiber diameters of about 7-10 μm and interwoven. The Fig. 3(a) is starting materials rockwool while the Fig. 3(f) is is P/R 0 or Rockwool account for 100 wt.%), so ther morphology is Rockwool and P/R0 is similar.

The microstructure of the PIR raw material shows that the plastic sheets are stacked on top of each other and there are microplastic particles scattered on the sheets. After hydrothermal treatment, sample P/R 100 still shows a surface structure similar to PIR because P/R 100 contains 100% PIR ratio, in addition, the prominent difference is the appearance of a rough surface on the surface of the samples. Sample P/R 0 also shows similarities with rockwooll raw material when the ratio of rockwool in this material is 100%, on the microscopic surface of P/R 0 there are fibers with a diameter of 7-10 μm interwoven with each other and CSH crystals also exist on the surface. Also the appear of CSH at the mixing ratio of P/RR 66 and P/R 34 was indicated be yellow arrow as in Fig. 3(d1) and 3(f1) at magification of 10.000×. At mixing ratio of P/R100 as shown in Fig. 3c), the PIR show the plate-like crystalm in contrast with P/R 66 show the filber of rockwool as well as the forming of round CSH crystasl (yellow arrow) on the surface of rockwool fiber as shown in Fig. 3(d1). Samples P/R 66 and P/R 34 to show the correlation of PIR and rockwool ratios, the microscopic surface structure of the two samples shows the appearance of PIR plastic sheet and rockwool fibers combined with each other.

Through the surface microstructure results, we can see the possibility of using PIR mineral as a filler in CSH mineral from rockwool when both materials have the ability to combine into composites with high surface area with versatile applications.

Fig. 4 shows the phase and crystalline composition of CSH by XRD analysis. For PIR and rockwool raw materials, the two materials have diffraction spectra showing the typical structure of amorphous materials [2]. P/R 0, P/R 33, P/R 66 have the diffraction spectral range of the amorphous phase, in addition to showing the characteristic diffraction patterns of Xonotlie mineral (PDF#23-0125), a common form of CSH mineral when synthesized in specific conditions such as high temperature >160°C with Ca/Si ratio ~1 in the mineral [6]. Characteristics of Xonotlite mineral at 2θ = 32°, 46° and exist

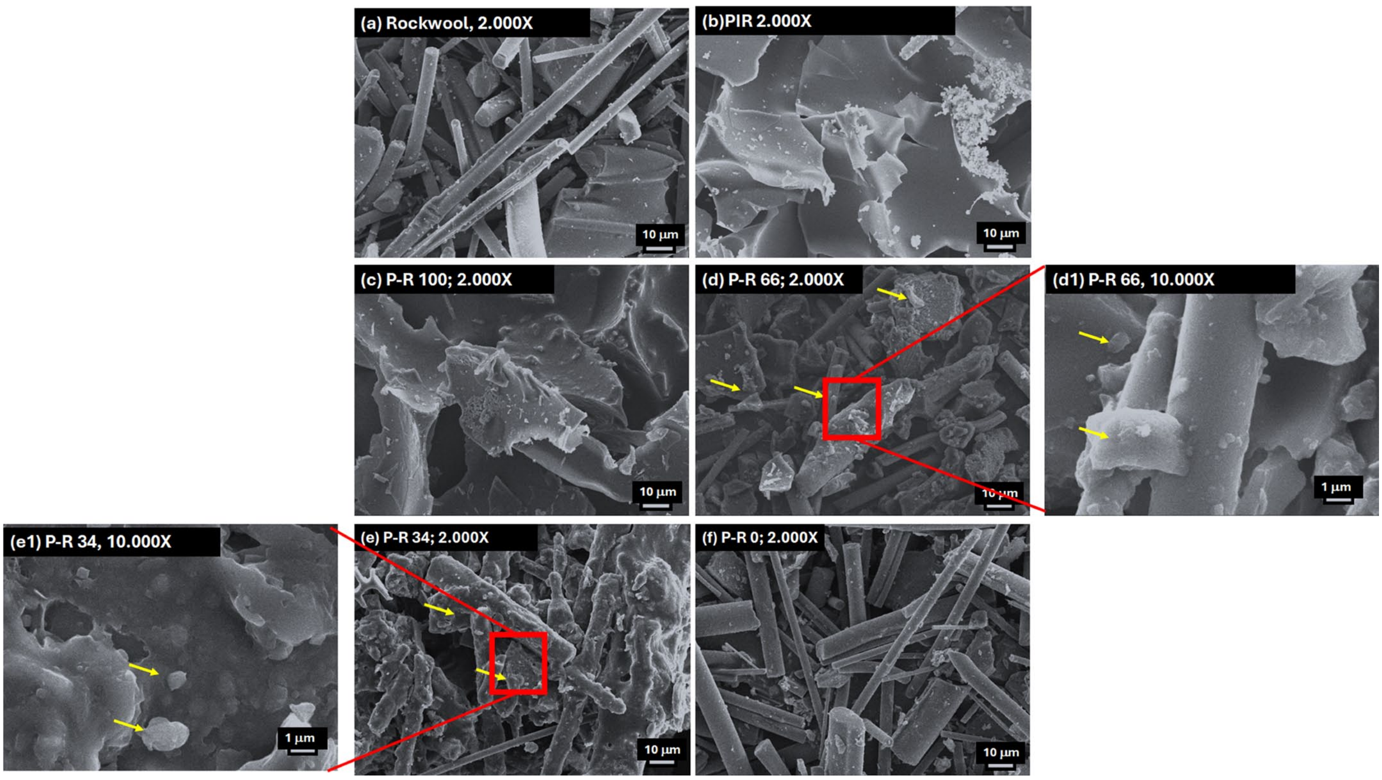

Fig. 3. SEM images of raw materials and P/R 100; P/R 66; P/R 34; P/R 00 at 2000 times magnification

in CSH materials containing rockwool (P/R 0, P/R 34, P/R 66). This also proved that Rockwool contains Ca and Si which play a major role in forming CSH minerals. The alkaline condition is also the important role to active the forming of CSH [9-11]. In this research, we used KOH 8M as an alkaline activator, and the present of trace element such as Na, Mg, Al also contributed the the formatin of CSH. In addition, sample P/R 100 also has an amorphous diffraction spectrum similar to PIR. Samples P/R 0, P/R 33, P/R 66 also have a peak in the diffraction spectrum of carbon due to the ratio of PIR in the sample. The characteristic diffractions of Xonotlite minerals and crystalized Carbon demonstrated the ratio of PIR and rockwool in the CSH samples.

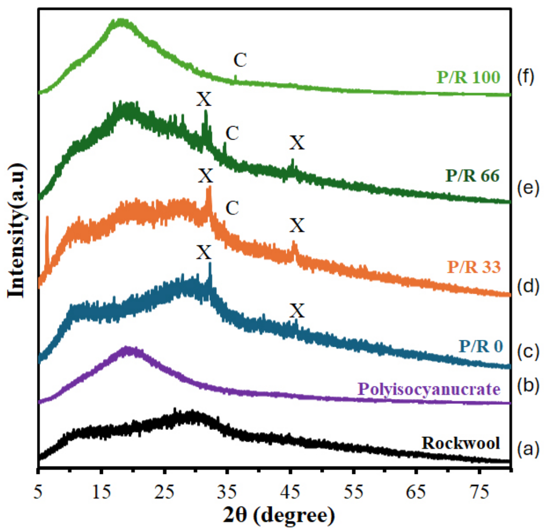

Fig. 4. XRD results of raw materials and CSH were synthesized at different ratios. C: Carbon (PDF#22-1069); X: Xonotlite (PDF#23-0125)

This research should be considered in the context of the experimental conditions and the potential applications of the findings. The main objective was to utilize the wasted PIR and rockwool to form Calcium Silicate Hydrate (CSH) mineral by hydrothermal reaction. As mentioned in introduction section, PIR is the main component of construction panel, after longuse it need to be recycle. The main component of PIR is C-H bonding, so it C chain can penetrate into the rockwool structure under pressure condition. In the other hand, rockwool was mainly used as thermal insulator with the main component of C (17.17 wt.%), Ca (21.56 wt.%) and Si (17.03 wt.%) as shown in TABLE 1. After certain used as heat insulator, wasted rockwool need to be recycle. Based on the needle-like shape morphology of rockwool (as shown in SEM data, Fig. 3a), it can be interlocked with PIR crystal to enhance the linkage chain between Ca-Si-C (as shown with P-R 66 in Fig. 3d and P-R34 in Fig. 3e). Thus, our research aim to utilize both PIR and rockwool as starting materials to form the new product by hydrothermal reaction. The main CSH mineral forming after hydrothermal reaction is Xonotlite as indicated in Fig. 4d and 4e with the needle-like morphology. It need to emphasized that the needle-like crystal size of xonotlite with diameter of 1 μm and length of 5 μm can be used as thermal insulator. This research shown the potential to recycle both wasted PIR and wasted rockwool to form CSH mineral toward the heat insulator in industry.

4. Conclusions

The hydrothermal adsorption process in 8M KOH of CSH minerals from PIR and rockwool has demonstrated the ability to synthesize waste source materials into CSH minerals with potential application value in many fields. Through XRD analysis results, the CSH mineral synthesized in the ratio of samples P-R 0, P-R 33, P-R 66 shows the CSH Xonolite can be successful obtained. SEM surface microstructure images of CSH have shown the typical structures of rockwood, PIR and the tendency to combine to form CSH materials with a highly porous structure with the pore size less than 10μm. In addition, FT-IR and EDX spectrum results also showed that CSH mineral after synthesis possesses chemical components and chemical functional groups corresponding to the PIR and rockwool ratios of CSH. In conclusion, CSH can be obtained when the amount of Rockwool vary from 33 to 100 wt.%. The next research direction is proposed to take advantage of different waste sources such as fly ash, steel slag, etc. to synthesize CSH minerals. The study can be extended to evaluate the porosity of CSH minerals such as adsorption applications.

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