Challenges in Chemistry for Sustainable Development

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Pure and Applied Chemistry International Conference 2010

January 21-23, 2010
Ubon Ratchathani University
Ubon Ratchathani
THAILAND

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JANUARY 21-23, 2010
UBON RATCHATHANI, THAILAND

ISBN: 978-974-523-230-3

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Inorganic Chemistry

Immobilization of Cr(VI) in rice husk ash based geopolymer

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Abstract: Geopolymer based on rice husk ash has been studied as an alternative eco-friendly cementitous material. Immobilization of Cr(VI) in its material was done for preventing toxicity effect of this species into human body. The rise husk ash based geopolimer was prepared using metakaolinite as alumina source and NaOH as the activator. The mixture of rice husk ask, kaolin and NaOH were autoclaving at temperature 115°C and pressure 10 Psi for 5 hours. The NaOH concentration was varied of 8, 10 and 12 M. The Cr(VI) of K_2CrO_4 salt was introduced in resulting geopolymer material with concentration of 15 to 25 ppm. The final resulting material was characterized by X-Ray Diffraction, Fourier Transform Infra Red (FTIR) Spectrophotometer and Porosity Analyzer. X ray diffraction pattern of the geopolymer indicates that the material is amorphous. The FTIR spectra show several peaks at certain wavenumbers, indicating the vibration band of Si-O-Al at 1016-1006 cm^{-1}, Al-O at 875 cm^{-1} and Si-O at 440-450cm^{-1}, respectively. After introduction of Cr in the system, the vibration stretching band of Si-O-Si shifted from 1004.20-1006.12cm^{-1} to 1010.70cm^{-1}. Porosity analysis shows the highest porosity was 16.57 % reached by sample prepared at 10M NaOH. TCLP (Toxicity Characteristic Leaching Procedure) tests showed that Cr(VI) was stable in the geopolymer material during at least 10 days.

Keywords: *geopolymer, rice husk ash, immobilization, Cr(VI), TCLP*

Introduction

Geopolymer, or Aluminosilicate Inorganic Polymers (AIPs) is a term of inorganic polymers group of aluminosilicates. Geopolymer shows the cement characters. It was designed to replace Portland cements in some applications. Development of geopolymer will also decrease the negative effect of cement production: emission of CO_2 which contributes to global warming [1].

Previous reports used the term of polysialate for describing the polymer structure of geopolymer. The sialate monomer represents SiO_4 and AlO_4 tetrahedra which connected by oxygen bridge [2,3]. Polisialate could be empirical formulated:

$M_n \{-(SiO_2)_z-(AlO_2)-\}_n$

The structure of geopolymer was also reported as SiO_4 and AlO_4 tetrahedra connected by oxygen bridge with hydrated Na^+ present in framework cavities. The structure is showed in Figure 1. [4,5]

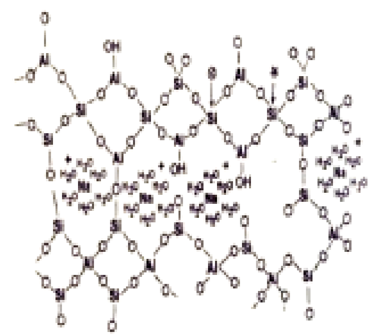

Fig.1. Proposed structure of a Na-polysialate polymer

Geopolymer will have advantages to replace Portland cement in ability of immobilization of toxic species from industrial waste water. Previous study of metakalonite based Geopolymer showed a high stability when exposed by aquadest, sea water, sodium sulphate and sulphuric acid [6].

Cr(VI) have known as a toxic species, with concentration of 10 mg/kg bodyweight can cause necrosis (breaking a part of tissues). Average Cr(VI) input in human body is 0,05 mg/day in their food consumption [7].

In this research, immobilization of Cr(VI) was applied in rice husk ash based geopolymer. Rice husk ash is an abundant waste from the rice production. The rice husk as based geopolymer have been prepared at the preliminary research. [8]

Materials and Methods

In the synthesis of geopolymers, there are two essentially types of raw materials, aluminosilicate-containing solids and alkali-silicate solutions. In this paper, rice husk ash were used as silica source and metakaolinite as alumina source.

The alkali-silicate solutions were prepared by diluting alkali-hydroxide solids in water, then added by rice husk ash to obtain certain silicate and alkali concentrations, expressed as SiO_2/M_2O and H_2O/M_2O ratios (where M = Na).[9]

Rice husk ash was made by calcinating dried rice husk at 800°C. Rice husk consist of 85-98 % of SiO_2. NaOH pellets were obtained from Merck. The concentration of activating solutions was varied according to get the best result in order to apply in immobilization.

Geopolymer Synthesis and Characterization

Geopolymer materials were made by mixing of alumina source material (metakaolinite) with alkali-silicate solution. Alkali silicates were first prepared by mixing of rice husk ash (silica source) with alkali solution (NaOH 8,10 and 12M).

The geopolymer binders were synthesized in a plastic container by hand mixing of geopolymer slurries for 5 minutes or longer and then poured into 3x3x3 cm cubic plastic moulds. The samples were then sealed and placed immediately in an air-circulated oven or autoclave at 115°C and 10 Psi for 5 hours.

The products (Na-geopolymer) were characterized by X-Ray Diffraction, Infrared Spectrophotometer and porosity test.

Immobilization of Cr (VI) in the Geopolymer

Immobilization of Cr(VI) was carried out similar to the preparation of the geopolymer. A portion of water used was replaced by simulation solution of 15,20 1nd 25 ppm Cr(VI) from K_2CrO_4. The resulting Cr-geopolymer were characterized by Infrared Spectrophotometer and TCLP test.

Results and Discussion

a.Geopolymer

Fig 2. Rice Husk Ash Based Geopolymer

Figure 2 showed the physical appearance of resulted Na-geopolymer in this research. It looks like a piece of chalk. The color of the material depends on the raw materials. Both rice husk ash and metakaolinite were resulting grayish white material. The shape of the geopolymer product came from the mould shape.

b.1.Characterization by X-Ray Diffraction (XRD)

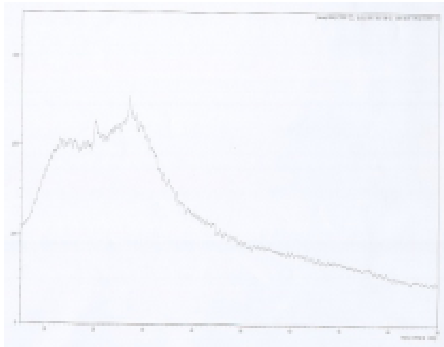

Figure 3. The XRD pattern of Na-geopolymer, made by NaOH 10M.

The XRD pattern showed that Na-Geopolymer is an amorphous material. There is no characteristic peaks correspond to the planes of crystalline solid.

b.2. Characterization by Infrared Spectrophotometer

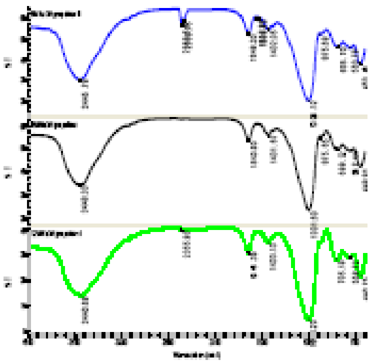

Fig.4. Infrared spectra of Na-Geopolymer made by 8,10,12 M NaOH.

In general, geopolymers consist of a short-range network of tetrahedrally-bonded Si-O-Si or/and Si-O-Al, loaded with water and carbonate species.The Infrared spectrophotometer spectra were shown at Figure 4. The characteristic wavenumbers of geopolymer was listed in Table 1.

Table 1. Assignment of wavenumbers (or frequencies) for molecular vibrations in absorption spectra of geopolymers.

Wavenumber (cm^{-1})	Vibrational assignments
3440-3480	Adsorbed O-H stretching
2855, 2930	Adsorbed O-H stretching
1650-1655	Adsorbed H-O-H bending
1420-1480	C-O stretching (carbonates)
865-875	O-C-O bending (carbonates)
950-1250	Asymmetric Si-O-Si and/or Al-O-Si stretching
950-880	SiO stretching (SiOM), M = Na or K
870	Si-OH stretching
600-800	Al-O bonds
797	Network Si-O-Si (or Si-O-Al) stretching
558	Network Si-O-Si (or Si-O-Al) symmetric stretching
481	Network Al-O-Si bending

b.3. Porosity Test

This test is based on the weight differences of the geopolymer before and after absorbtion of water. Porosity (P) was expressed by percentage as following equation:

$$P = \frac{\text{total weight-dry weight}}{\text{total weight-weight of geopolymer in water}} \times 100\%$$

The highest porosity of geopolymer material was 16.57 %, reached by Na-geopolimer with 10M NaOH. This product was applied in immobilization of Chromium (VI). The result was listed at Table 2.

Table 2. The result of the porosity test

Code	Dry weight (g)	Concentrated/ total weight (g)	Water weight (g)	Porosity (%)
Na-PS 8M	39,08	42,43	14,56	12,02
Na-PS 10M	38,76	43,48	15,0	16,57
Na-PS 12M	55,98	58,07	21,44	5,79
K-PS 8M	56,52	61,57	22,00	12,76
K-PS 10M	78,20	85,36	31,77	13,36
K-PS 12M	77,02	83,88	31,00	12,97

c. Immobilization of Cr(VI) in Geopolymer

The concentration of introduced Cr (VI) in the geopolymer matrix was varied by 15, 20 and 25 ppm. The resulting Cr-Geopolymers were characterized using Infrared spectrophotometer, giving 3 spectra as expressed at Fig.5a-5c:

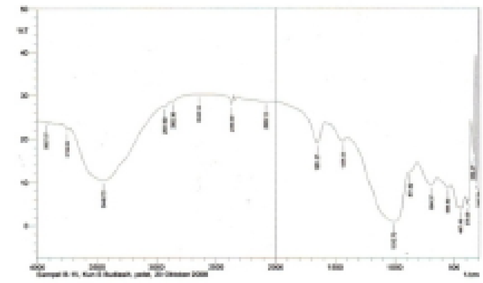

Fig 5.a. Infrared Spectra of of Na-Geopolymer-Cr (15ppm Cr)

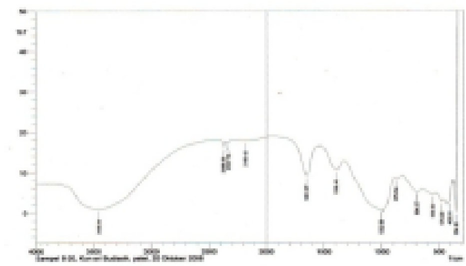

Fig 5b. Infrared Spectra of Na-Geopolymer-Cr (20ppm Cr)

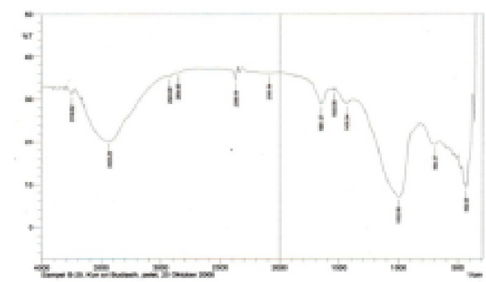

Fig 5c. Infrared Spectra of Na-Geopolymer-Cr (25ppm Cr).

There are no significant differences in infrared pattern of Na-Geopolymer-Cr compared to the original geopolymer, except a shifting of several peaks. For example,The strectching vibration peak of Si-O-Si was shifted from 1004,20- 1006.12cm^{-1} to 1010.70cm^{-1}.

There were two interpreted facts: First, there isn't a bond produced between Cr and geopolymer only physical interaction. The second, the Cr-O bonding was not detected until the wavenumber 500cm^{-1}. It coresponds to vibration of ionic bond which absorb higher energy and lower wavelength.

TCLP (Toxicity Characteristic Leaching Procedure) was done for determining the concentration of Cr (VI) diluted from the geopolymer matrix in a certain time. The procedure was adopted from Japan Environmental Agency [10].

The leaching agents were aquadest, well water, rain water and sea water. The effect of impregnated Cr(IV) concentration also studied. In 10 days, there is

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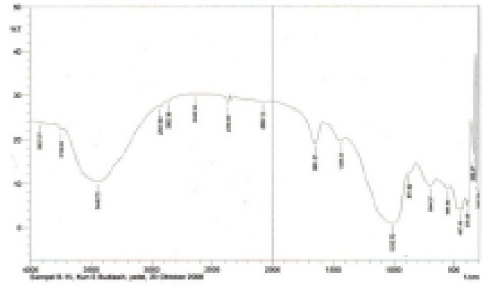

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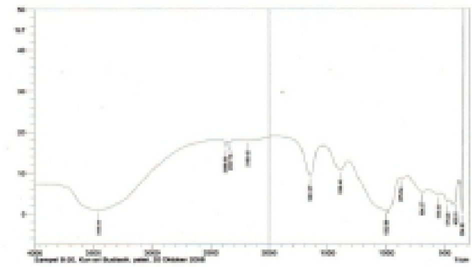

Fig 5b. Infrared Spectra of Na-Geopolymer-Cr (20ppm Cr)

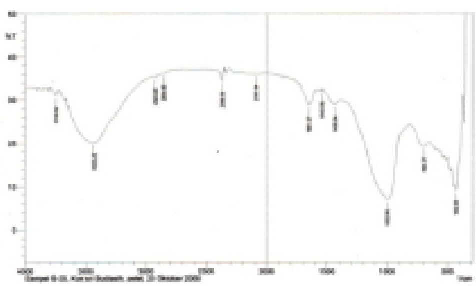

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Table 3. TCLP test of Cr (VI) in rice husk ash geopolymer (Na-Geopolimer for 10 days

Variables	code (ppm)	Amount of Cr
Cr (VI) introduced/ impregnated	C15 (15 ppm)	Undetected
	C20 (20 ppm)	Undetected
	C25(25 ppm)	Undetected
	C0 (blank)	Undetected
Leaching agents	A1 (well water)	Undetected
	A2 (rain water)	Undetected
	A3 (sea water)	Undetected
	A4 (aquadest)	Undetected

Conclusions

Immobilization of Cr(VI) in NaOH–rice husk ash geopolymer obtain a good result up to 25 ppm of Cr(VI). TCLP in 10 days showed that there is no Cr(VI) detected in the leachate water.

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