

Influences of thermal excitation on volcanic activity and mechanism of rich-silicon IOTP

Beixing Li^{1,a}, Fengshou Tang^{2,a}, Zhigang Zhu^{3,a}

State Key Laboratory of Silicate Materials for Architecture, Wuhan University of Technology,
Wuhan ,430070, China.

libx0212@126.com, jblzm4@163.com, 312378964@qq.com

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Abstract. In order to study the influences of different thermal curing methods on volcanic activity and mechanism of rich-silicon iron ore tailing powder (IOTP), different specific surface area and curing conditions of IOTP were tested, at the same time, the strength, pore size distribution(MIP) and the structure character of hydration product(SEM) were measured. Test results show that IOTP do not have activity cured by room temperature. IOTP cured by thermal conditions shows different degrees of volcanic activity, hot-wet curing systems can obviously reduce the porosity and pore diameter size of IOTP mortars, improve the compactness of hydration products at the same time, the autoclaved curing systems is the best.

Introduction

IOT is the major component of industrial solid waste. According to incomplete statistics, there are more than 10 billion tons of ore tailing discharged around the world every year, the stock of ore tailing in China is more than 10 billion tons and nearly one half is IOT. However, it is growing at a rate of 500 million tons every year[1]. The stored IOT causes many sorts of environmental pollution, moreover, some IOT ponds are at risk of dam break[2-5].

The physical and chemical properties of IOT were similar with some building materials, many researches about comprehensive utilization of IOT have been carried out in recent years[6], such as using IOT as building aggregates and binding materials, recovering valuable metals, soil conditioner, reclamation and so on[7-14]. The particle size of IOT is smaller and smaller along with the improvement of mineral processing technology, and the superfine IOT is no longer suitable for some building products[15].

In view of some IOT are rich in SiO₂, some researchers have studied the potential volcanic activity and value of rich-silicon IOT. YI Zhonglai[16] heated IOT in 700°C condition and milled to 400m²/kg, after that the IOT powder was mixed with clinker, gypsum, slag as binding materials. NI Wen[17] used some microscopic methods such as IR and SEM to test the crystal shape change of IOT, the results showed mechanical grinding was useful for stimulating the activity of IOT but the activity is very low. FENG Xiangpeng[18] studied the influence of red mud on the thermal activation of IOT, the results showed the red mud can partly inspire the activity.

Many researches judged the activity of IOTP only depend on the 28d strength ratio and lose sight of the filling effect when powders get high specific surface area, they failed to distinguish the filling effect and volcanic activity in concrete. In this paper, inert quartz powder is introduced as correction standard, the activity is tested by the China GB/T12597-2005 standard and GB 2847-2005-T standard, the influences of mechanical grinding, calcination, thermal curing systems

and some other factors on the activity of IOT are also studied.

Experiment

Materials

The 52.5 ordinary Portland cement is from Huaxin, its physical properties and chemical composition are shown in table 1 and table 2. The IOT is from Miyun area, its main chemical composition is SiO₂ and it belongs to rich-silicon IOT, the main mineral composition are quartz, feldspar minerals and magnetite, all of them are shown in table 2 and figure 1. The SiO₂ content of inert quartz sand is more than 90%. The water is tap water from Wuhan city. Grinding agent is melamine and quality content is 0.035%.

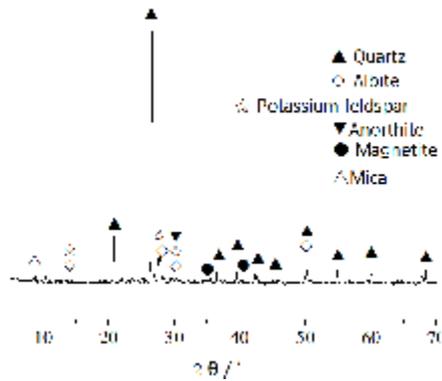


Fig 1 The XRD pattern of IOT

Table 1 The basic physical properties of cement

Water requirement of Normal consistency/%	Setting time/min		Compressive strength/MPa			Flexural strength /MPa		
	Initial	Final	3d	7d	28d	3d	7d	28d
27.6	104	176	30.0	48.5	55.2	5.7	8.8	9.5

Table 2 The chemical composition of cement and IOT(%)

Name	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	SO ₃	Na ₂ O	K ₂ O	Loss
Cement	19.95	5.06	3.34	2.54	63.30	2.29	0.14	0.53	1.09
IOT	65.27	7.46	11.80	5.27	3.80	0.24	/	/	2.13

Table 3 Particle size distribution data of different powder

比表面积 / $m^2 \cdot kg^{-1}$	<1 μm /%	1-10 μm /%	10-30.2 μm /%	>30.2 μm /%	$D_{10} / \mu m$	$D_{50} / \mu m$	$D_{90} / \mu m$
Q (402)	3.57	45.55	35.07	15.81	1.659	10.331	37.092
T (410)	3.93	39.74	32.82	23.51	1.403	12.611	49.906
Q (608)	4.70	46.08	33.07	16.15	1.433	9.696	37.989
T (595)	6.64	41.65	30.23	21.48	1.257	10.755	47.515
Q (797)	4.71	48.19	32.13	14.97	1.403	8.896	36.727
T (813)	7.50	44.02	29.27	19.01	1.150	9.273	44.122
Q (1010)	5.31	53.78	30.42	10.49	1.293	7.033	30.894
T (1001)	8.78	45.06	27.62	18.00	1.037	8.171	42.756

Preparation and tests of powder

The powder is made by ball mill which size is SM Φ 500mm \times 500mm. Specific surface area is tested by BET surface area, powder particle size is tested by Mastersizer 2000 laser particle size analyzer made by England, the activity of IOT is tested by China GB/T12597-2005 standard and GB2847-2005-T standard.

Preparation of mortars and curing systems

Preparation of mortars is according to the GB/T17671-1999, cement-sand ratio is 1:3, water-cement ratio is 0.5, cement is replaced 30% by IOT powder or quartz powder, the size of mortar specimen is 40mm \times 40mm \times 40mm. The formed specimen are cured under room temperature which relative humidity is above 95% for about 24h, then ejected and cured in different ways till to defined period.

Table 4 Four different curing systems

Curing Name	Curing systems	Age/d
Standard	Standard curing	3、28
Hot water	90 $^{\circ}C$ hot water for 2d+standard curing	3、28
High temperature	90 $^{\circ}C$ heat water for 1d+200 $^{\circ}C$ High temperature for 8h+standard curing	3、28
Autoclave	90 $^{\circ}C$ heat water for 1d +1.3MPa autoclave for 6h+standard curing	3、28

Results and discussion

Influence of thermal curing systems on the mortar strength with IOTP

Figure 2 is about the influence of thermal curing system on 28d strength. The results show that, the strength of IOT mortars is lower than the strength of quartz mortars in room temperature condition. When specimen cured by hot water, high temperature or autoclave, the strength of IOT mortars is higher than the strength of quartz mortars. Especially when specific surface area of IOT powder is 813m²/kg and in autoclave condition, the strength of IOT mortars is even higher than the strength of cement mortars.

It is known in section 2.1, the particle size distribution of IOT powder and quartz powder are similar and the strength of quartz mortars is higher than the strength of IOT mortars in room

temperature condition. However, when mortars are cured by thermal curing condition, the strength of IOT mortars is higher than the strength of quartz mortars. It can be explained by that thermal curing system can stimulate the volcanic activity of IOT in concrete, the most efficient way is cured in autoclave condition and strength reaches the highest values when specific surface area is 813m²/kg, all of the rest tests depend on the same specific surface area.

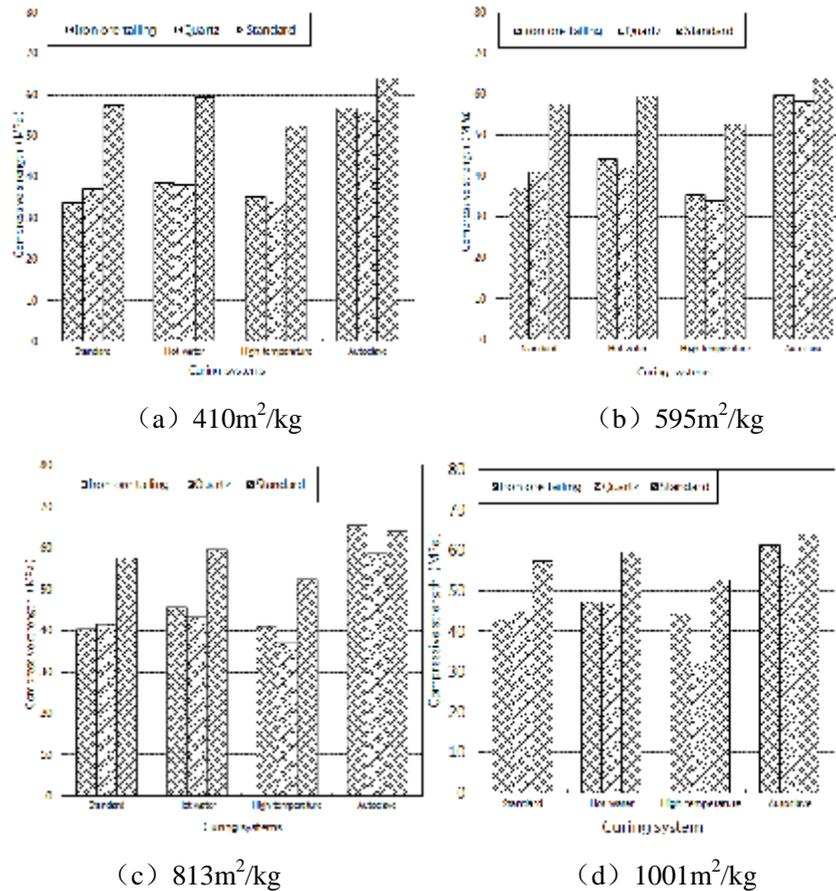


Fig.2 The influence of curing system on 28d compressive strength

Influence of thermal curing systems on pore structure of mortars

Figure 3 is about the MIP results of 28d age mortars, the specific surface area of IOTP and quartz powder is about 800m²/kg. It can be seen from the four figures:

In room temperature condition, accumulated mercury injection of mortars with IOTP or quartz powder is lower than the accumulated mercury injection of mortars with pure cement. It can be explained by that the specific surface area of the two different powder is bigger than the specific surface area of cement, they can play the filling role more successfully. For pore size which is above 0.02nm, the content of mortars with IOTP or quartz powder is higher than the content of control mortars, it can be explained by that the two kinds of powder have no pozzolanic activity in room temperature, it reduced hydration products.

When mortars cured in 90°C hot water, accumulated mercury injection of mortars with pure cement had a significant decrease, but the accumulated mercury injection change of mortars with IOTP or quartz powder was small, and for pore size which is above 0.4nm, the content of mortars with IOTP or quartz powder is higher than the control mortars. It can be explained by that the 90°C hot water inspired the pozzolanic activity of IOTP and quartz powder, accelerated the hydration of cement and improved the pore structure.

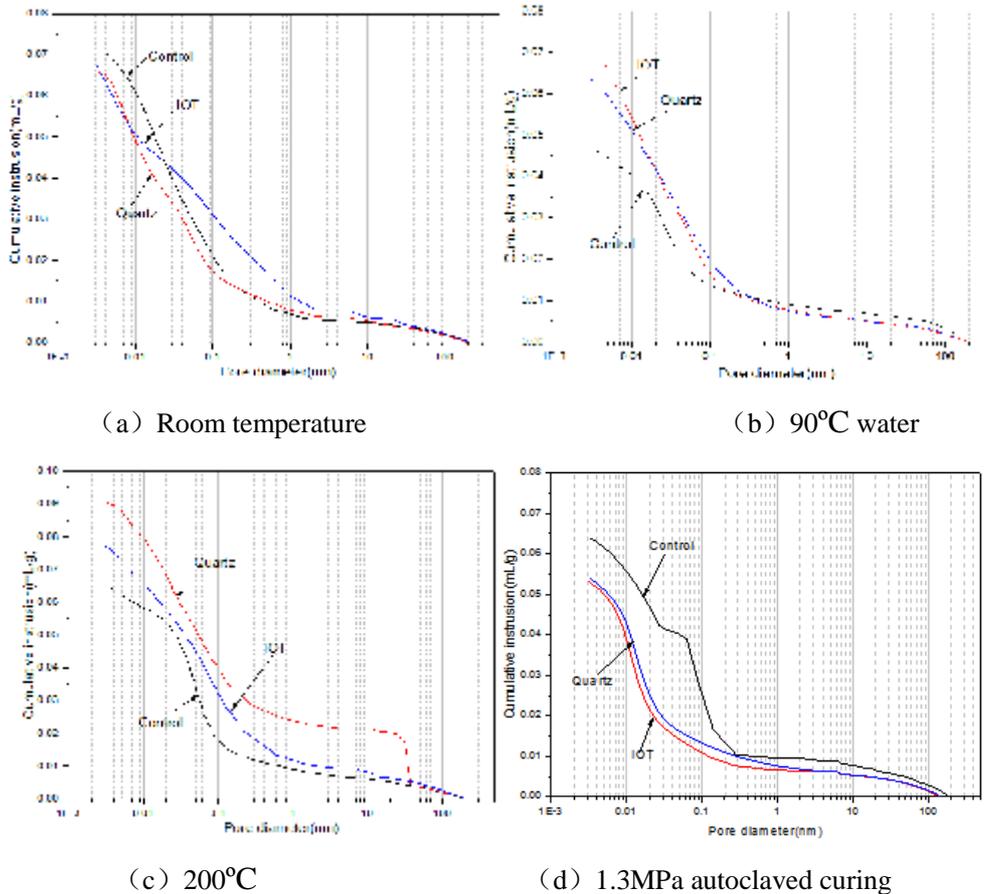


Fig.3 MIP of mortars cured by different curing system

When mortars cured in 200°C condition, the accumulated mercury injection of control mortars was higher than the mortars' cure in 90°C hot water and lower than the mortars' cured in room temperature condition. However, the accumulated mercury injection of mortars with IOTP and quartz powder had a significant increase, it maybe caused by that cement was instead by IOTP and quartz powder, it led to a lot of free water in mortar, the mortars in so high temperature condition and the inner structure would be degraded with the evaporation of water. Some researches show that high temperature curing system can improve pore structure, that is because of low water-binder ratio. It also can be found that the accumulated mercury injection of mortars with IOTP is lower than the accumulated mercury injection of mortars with quartz powder which had different law unlike cured in 90°C hot water and room temperature condition, it was because that pozzolanic activity of IOTP was inspired in 200°C condition and its activity was higher than quartz powder.

When mortars cured in 1.3MPa autoclaved curing system, accumulated mercury injection of mortars with IOTP or quartz powder had an obvious decreased and far below than the control mortars'. It showed that autoclaved curing system could effectively stimulate the activity of IOTP and quartz powder, which would accelerate hydration of cement, consume large amounts of calcium hydroxide and produce more CSH gel, all of above improved the pore structure. On the other side, it also can be seen that accumulated mercury injection of mortars with IOTP is lower than accumulated mercury injection of mortars with quartz powder, it also showed pozzolanic activity of IOTP was higher than quartz powder when cured in 1.3MPa autoclaved curing condition.

The laws of accumulated mercury injection of mortars was same with the strength of mortars, the two kinds of tests proved that 200°C and 1.3MPa autoclaved curing systems could inspire

pozzolanic activity of them and IOTP had higher pozzolanic activity.

Influence of thermal curing system on hydration

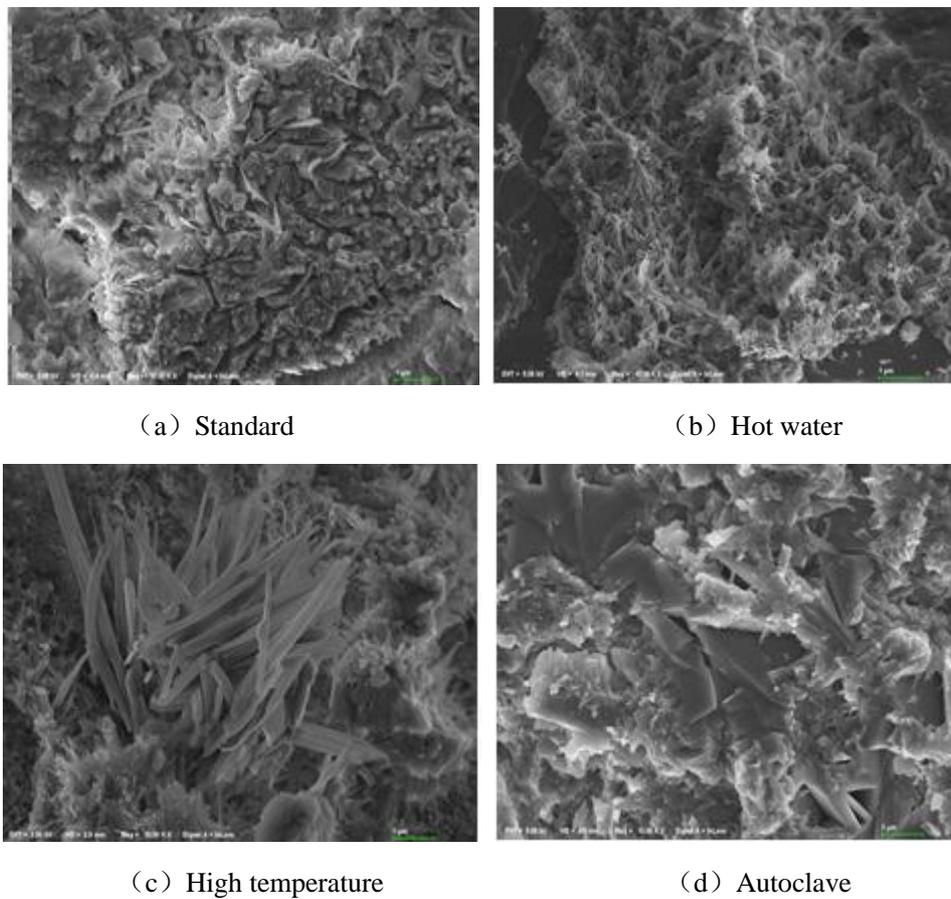


Fig.4 Influence of curing system on morphology of hydration

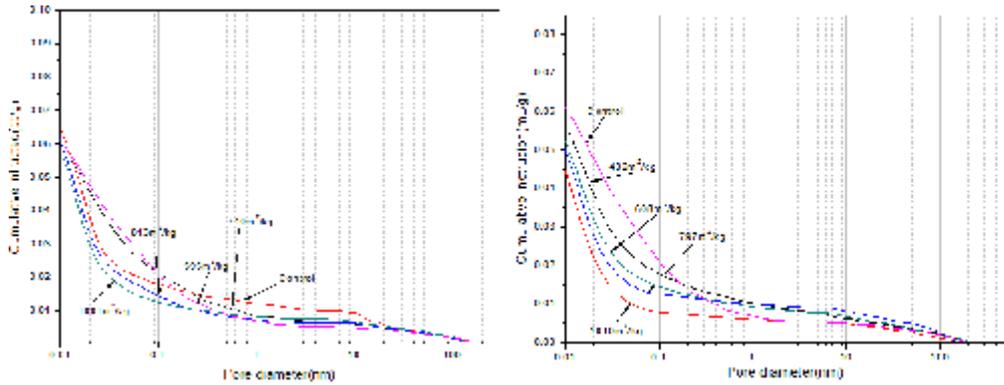
It can be seen from figure 4, slurry cured by standard condition has some $\text{Ca}(\text{OH})_2$, poorly and evenly distributed CSH gel, erosion acreage of the aggregate surface is little. Slurry cured by 90°C hot water appears lots of corrugated CSH gel, the part of acicular crystal is CHS gel, its structure is relatively even, gel overlays of each other. Slurry cured by high temperature condition has some tobermorite(coral shape part), but the hydration products are uneven distribution and different thickness. However, slurry cured by autoclave condition has lots of even and compact hydration products, from figure (d) can see a large area of hard CSH gel.

It is visible that thermal curing conditions have a positive effect on accelerating the hydration rate and expanding the content of $\text{Ca}(\text{OH})_2$, high temperature curing system also plays the same role but likely destroy the even distribution of hydration products.

The influence of autoclaved curing system on mortar with IOTP

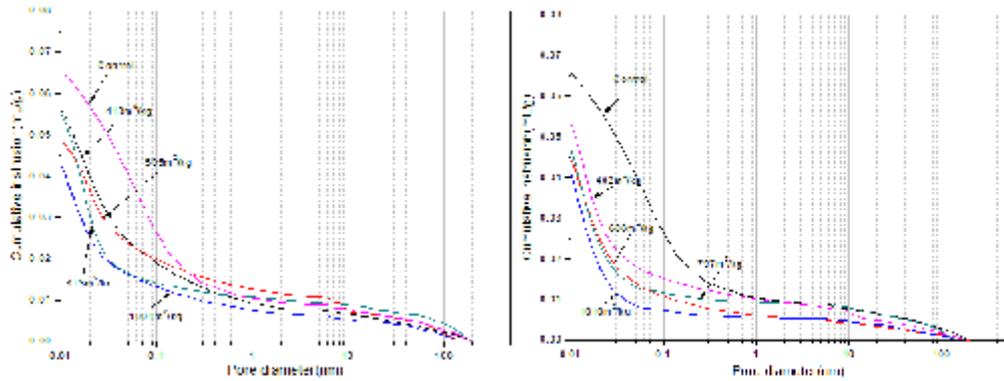
Pore structure of mortars with different powder

Figure 5 is about 7d and 28d aged MIP results of mortars with IOTP or quartz powder cured in 1.3MPa autoclaved curing condition. The four pictures showed that with the growth of specific surface area of powder, the content of pore size which is less than 1nm was lower, all of them was lower than control mortars. It indicated that when mortars cured in autoclaved curing condition, pore structure, pore size and compactness of mortars could be improved by introducing IOTP or quartz powder, it also proved autoclaved curing systems could inspire pozzolanic activity of IOTP.



(a) 7d pore size distribution with IOTP

(b) 7d pore size distribution with quartz powder



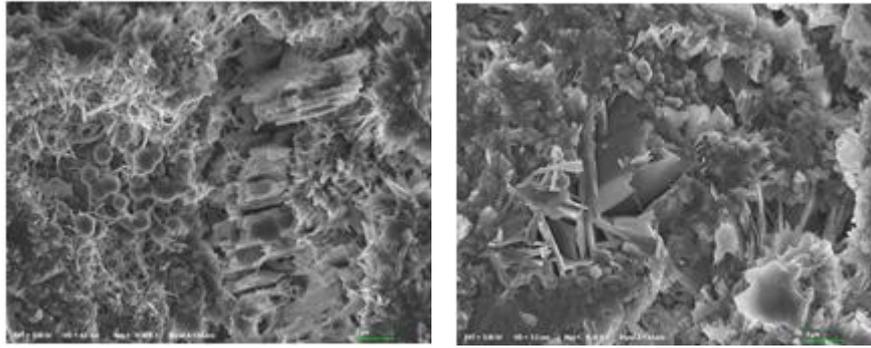
(c) 28d pore size distribution with IOTP

(d) 28d pore size distribution with quartz powder

Fig.5 MIP of different mortars cured by autoclave

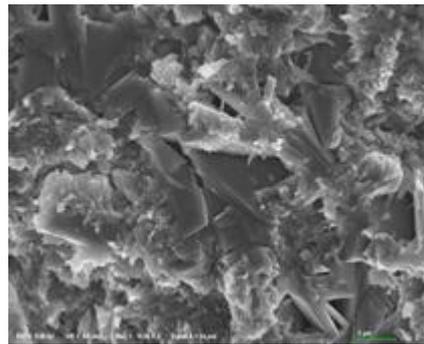
Hydration characteristics of mortars with different powder

Figure 6 is about SEM images of 28d mortars which cured in autoclave curing condition. Figure (a) can be obviously found cement particles, Ca(OH)_2 , CSH gel and connected pores between hydration products, the structure of slurry is loose. Figure (b) can be found smaller cement particles, a small number of tobermorite, general CSH and hard CSH gel, Ca(OH)_2 crystals almost can't be found. Figure (c) can not be found cement particles or Ca(OH)_2 crystals, there are a lot of compact hard CSH gel. The results show that when specimen cured by autoclave, the volcanic activity of quartz powder and IOTP is motivated, a large sum of Ca(OH)_2 crystal is consumed by active SiO_2 and hard CSH gel is generated in this thermal condition. Comparing figure(b) with figure(c), figure(c) does not have Ca(OH)_2 , larger area of CSH gel, it indicated that IOTP have more motivated SiO_2 , the volcanic activity of IOTP is higher than quartz in autoclaved condition.



(a) 100% cement

(b) 30% quartz powder+70% cement



(c) 30% IOTP+70% cement

Fig.6 SEM patterns of mortars

Conclusions

(1) In room temperature condition, mortar strength increased with the growth of IOTP content, the compressive strength than even reached 75, but its strength was lower than mortar strength with inert quartz powder. It showed IOTP does not have pozzolanic activity in normal temperature condition, it is unreasonable to judging its activity by 28d compressive strength ratio.

(2) In thermal curing condition, the mortar strength with IOTP was higher than mortar strength with quartz powder. Through SEM and MIP test methods scanning mortars cured by thermal curing systems, $\text{Ca}(\text{OH})_2$ almost disappeared in mortar added IOTP, content of CSH gel was increased, most compact mortar structure and large number of tobermorite. Its strength was even higher than control mortar strength when the specific surface area of IOTP was $813\text{m}^2/\text{kg}$. It proved that thermal curing can arouse activity of IOTP and autoclaved curing was the most effective mean.

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