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Recycling

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A study on the MSWI fly ash modifying for inorganic gel of cement admixtures

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Outline

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2 Methods

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4 Conclusions

Background

Background

- Municipal solid waste incinerator (MSWI) fly ashes contain high concentrations of heavy metals and dioxins, which are defined as hazardous wastes usually.
- Solidification followed by designated landfilling has been popular used in the world, but the long term stability still be worried about.
- Zero-Waste or Zero-Landfill policy has been ask in many countries, therefor, there were many studies discussed with the recycling of the MSWI fly ash, while seldom of then were commercialized.

Background

- Eco-cement and melting technologies have been developed in Japan for three decades already, but still been questioned a lot today.
- Dioxin could be destroyed in the high temperature of cement kiln, but most of the heavy metals will evaporated in the form of chloride compounds, increased the hazard of fly ash in the APCD.
- MSWI fly ashes have the characteristics of pozzolanic property, but applied as the substitute of cement directly is not feasibly due to the impurities in it.

Background

- Washing followed by wet ball milling had been proved to have the ability to elevate the pozzolanic property and destroy Dioxin effectively, due to the mechno-chemical reaction.
- The pozzolanic material could be activated by alkali hydroxide accompanied with sodium silicate, which could produce an inorganic gel material to elevate the strength during cementing.

Background

- In this study, the silicate component comes from metakaolin, calcium comes from washed MSWI fly ash, and the activation were executed by wet ball milling under the sodium hydroxide solution, after drying, the product was used as the cement admixture.

Methods

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Methods

- Fly ash was collected from the reaction product of a 1,350 ton/d MSW mechanical grate incinerator operated around 950 ^{o}C, with semi-dry and bag-filter system.
- Ash washing was carried out twice with distill water in a liquid to solid ratio 5 for 5 min.

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Methods

- Metakaolin was adopted the industrial grade of kaolin from Yun-nan China. After drying, calcining at 550 ^{o}C for 1.5 hr, then 700 ^{o}C 3hr.
- Conventional ball-milling machine were used, the liquid to solid ratio was 9 during the milling of the mixed ash, the ball miller were operated below the critical speed.

Results and Discussion

Table 1 The properties of MSWI fly ash and metakaolin

	pH	Moisture content (%)	Ignition loss (%)	D_{50} (μm)
Raw fly ash	11.28	1.03	3.38	7.38
Washed fly ash	**12.15**	2.8	-	**7.07**
Metakaolin	4.37	0.5	-	**8.92**

Table 2 Elements

Elements	Washed fly ash	metakaolin
Ca	**32.4**	0.09
Si	2.03	**19.3**
Al	0.61	**16.7**
Mg	1.06	0.07
Fe	0.72	0.71
Na	0.62	0.54
K	0.46	1.22
		Unit : wt.%

Table 3 Heavy metals content

Elements	Washed fly ash	metakaolin
Zn	**18,400**	124
Pb	**3,170**	352
Cd	207	N.D. [a]
Cr	281	90
Cu	**3,450**	438
[a]N.D. : Not detectable		Unit : mg/kg

Table 4 TCLP leaching concentration

Elements	Washed fly ash	metakaolin	Hazardous waste standard
Zn	1.84	0.14	-
Pb	7.69	0.3	5
Cd	N.D.[a]	N.D.	1
Cr	0.06	N.D.	5
Cu	0.11	N.D.	15

[a]N.D. : No detectable (Pb=5 ppb, Zn=0.3 ppb, Cu=0.6 ppb, Cd=0.35 ppb, Cr=0.5 ppb)

Unit : mg/L

Fig. 1 XRD pattern

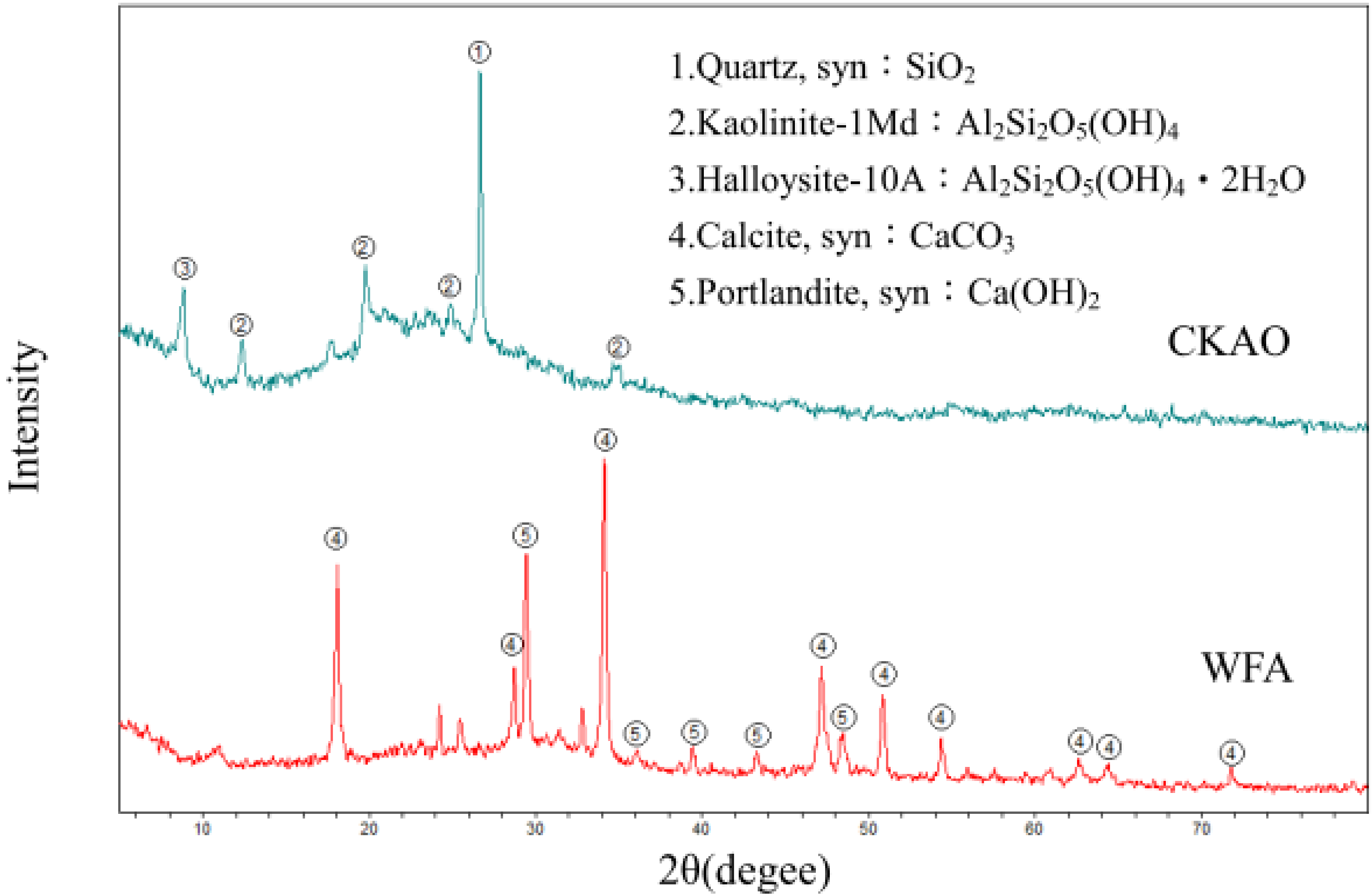

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Fig. 2 XRD pattern of active powder (1M NaOH, 24h)

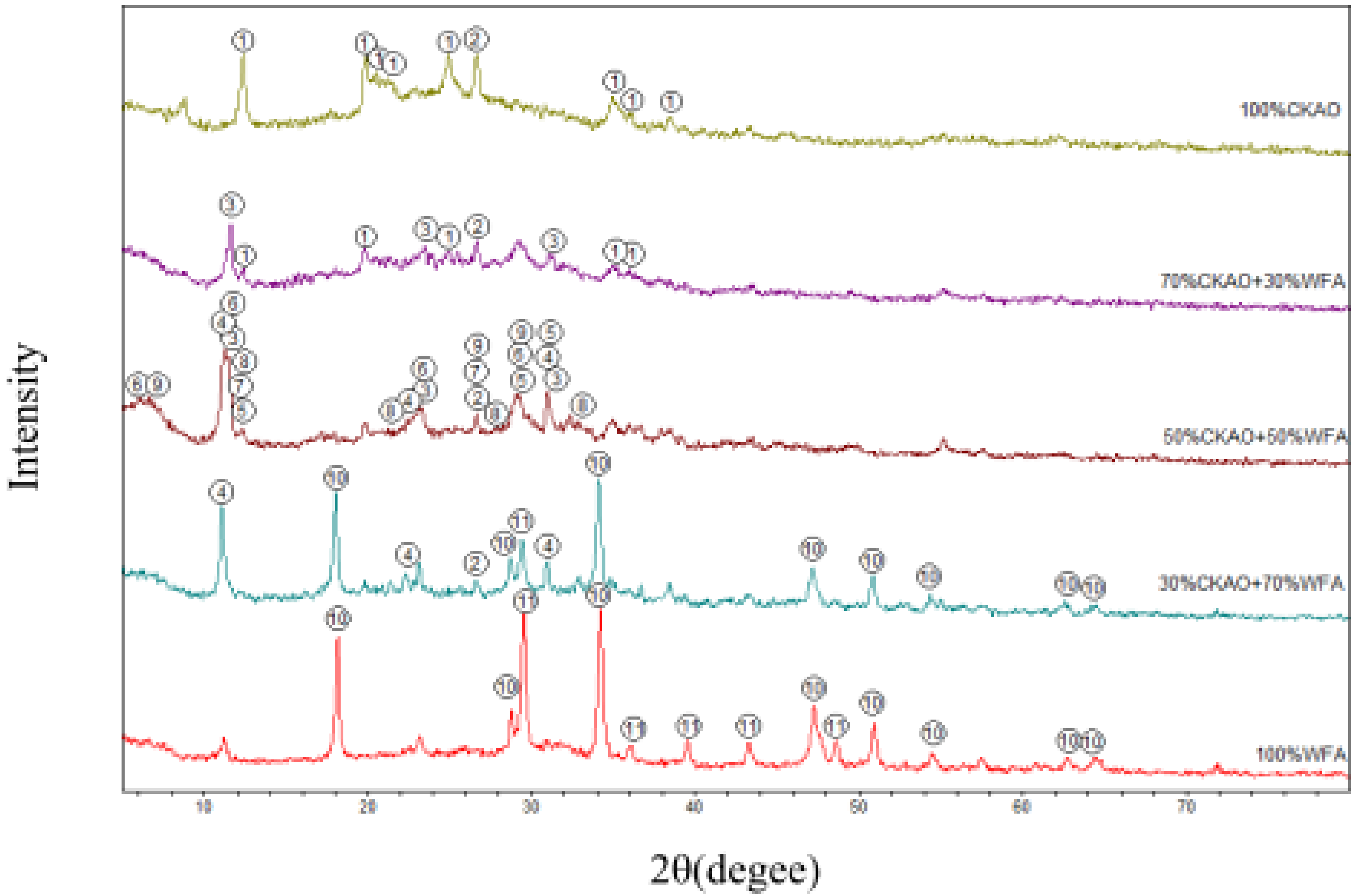

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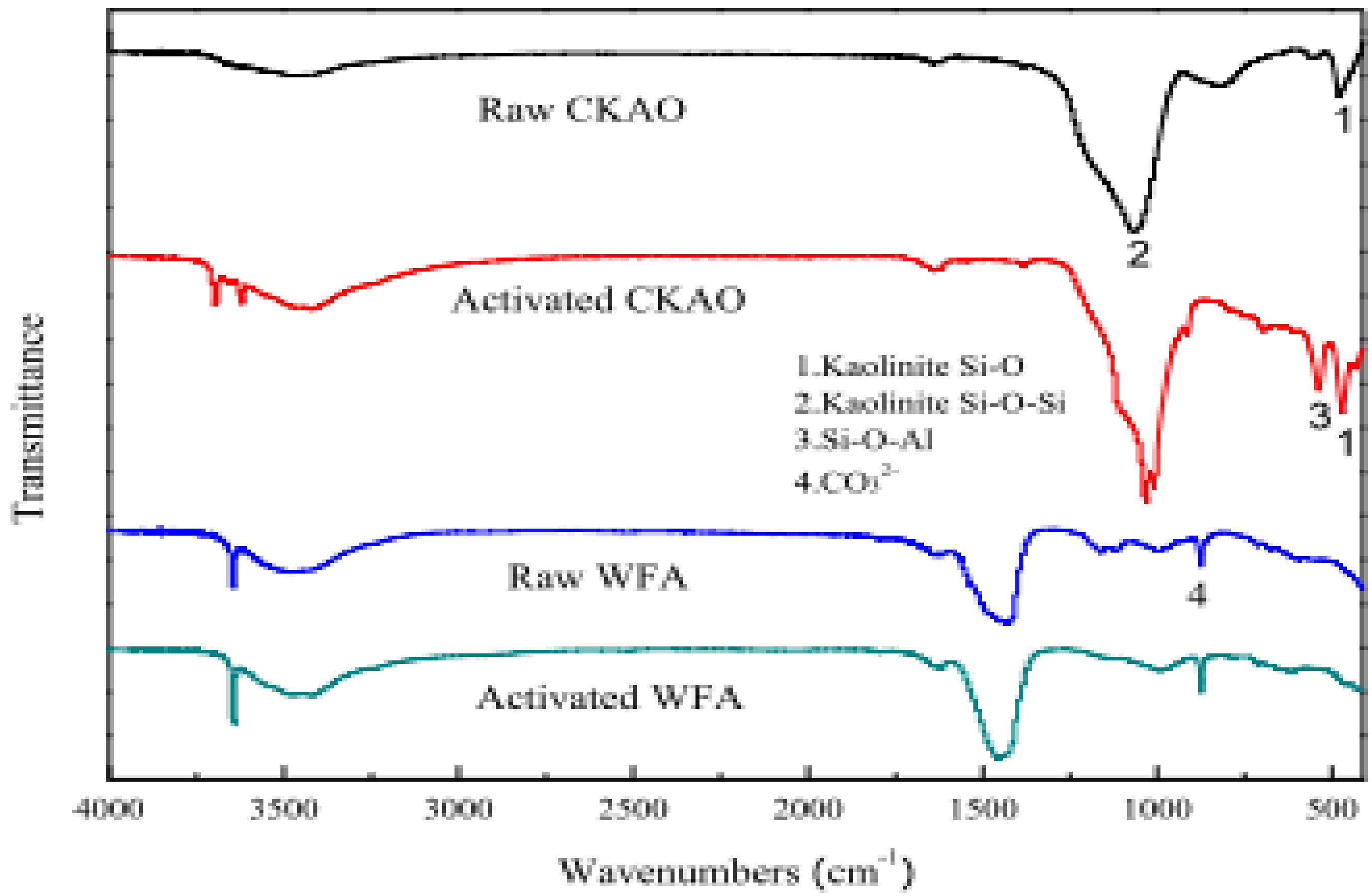
Fig. 5 XRD crystalline of milling activation

XRD crystalline phase	CKAO	WFA	KA-73	KA-55	KA-37
① Kaolinite-1A：$Al_2Si_2O_5(OH)_4$	○		○		
② Quartz, syn：SiO_2	○		○		
③ Calcium Aluminum Oxide Carbonate Hydrate：$Ca_4Al_2O_6CO_3 \cdot 11H_2O$			○		
④ Hydrocalumite：$Ca_2Al(OH)_6Cl \cdot 2H_2O$				○	○
⑤ Zeolite K-F, (Na)：$Na_5Al_5Si_5O_{20} \cdot 9H_2O$				○	
⑥ Faujasite-Na, syn：$Na_2Al_2Si_{2.4}O_{8.8} \cdot 6.7H_2O$				○	
⑦ Gismondine：$CaAl_2Si_2O_8 \cdot 4H_2O$				○	
⑧ Gobbinsite：$Na_4Ca(Si_{10}Al_6)O_{32} \cdot 12H_2O$				○	
⑨ Tacharanite：$Ca_{12}Al_2Si_{18}O_{51} \cdot 18H_2O$				○	
⑩ Portlandite, syn：$Ca(OH)_2$		○			○
⑪ Calcite：$CaCO_3$		○			○

*K：CKAO，A：WFA，KA-73：70%CKAO+30%WFA and so on

* **Activation： 1M NaOH 24h**

Fig. 3 FTIR pattern (1M NaOH, 24h)



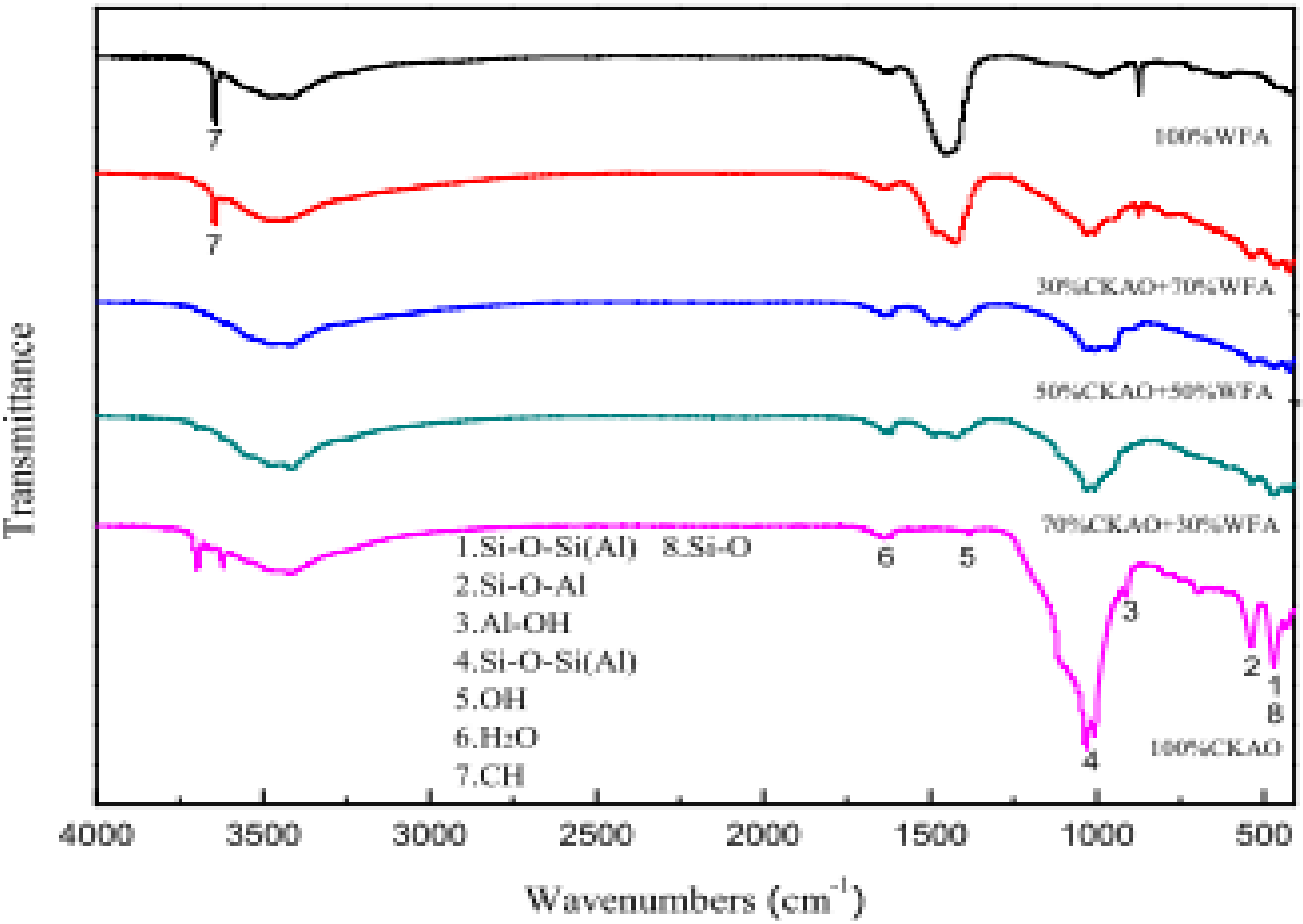

100%WFA
30%CKAO+70%WFA
50%CKAO+50%WFA
70%CKAO+30%WFA
100%CKAO
1.Si-O-Si(Al) 8.Si-O
2.Si-O-Al
3.Al-OH
4.Si-O-Si(Al)
5.OH
6.H2O
7.CH
Transmittance
4000 3500 3000 2500 2000 1500 1000 500
Wavenumbers (cm-1)

Table 6 TCLP leaching the activation powder (1M NaOH 24h)

Powder ratios	Zn	Pb	Cd	Cr	Cu
Regulation	-	5	1	5	15
100%CKAO	0.44	0.03	N.D.[a]	0.01	N.D.
70%CKAO+30%WFA	N.D.	0.07	N.D.	0.05	N.D.
50%CKAO+50%WFA	0.02	0.1	N.D.	0.06	N.D.
30%CKAO+70%WFA	0.37	0.38	N.D.	0.04	N.D.
100%WFA	1.87	2.93	N.D.	0.01	0.02

[a]N.D.： Not detectible .(Pb=5 ppb, Zn=0.3 ppb, Cu=0.6 ppb, Cd=0.35 ppb, Cr=0.5 ppb)

Unit：mg/L

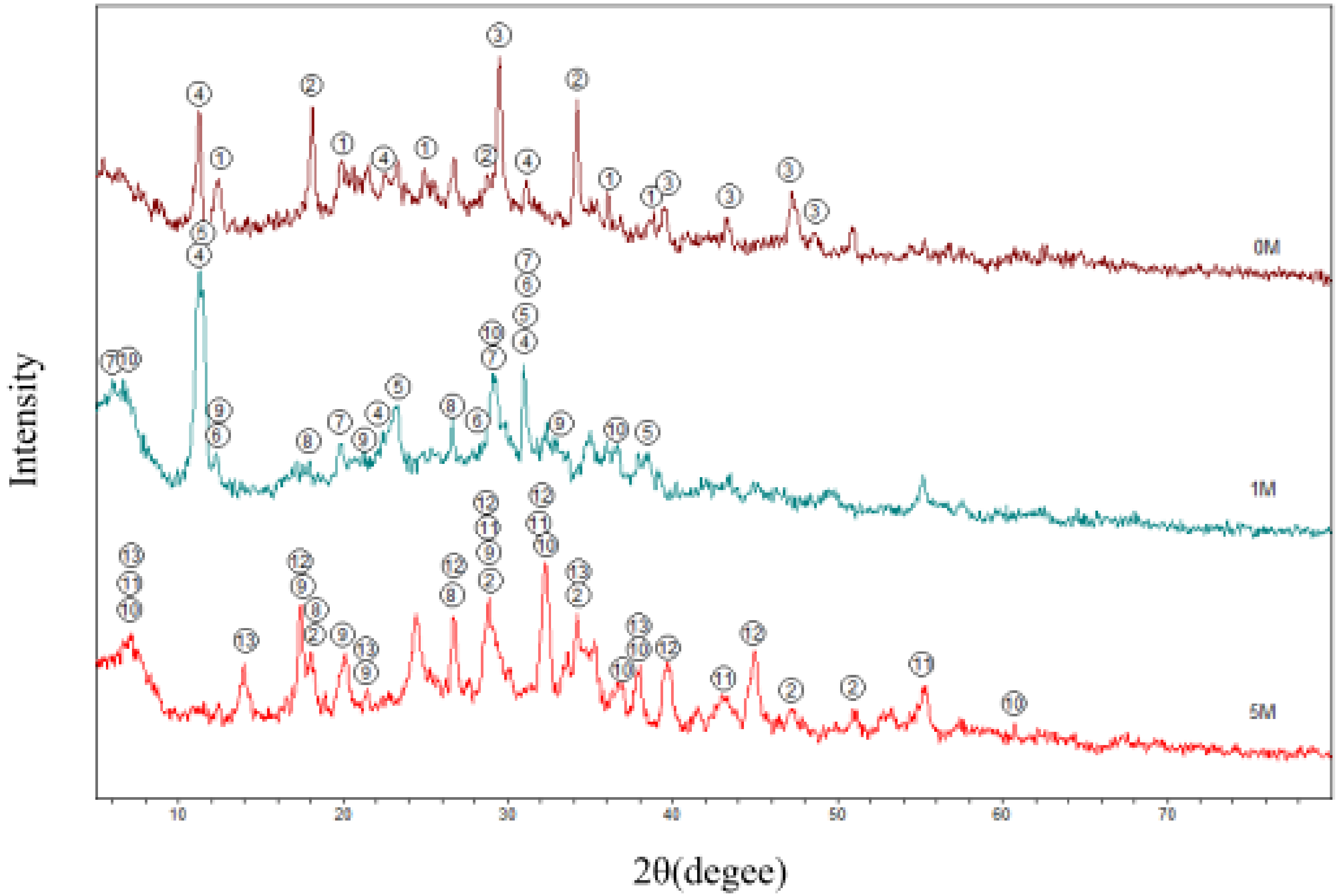


Fig. 4-8 The XRD pattern of milled active powder treated by NaOH active solution (50% CKAO + 50%WFA, 24h)

Table 7 XRD crystalline of milling activation powder in NaOH solution

XRD crystalline phase	0M	1M	5M
①Kaolinite-1Md：$Al_2Si_2O_5(OH)_4$	○		
②Portlandite, syn：$Ca(OH)_2$	○		○
③Calcite, syn：$CaCO_3$	○		
④Hydrocalumite：$Ca_2Al(OH)_6Cl2H_2O$	○	○	
⑤Calcium Aluminum Oxide Carbonate Hydrate：$Ca_4Al_2O_6CO_3 \cdot 11H_2O$		○	
⑥Zeolite K-F, (Na)：$Na_5Al_5Si_5O_20 \cdot 9H_2O$		○	
⑦Faujasite-Na, syn：$Na_2Al_2Si_{2.4}O_{8.8} \cdot 6.7H_2O$		○	
⑧Gismondine：$CaAl_2Si_2O_8 \cdot 4H_2O$		○	○
⑨Gobbinsite：$Na_4Ca(Si_{10}Al_6)O_{32} \cdot 12H_2O$		○	○
⑩Tacharanite：$Ca_{12}Al_2Si_{18}O_{51} \cdot 18H_2O$		○	○
⑪Calcium Silicate Hydrate：$CaOSiO_2 \cdot H_2O$			○
⑫Katoite, silicatian：$Ca_3Al_2(SiO_4)(OH)_8$			○
⑬Stratlingite, syn：$Ca_2Al_2SiO_7 \cdot 8H_2O$			○

Activation: 50% CKAO + 50%WFA, 24h of milling

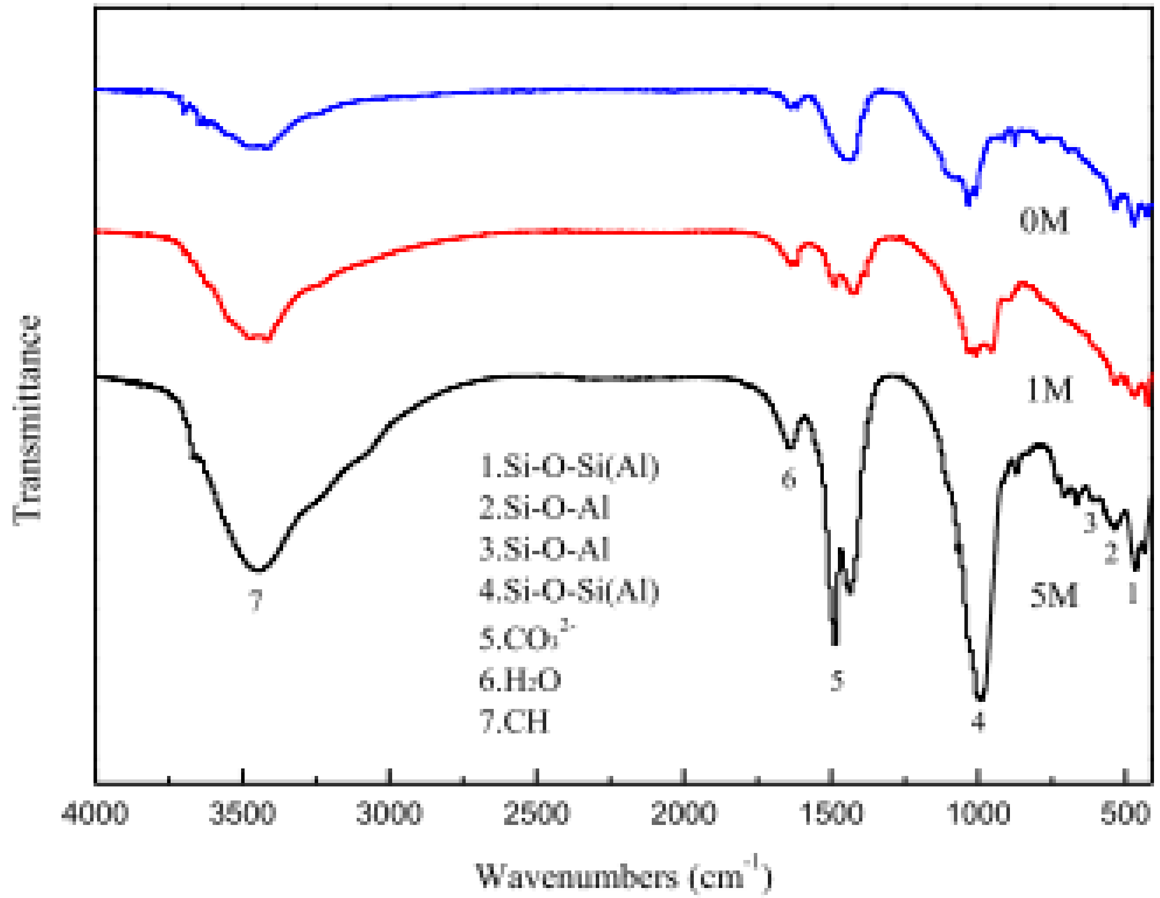


Fig. 4-9 FTIR pattern of the milling activation (50% CKAO + 50%WFA, 24h)

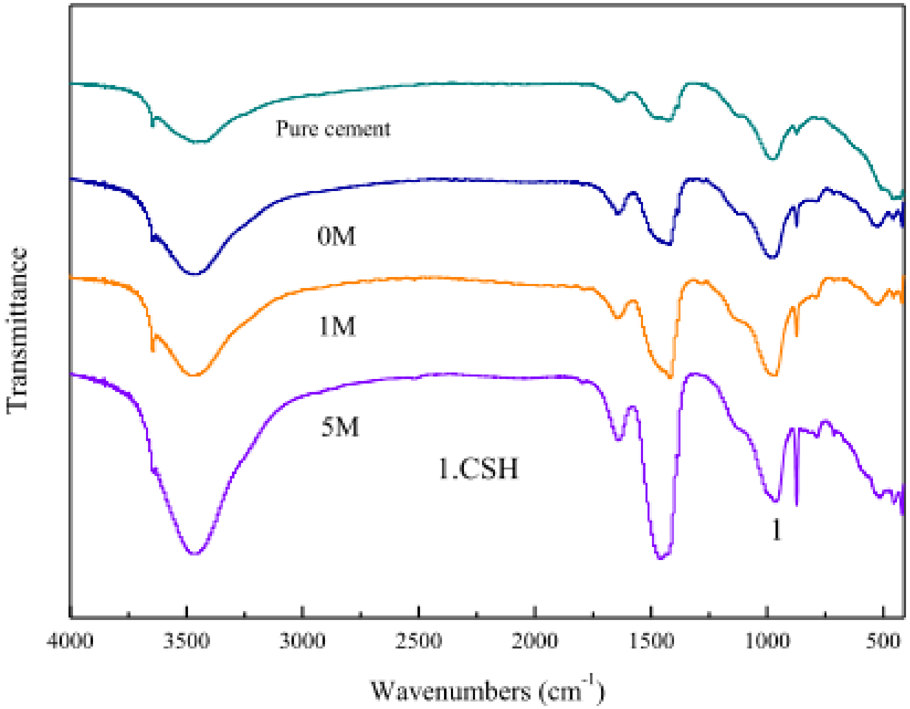
Table 8 The TCLP leaching of the milling activation powder

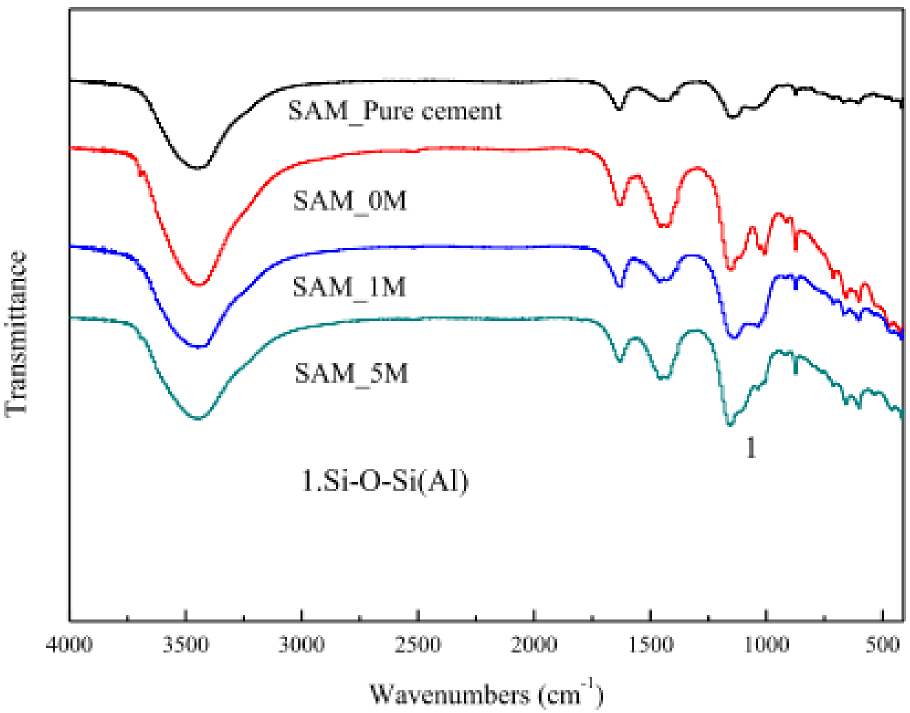
NaOH active solutions	Zn	Pb	Cd	Cr	Cu
Limitation	-	5	1	5	15
0M	N.D.[a]	0.03	N.D.	0.07	N.D.
1M	0.02	0.1	N.D.	0.06	N.D.
5M	0.38	0.24	N.D.	0.08	N.D.

[a]N.D.： Not detectible (Pb=5 ppb, Zn=0.3 ppb, Cu=0.6 ppb, Cd=0.35 ppb, Cr=0.5 ppb)

Unit：mg/L

* Active parameter： 50% CKAO + 50%WFA, 24h of active time





活化液濃度對活化粉取代水泥之影響(1/1)

- NaOH活化液濃度對研磨活化粉取代水泥10%之28天水泥漿體與28天水泥漿體經SAM前處理之FTIR分析

- 活化粉條件：
  1.50%CKAO+50%WFA
  2.活化24 hr

- Pure cement ：養護28天純水泥漿體
- SAM：水楊酸-甲醇萃取前處理

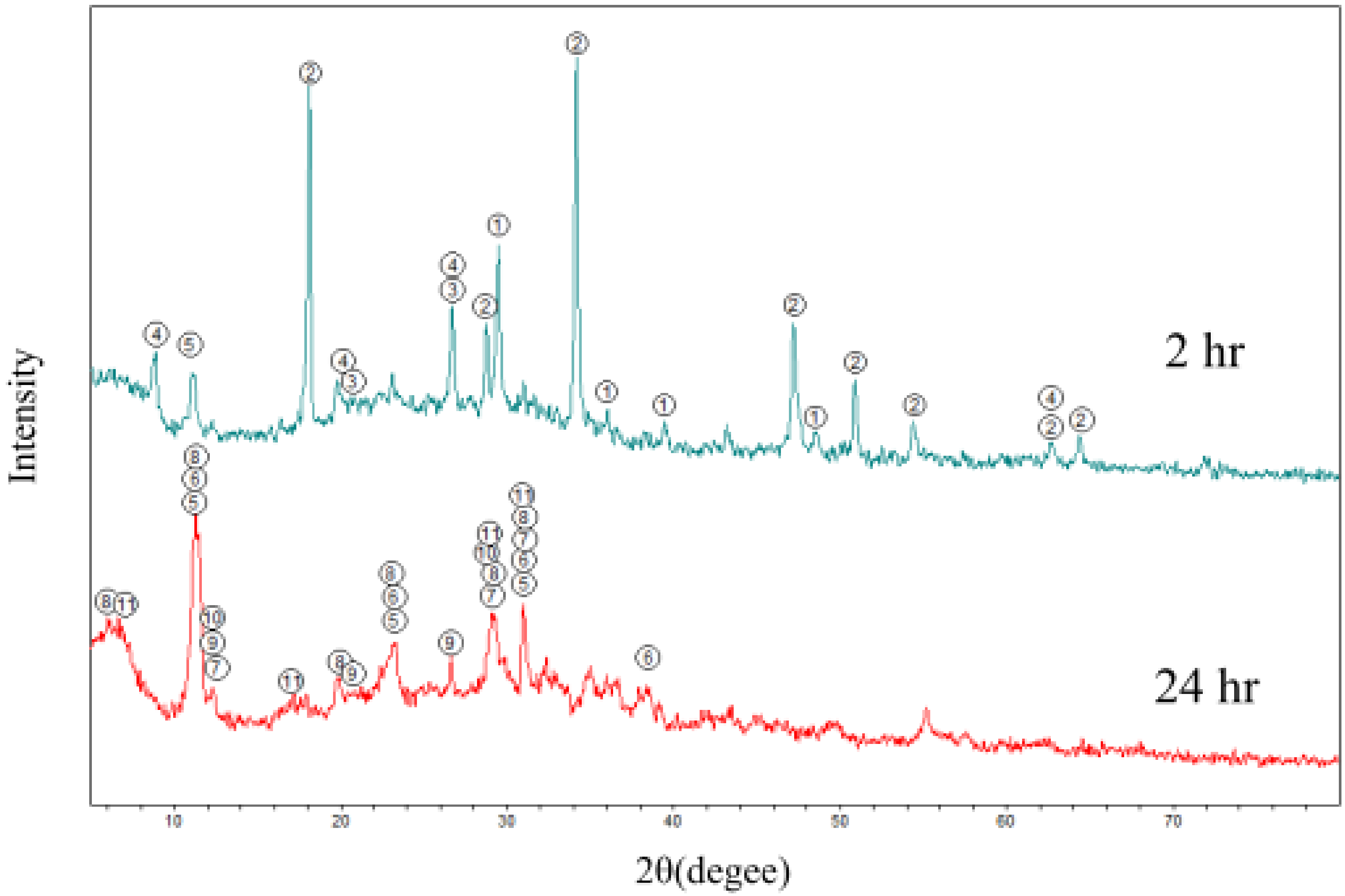


Fig. 4-12 XRD pattern of milled active powder in different active time (50% CKAO + 50%WFA, 24h)

Table 9 XRD crystalline of milling activation powder

XRD crystalline phase	*CKAO	*WFA	2 hr	24 hr
①Calcite, syn：$CaCO_3$		○	○	
②Portlandite, syn：$Ca(OH)_2$		○	○	
③Quartz, syn：SiO_2	○		○	
④Halloysite-10A：$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$	○		○	
⑤Hydrocalumite：$Ca_2Al(OH)_6Cl_2H_2O$			○	○
⑥Calcium Aluminum Oxide Carbonate Hydrate：$Ca_4Al_2O_6CO_3 \cdot 11H_2O$				○
⑦Zeolite K-F, (Na)：$Na_5Al_5Si_5O_{20} \cdot 9H_2O$				○
⑧Faujasite-Na, syn：$Na_2Al_2Si_{2.4}O_{8.8} \cdot 6.7H_2O$				○
⑨Gismondine：$CaAl_2Si_2O_8 \cdot 4H_2O$				○
⑩Gobbinsite：$Na_4Ca(Si_{10}Al_6)O_{32} \cdot 12H_2O$				○
⑪Tacharanite：$Ca_{12}Al_2Si_{18}O_{51} \cdot 18H_2O$				○
⑫Kaolinite-1Md：$Al_2Si_2O_5(OH)_4$	○			

* metakaolin and extracted fly ash before active process

* **Milling activation： 50% CKAO + 50%WFA, 1M of NaOH**

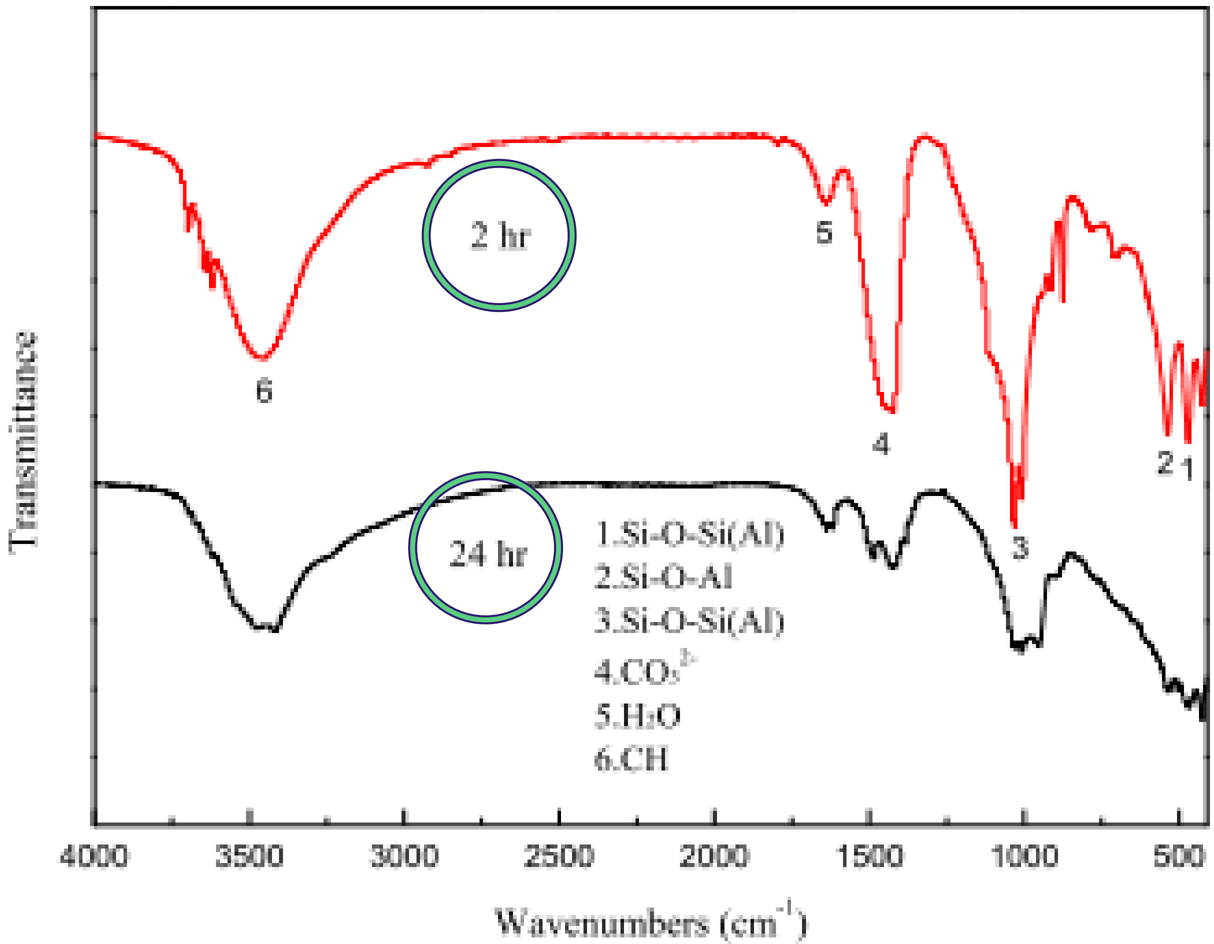


Fig. 4-12 FTIR pattern of milling activation powder (Active parameter： 50% CKAO + 50%WFA, 1M of NaOH)

Table 10 The TCLP of the milling activation powder at different activation time

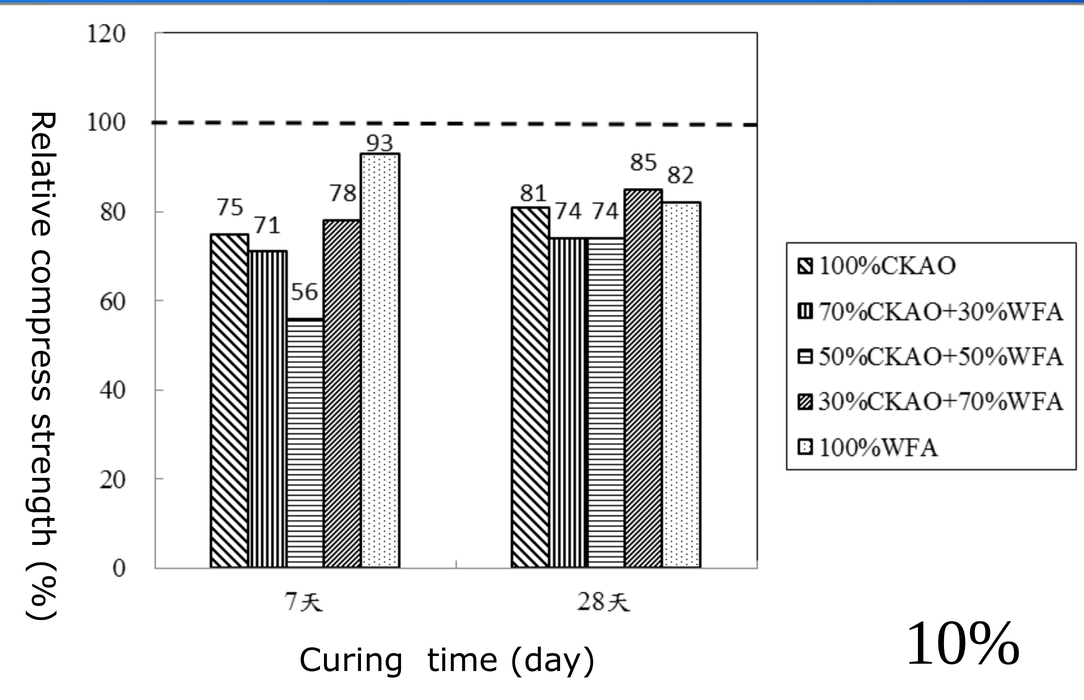
active time	Zn	Pb	Cd	Cr	Cu
Regulation	-	5	1	5	15
2hr	0.1	0.08	N.D.[a]	N.D.	N.D.
24hr	0.02	0.1	N.D.	0.06	N.D.

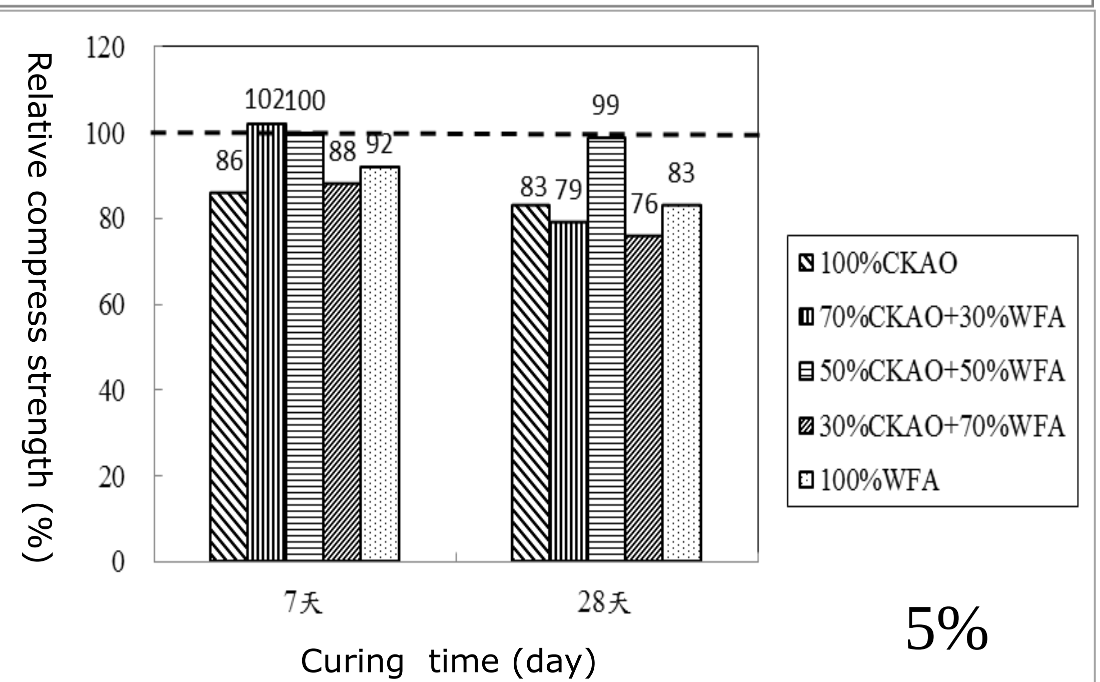
[a]N.D.： Not detectible (Pb=5 ppb, Zn=0.3 ppb, Cu=0.6 ppb, Cd=0.35 ppb, Cr=0.5 ppb)

Unit：mg/L

* **Activation： 50% CKAO + 50%WFA, 1M of NaOH**

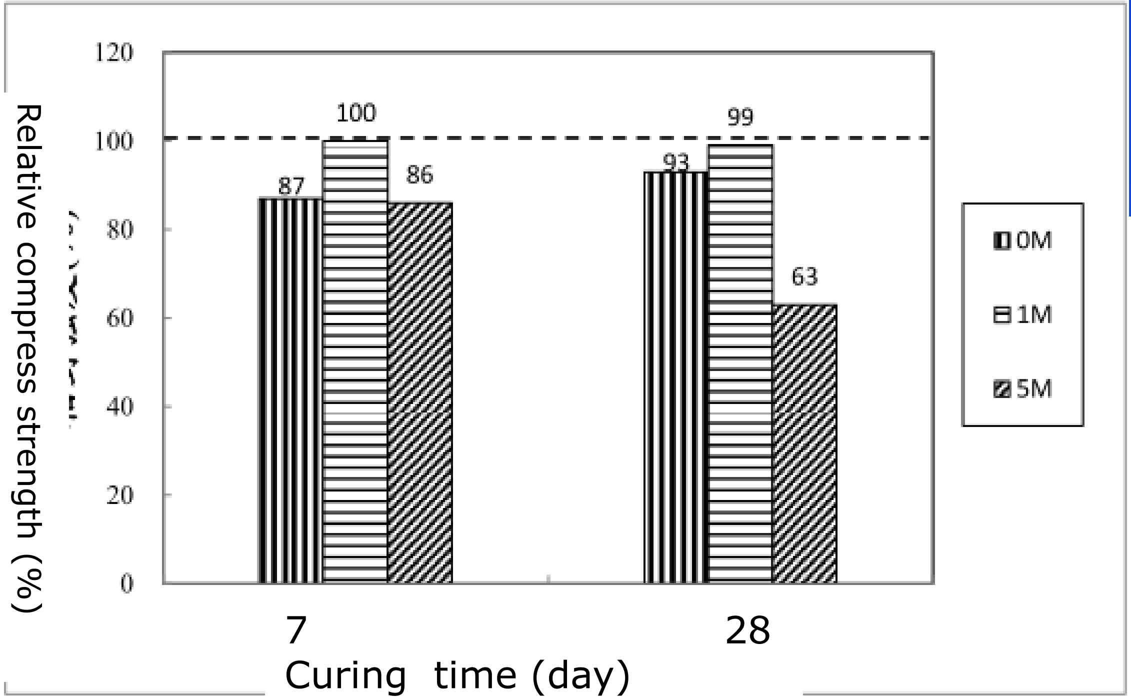
Relative compressive strength



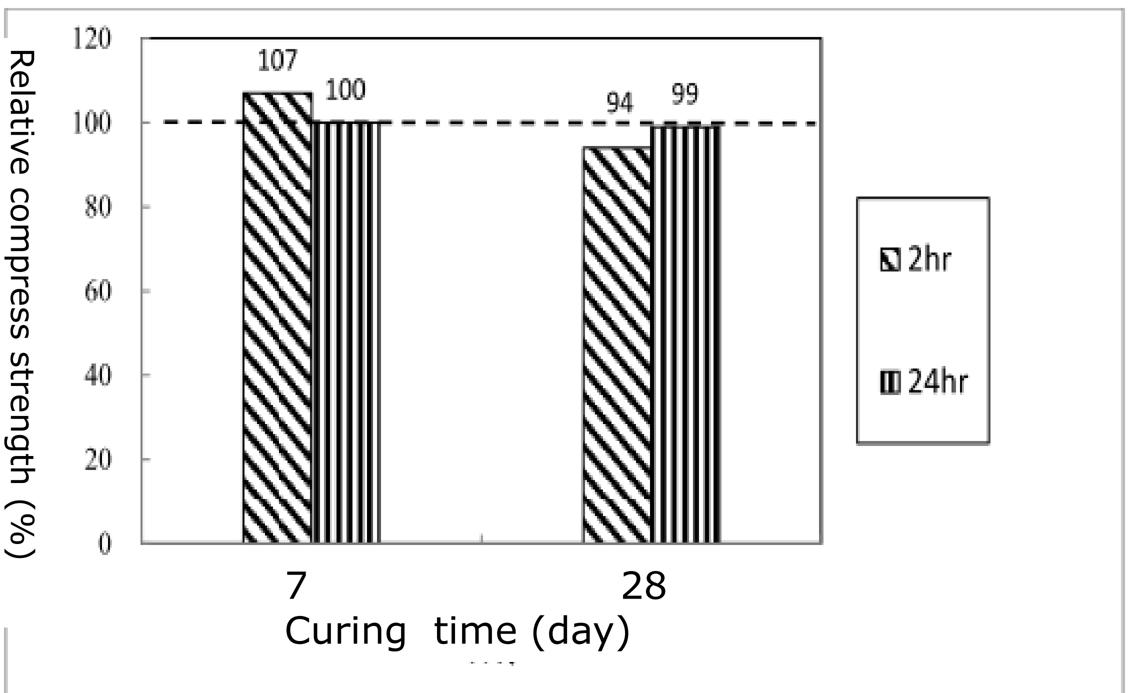


Activation:
1 M NaOH, milling 24 hr

Relative compressive strength



- Cement additive 5%
- Activation 24 hr
- 50%CKAO+50%WFA



- Cement additive 5%
- Activation:1M NaOH
- 50%CKAO+50%WFA

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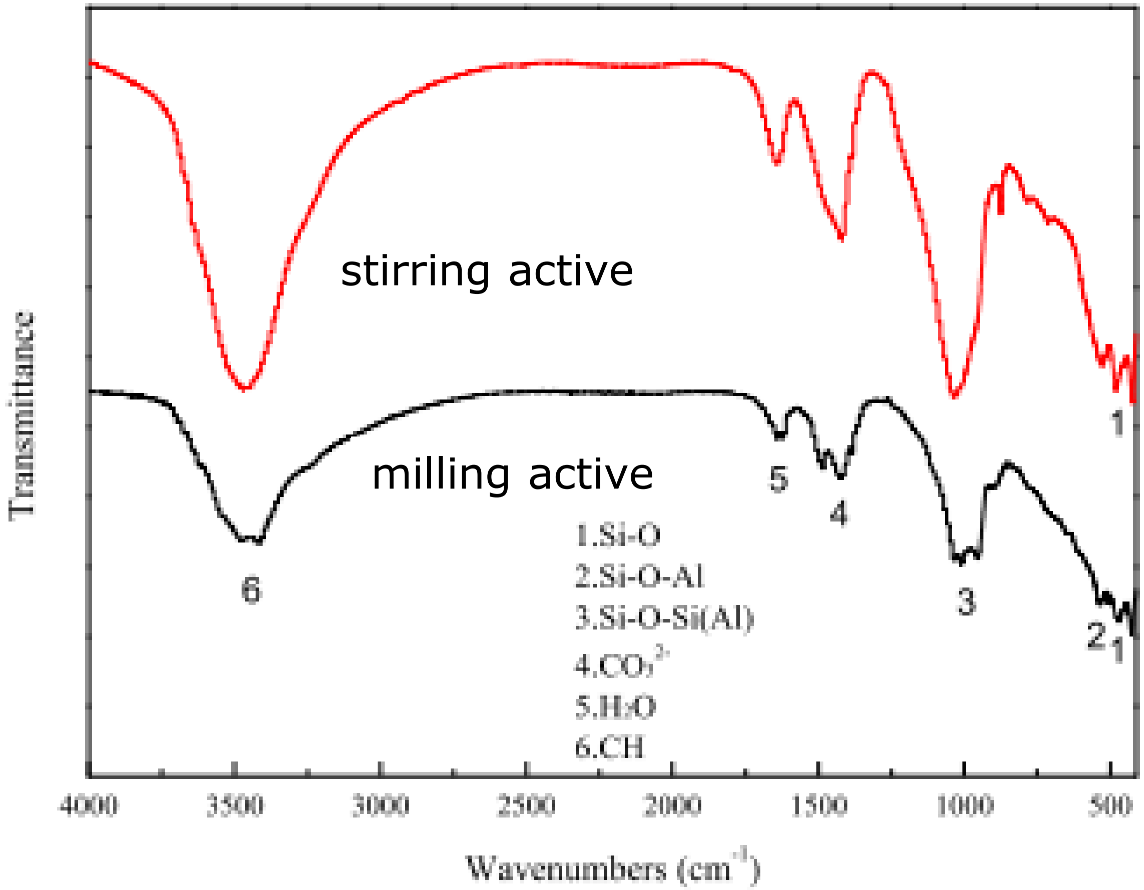
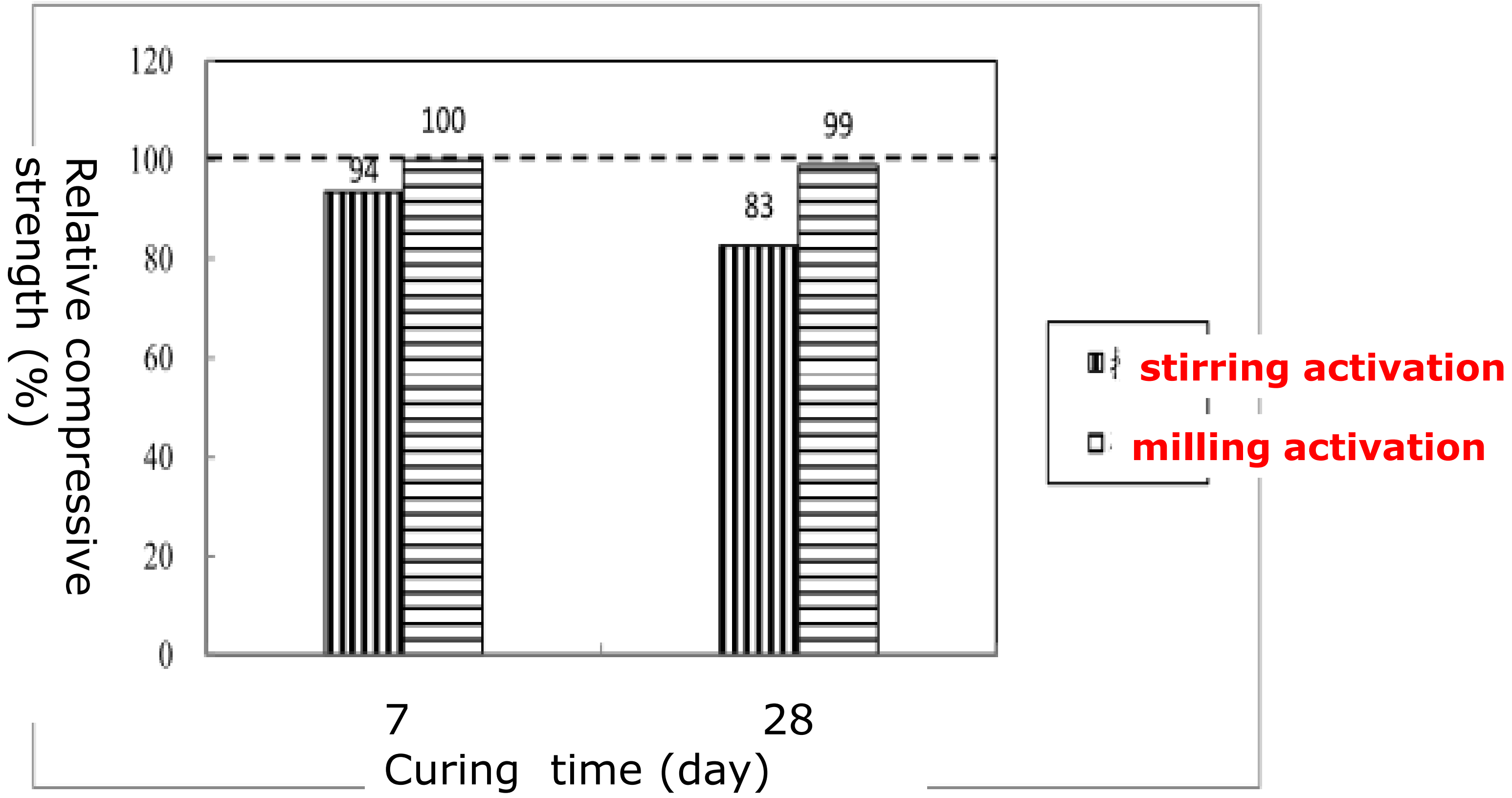


Fig. 4-22 FTIR pattern of active powder with stirring and milling activation(50% CKAO + 50%WFA, 1M of NaOH 24h)



Cement additive 5%

Conclusions

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Conclusions(1/3)

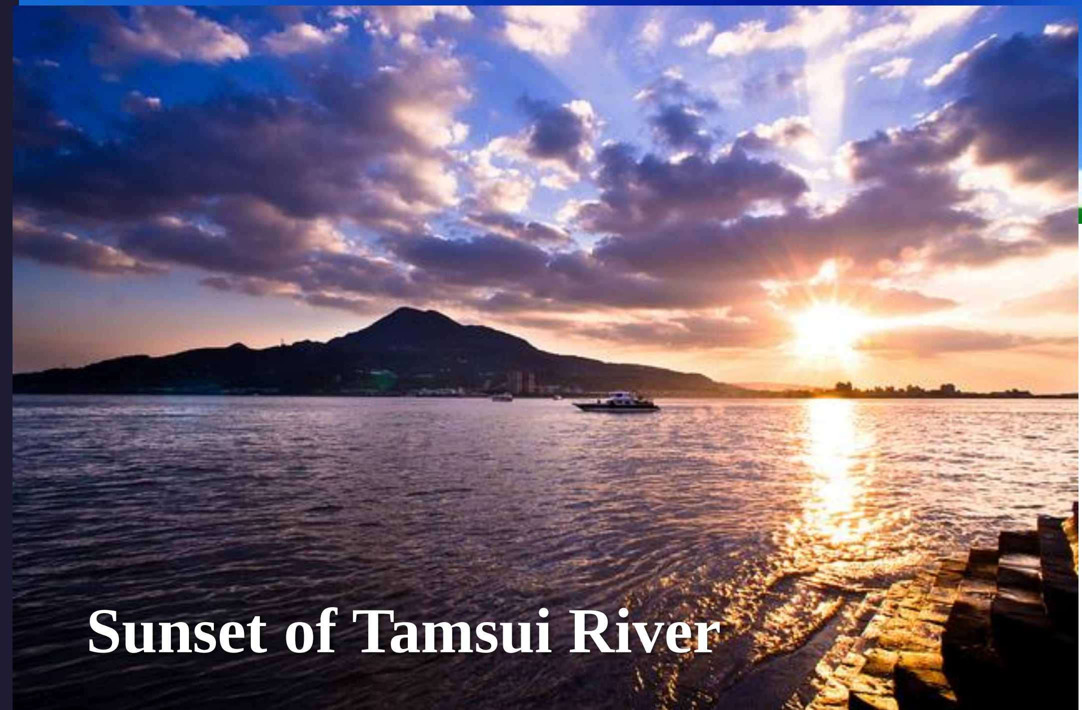
- The reaction of 50% metakaolin, 50% washed fly ash (5C5W) with 1M NaOH solution after 24 hr milling produces multiple crystal species of inorganic gel.
- TCLP test showed that, the activated powder were far below the hazard waste limitations of heavy metals.

Conclusions(2/3)

- The milling activation powder were replaces 10% of cement, low workability caused lower relative compressive strength.
- Replacing 5% cement grouting to cure 7 days and 28 days, could form inorganic gels in the cured cement evidently, which raised the relative compressive strength up to 100% compared to the pure cement sample.

Conclusions(3/3)

- For the activated powder process, milling activation has more contribution than stirring activation in the formation of inorganic gel and helps the growth of inorganic gel in cement curing.



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Thank you for your Attention

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