

# Evaluation of Activation and Action Mechanism of Calcined Coal Gangue

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Abstract:

Mineral compositions of coal gangue are basically quartz and clay minerals. During calcination clay minerals dehydrate, decompose and create amorphous SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> which can improve the activity of coal gangue.

Coal gangue, limestone and gypsum were used as raw materials. Blended coal gangue according to two batches was calcined at 850-1200°C for 1h. Mineral compositions and microstructure variations were analyzed before and after calcination by X-ray diffraction and method of mercury intrusion pore measurement, which was propitious to search after calcination mechanism.

XRD results show that amorphous SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> took part in chemical reaction and created hydraulic-activity C<sub>12</sub>A<sub>7</sub> and C<sub>2</sub>S with gypsum and enough calcium. During calcinations F<sup>-</sup> and [SO<sub>4</sub>]<sup>2-</sup> come into the framework and react with CaO at 900-950°C to create 3C<sub>2</sub>S•3CaSO<sub>4</sub>•CaF<sub>2</sub> which took into fluid when the temperature became high.

Pore structure analysis of the samples indicates that adding gypsum and fluorite into coal gangue is more propitious to strengthen the slurry and optimize the pore distribution than only of gypsum.

Key words: coal gangue; calcination; activation

## 1 Introduction

Coal gangue is composed of various minerals and accretes with coal stratum. Its dominant minerals are quartz and silicate layered clay minerals. Fresh coal gangue has stable crystal structure. All particles in lattice arrange rigidly, so that its chemical composition is fixed and the activity is poor. But calcined coal gangue, especially under the condition

of rapid cooling, has no enough time to form new crystal nucleus in highly viscous liquids. So it is very difficult to grow up for the crystal. Particles can not arrange regularly, and vitreous minerals may appear.

Now it is necessary to solve pollution problem from pileup of coal gangue. Calcining coal gangue to improve activity is an important method to develop its application as cement additive [1]. America, France, England, Poland and other countries have already taken into account and obtained some achievement [2,3]. Chinese government also has thought much of it, brought forward the idea of “ adjusting measures to fit local conditions”, and set down some policies to facilitate an effective utilization of coal gangue[4].

In this paper, coal gangue was calcined at seven chosen temperature ranges. Its activity and microstructure before and after calcinations are discussed. A certain modern methods of testing are carried out to support theory basis. The optimal calcining temperature is determined to activate coal gangue.

## 2 Experimental

### 2.1 Raw materials and patches

Coal gangue comes from Shandong and Huainan. Its fineness is below 6.3% (residue on 0.08mm sieve). Both gypsum and limestone are natural minerals. Fluorite is chemical reagents with AR grade. Chemical composition of raw material is shown in Table 1.

Table1 Chemical compositions of raw materials w/%

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Loss
Huainan	58.90	8.79	5.96	0.85	0.81	1.67	1.85	1.82	18.59
Shandong	48.82	19.03	4.47	2.03	2.29	---	0.19	1.43	16.78
Limestone	1.09	0.77	0.20	53.60	0.61	0.04	0.11	0.06	42.19
Gypsum	9.02	0.77	0.15	33.23	3.93	40.97	0.47	0.36	3.08

### 2.2 XRD analysis

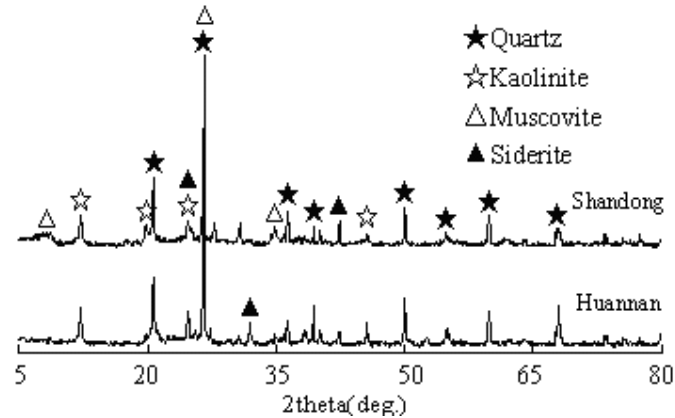


Fig.1 XRD patterns for raw coal gangue

Fig.1 shows XRD patterns of Shandong and Xuzhou coal gangue. Main minerals of coal gangue are quartz [ $\text{SiO}_2$ ], kaolinite [ $(\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH}))$ ], muscovite [ $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ ] and siderite [ $\text{FeCO}_3$ ]. Characteristic peak of quartz is speculate, which illuminates crystal consideration is high and crystal lattice is whole.

Kaolinite and muscovite with clay-mineral character can dehydrate and decompose at  $700\text{-}1000^\circ\text{C}$  to create metakaolinite or amorphous  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , which is propitious to activate coal gangue [5,6].

### 2.3 Experimental patches

The experimental patch in single-addition system is  $w(\text{coal gangue}) : w(\text{limestone}) : w(\text{gypsum}) = 50:50:4.5$  and the one in compound-addition system is  $w(\text{coal gangue}):w(\text{limestone}):w(\text{gypsum}):w(\text{fluorite}) = 50:50:4.5:2$ .

## 3 Experimental results and discussion

### 3.1 XRD analysis

#### 3.1.1 Mineral composition analysis of calcined coal gangue in single-addition system

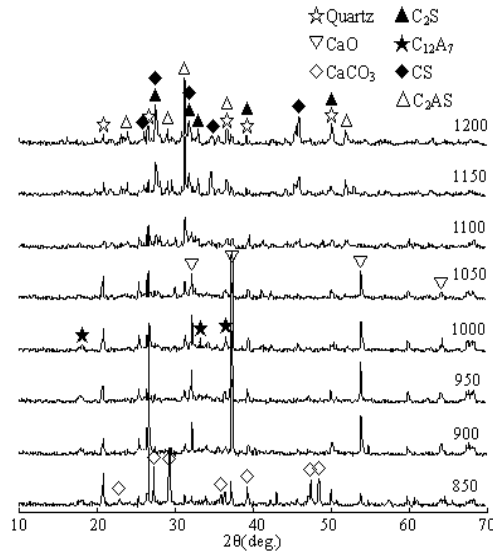


Fig.2 XRD patterns for calcined Huainan in single-addition system

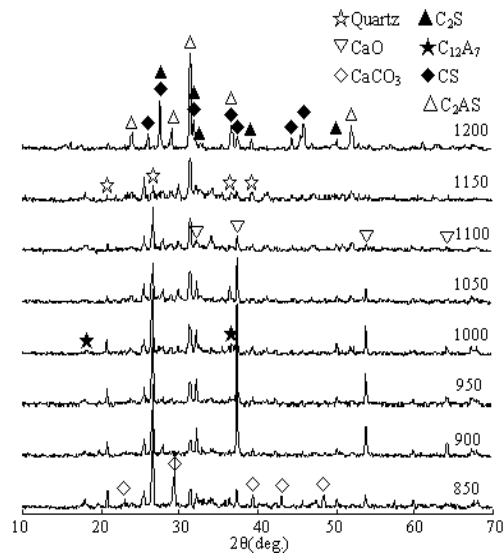


Fig.3 XRD patterns for calcined Shandong in single-addition system

Mineral composition varieties of coal gangue from Huainan during calcinations at 850-1200°C are shown in Fig.2. At 850°C characteristic peaks of  $\text{CaCO}_3$  is evident, but at 900°C those can not be seen. So  $\text{CaCO}_3$  had decomposed entirely at 850-900°C to create  $\text{CaO}$  and  $\text{CO}_2$ . At the same time  $\text{CaO}$  and amorphous  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  from that kaolinite dehydrating and decomposing created and created new minerals  $\text{C}_{12}\text{A}_7$  and  $\text{C}_2\text{S}$ , which explains XRD patterns at 900 -1050°C is similar. Quartz,  $\text{CaO}$ ,  $\text{C}_{12}\text{A}_7$  and  $\text{C}_2\text{S}$  are dominant after calcinations. At 1050-1100°C

those minerals created at low temperature went on reaction. In XRD patterns characteristic peaks of  $C_{12}A_7$  and CaO disappear, quartz peak becomes gently obviously and  $C_2AS$  and CS are created.

Mineral composition varieties of coal gangue from Shandong are shown in Fig.3. In 850°C raw minerals still exist largely. At 900-1100°C those minerals created at low temperature such as CaO,  $C_{12}A_7$  and  $C_2S$  were created, consumed and vanished. At 1150-1200°C the content of crystal quartz decreased and simultaneity  $C_2AS$  and CS without activity were created.

### 3.1.2 Mineral composition analysis of calcined coal gangue in compound -addition system

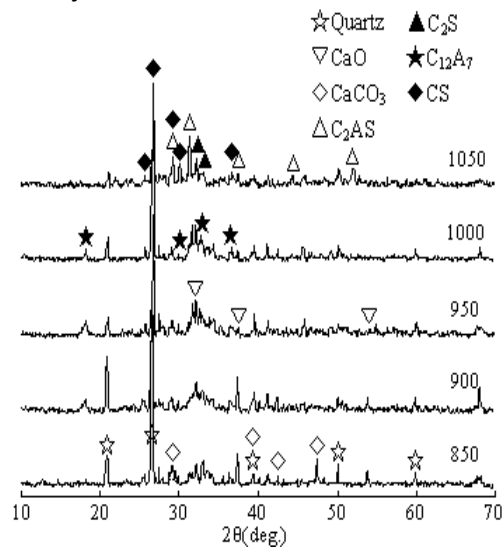


Fig.4 XRD patterns for calcined Huainan in compound -addition system

Mineral composition varieties of coal gangue from Huainan during calcinations at 850-1050°C are shown in Fig.4. It is obvious that mineral composition is different after calcinations at different temperature. In 850°C quartz is dominant and its diffraction peaks are specular. Characteristic peaks of  $CaCO_3$  are gentle, so  $CaCO_3$  had decomposed largely. At one time characteristic peaks of CaO and  $C_2S$  are remarkable. At 900°C those peaks of  $CaCO_3$  can not be seen, so  $CaCO_3$  had decomposed entirely. Quartz, CaO and  $C_2S$  still exist, and  $C_{12}A_7$  as a new mineral appears. So amorphous  $Al_2O_3$  from kaolinite's dehydrating and decomposing had taken part into reactions. The XRD pattern in 950°C is similar with that in 900°C, but obviously the content of minerals is different. The content of quartz and CaO reduced, and that of  $C_2S$  and  $C_{12}A_7$  increased. Creating reaction of  $C_2S$  and  $C_{12}A_7$  with cementitious activity went on. In 1000°C mineral compositions evidently changed.

The characteristic peaks of CaO disappeared. Those of  $C_2S$  and  $C_{12}A_7$  became gentle. But  $C_2AS$  and CS are created. When calcining temperature went on increasing,  $C_2AS$  and CS were dominant, and  $C_{12}A_7$  disappeared.

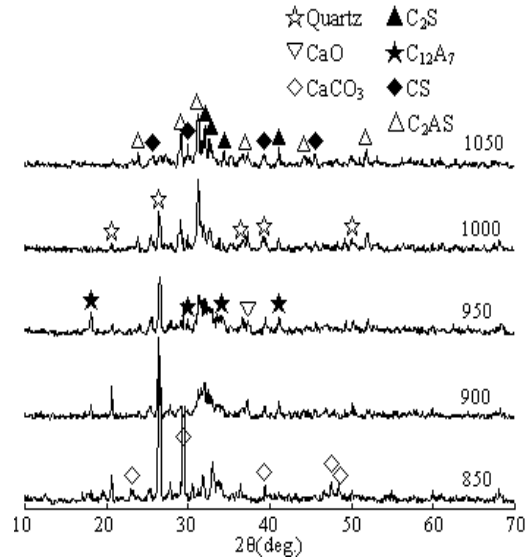


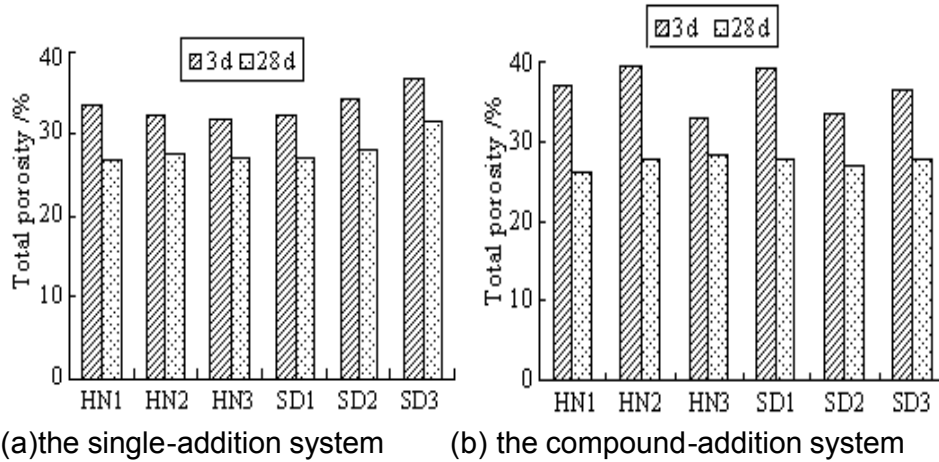
Fig.5 XRD patterns for calcined Shandong in compound -addition system

At 850-900°C  $CaCO_3$  decomposed entirely during calcining coal gangue from Shandong to create  $CaO$ ,  $C_{12}A_7$  and  $C_2S$ . At 950-1000°C  $C_{12}A_7$ ,  $CaO$  and  $SiO_2$  went on reaction to create  $C_2AS$  and CS. At 1000-1050°C diffraction intensity of quartz ( $d=0.33532nm$ ) is decreased evidently and even disappeared in 1050°C.

Comparing the two systems, decomposing temperature of  $CaCO_3$  is not changed, but the consuming temperature of  $CaO$  and the creating one of  $C_2AS$  and CS is affected evidently. In single-addition system at 1050-1150°C the characteristic diffraction intensity of  $CaO$  is reduced, and  $C_2AS$  and CS are created. In compound-addition system at 950-1000°C diffraction intensity of  $C_{12}A_7$ ,  $CaO$  and  $SiO_2$  is lower and even to zero. It is concluded that in compound-addition system common melting point is reduced, which is more propitious to activate. That is explained that  $F^-$  and  $[SO_4]^{2-}$  came into the framework, and reacted with  $CaO$  at 900-950°C to create  $3C_2S \cdot 3CaSO_4 \cdot CaF_2$  which took into fluid when the temperature became high.

### 3.2 Characterization of pore structure

Coal gangue calcined in is mixed with gypsum and cement. The batch is  $w(\text{coal gangue}):w(\text{cement}):w(\text{gypsum})= 95:100:5$ .  $W/F = 0.4$ . The samples with  $2\text{cm} \times 2\text{cm} \times 2\text{cm}$  were cured at  $20\pm 2^\circ\text{C}$  for 3d and 28d. The uncalcined coal gangue was only for comparison. Then hydration reaction is terminated by ethanol. After vacuum dryness the samples are tested for pore structure.



(a) the single-addition system (b) the compound-addition system  
 Fig.6 relationship between curing time and total porosity  
 Note: HN1, HN2, HN3—Huinan coal gangue differently caicined at 850, 900, 950°C; SD1, SD2, SD3—Shandong coal gangue differently caicined at 850, 900, 950°C.

Comparing total porosity of hydrating samples, it is showed that with the same conditions of calcination temperature and curing age the total porosity is evident to decrease as the curing age is extended both in single-addition system and in compound-addition system. It can be explained that during hydration cementitious minerals hydrolyze to create lots of hydrating production which fills in the holes. The big holes become small. These are not connecting. So the porosity decreases and the samples are compacter.

Comparing the single-addition system with the compound-addition system, curing for 3days total porosity of the samples calcined in the same temperature is close, but for 28 days the porosity of compound-addition system is lower than that of single-addition system. It is confirmed that when the curing time is extended, the samples of compound-addition system are compacter than that of single-addition system.

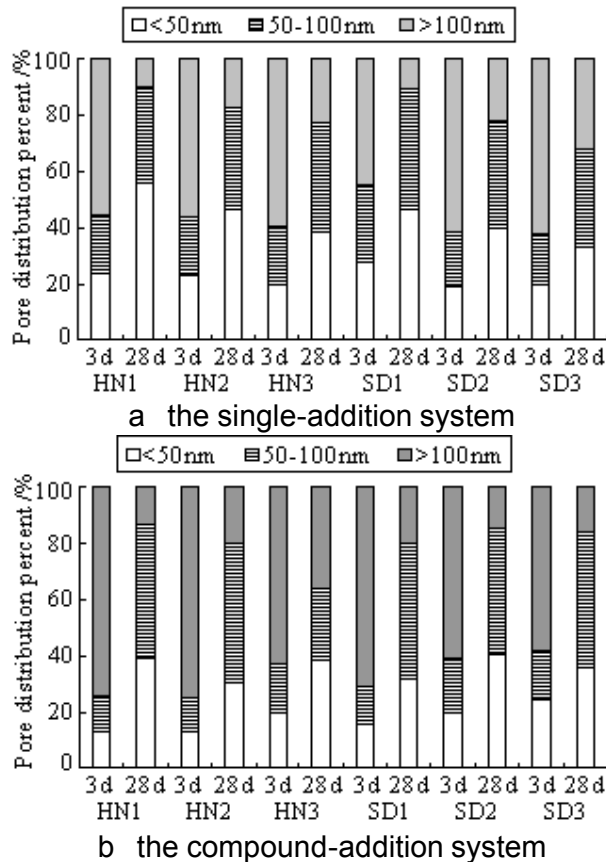


Fig.7 relationship between curing time and pore distribution

In theory, the pore in the slurry can be disported into air hole, stoma and gel hole. As the proportion of gel holes increase, the strength is higher and the performance is better. Generally speaking, the hole in 0.5~50nm is called gel hole and that in 50~100nm is stoma. The others whose diameter is bigger than 100nm are air hole. The air holes are usually taken for being harmful to the strength.

In single-addition system when the sample has cured for 3 days, the proportion of the holes >100nm is 44.82~62.04%, that <50nm is 18.91~27.4%. For 28 days the proportion of the holes >100nm is 9.78~31.58%, that <50nm is 33.29~55.46%.

It is obvious that when the curing age is extended, pore distribution inclines to reduce. The harmful holes have decreased 49.1 ~82.4%. The gel holes have increased 67.3~134.2%. In compound-addition system when the sample has cured for 3 days, the proportion of the harmful holes is 58.26~75.08%, that <50nm is 13.1~24.5%. For 28 days the proportion of the holes >100nm is 13.0~36.0%, that <50nm is 30.3~40.8%. So when the curing age is extended, pore distribution is the same trend with the single-addition system. The harmful holes have



decreased 43.1~82.5%. The gel holes have increased 46.6~197.8%.

### 3.3 Mechanical performance

#### 3.3.1 Compressive strength in single-addition system

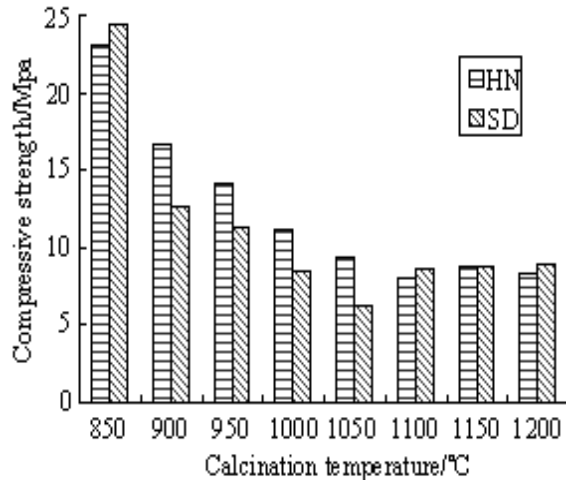


Fig.8 The chart of 3d compressive strength

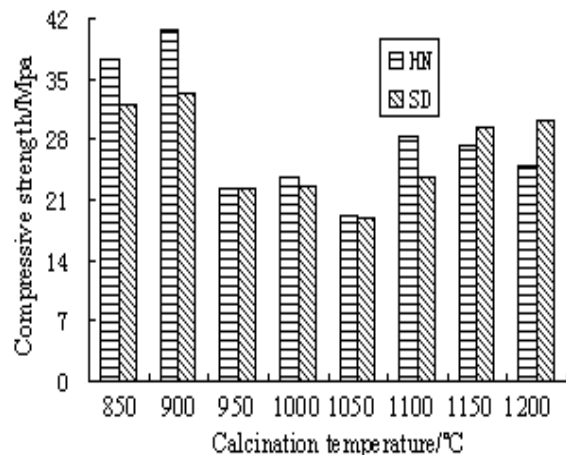


Fig.9 The chart of 28d compressive strength

Fig.8 and Fig.9 are the charts of 3d and 28d compressive strength of Shandong and Huainan coal gangue in single-addition system.

Compressive strength of coal gangue in the early stage at low temperature is higher evidently than that at high temperature. In the early stage it was at 850°C that compressive strength came highest. The highest compressive strength of Shandong coal gangue is 24.5MP and that of Huainan coal gangue is 23.1MP. In the late stage it was at 850°C that compressive strength came highest. The highest compressive strength of Shandong coal gangue is 31.7MP and that of Huainan coal

gangue is 40MP.

### 3.3.2 Compressive strength in compound-addition system

Fig.10 and Fig.11 are the charts of 3d and 28d compressive strength of Shandong and Huainan coal gangue in compound-addition system.

In the early stage Compressive strength of coal gangue at low temperature is higher similarly than that at high temperature. The highest compressive strength of Shandong coal gangue is 14.4MP at 950°C and that of Huainan coal gangue is 15.1MP at 900°C. In the late stage the highest compressive strength of Shandong coal gangue is 36.4MP at 950°C and that of Huainan coal gangue is 39.7MP at 900°C.

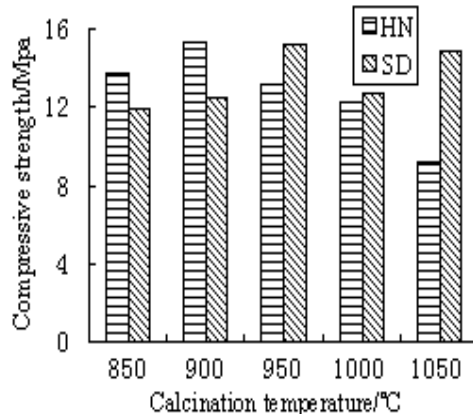


Fig.10 The chart of 3d compressive strength

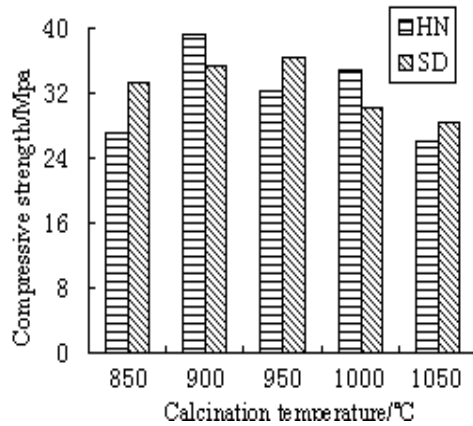


Fig.11 The chart of 28d compressive strength

## 4 Conclusions

1. During calcinations at 850-1200°C two conversions exist: one is low-temperature creating section of cementitious minerals.  $\text{CaCO}_3$  entirely decomposed at 850-900°C to create  $\text{C}_{12}\text{A}_7$  and  $\text{C}_2\text{S}$  with

cementitious activity in favor of activating coal gangue. The other is high-temperature creating section of inert minerals. At 1050-1150°C C<sub>2</sub>AS and CS without cementitious activity created.

2. F<sup>-</sup> and [SO<sub>4</sub>]<sup>2-</sup> come into the framework and react with CaO at 900-950°C to create 3C<sub>2</sub>S•3CaSO<sub>4</sub>•CaF<sub>2</sub> which took into fluid when the temperature became high.

3. Pore structure analysis of the samples indicates that adding gypsum and fluorite into coal gangue is more propitious to strengthen the slurry and optimize the pore distribution than only of gypsum.

#### References

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