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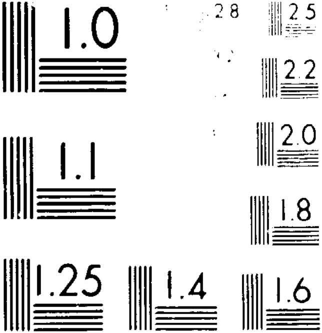
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STRUCTURE AND NATURE OF POZZOLANAS AND THEIR APPLICATION IN THE CEMENT INDUSTRY IN CHINA *

by

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STRUCTURE AND NATURE OF POZZOLANAS AND THEIR APPLICATION IN CEMENT INDUSTRY IN CHINA

It is known that what we call pozzolanas means more than natural pozzolana. It is in fact the general term for a large variety of materials which enjoy the following characteristics. Firstly, the principal constituent is acidic oxide (SiO_2) whose percentage reaches 50% to 70% and above. Secondly after combining with lime and mixing with water at normal temperatures, they can harden in moist contitions and further harden in water. These are the two common characteristics of pozzolanas.

Pozzolanas are a kind of material traditionally used in cement industry. Much investigation has been made in many countries with a great many treatises and articles written on pozzolanas.

There is a great variety and an abundant supply of pozzolanas in China. Not long after the founding of the People's Republic of China, pozzolanas were used in cement industry and pozzolanic cement was produced. At present pozzolanic cement is one of the most important cement sorts in China. Systematic investigation has been made on pozzolanas and pozzolanic cement. This paper deals in brief with the structure and nature of pozzolanas and their application in cement industry in China.

PHYSICOCHEMICAL PROPERTIES OF POZZOLANAS

There are different kinds of pozzolanas in China. They can be divided into three groups according to their mineralogical characteristics: hydrous siliceous materials, volcanic glassy materials and burnt clays. But nowadays, according to their sources they usually fall into two categories: natural and artificial .

In China pozzolanas which are being used or will be used are as follows:

Natural ---- volcanic ash, trass, zeolite and diatomaceous earth;

artificial ---- mainly industrial by-products: fly ash (from power industry), spent oil shale (from oil industry), carbonaceous shale (from coal industry), burnt clay (from building material industry) and siliceous residue (from alumina industry) etc..

1. Chemical composition

The chemical composition of pozzolanas commonly used in China is shown in Table 1. In spite of their different variety, pozzolanas, it can be seen from the table, are siliceous materials containing high silica. In general, they contain 50 - 70% SiO_2, about 80% SiO_2 + Al_2O_3 and less than 10% CaO, which proves that pozzolanas are acidic materials. It can also be seen that the ignition loss of natural pozzolanas is quite high while artificial pozzolanas have a high Al_2O_3 content, generally above 20%. It is significant that natural pozzolanas contain a relatively large amount of alkali as compared with artificial ones. This is because on the one hand natural pozzolanas contain a certain amount of feldspar and, on the other hand, a part of alkali in artificial ones is volatilized during heat treatment. It is considered that the alkali in pozzolanas is harmless when used in cement production.

2. Physicochemical properties

The most important physicochemical characteristic of pozzolanas lies in their structure. Usually, they have a large number of micro pores in their structure, especially natural pozzolanas, with the exception of fly ash and liquefied residue which have a dense structure. The test value of the internal surface area of several pozzolanas is shown in Table 2.

Table 1. Percentage composition of pozzolanas in China

Pozzolanas	Ignition Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Total
Diatomaceous earth	6.57	67.78	14.78	4.30	1.96	0.78	—	0.42	1.31	100.10
Volcanic ash	1.82	45.51	16.50	11.86	10.60	5.13	trace	3.93	1.49	97.34
Trass 1	4.63	64.67	17.03	4.20	3.48	1.21	"	2.04	3.14	100.40
Trass 2	3.77	74.27	13.38	1.82	1.05	0.76	0.21	0.45	3.43	99.36
Zeolite 1	10.44	67.55	11.31	0.59	3.30	0.78	0.04	1.10	2.65	97.76
Zeolite 2	12.35	67.02	11.11	0.67	2.81	0.93	0.03	1.09	2.76	99.37
Fly ash	4.77	52.40	26.37	6.95	4.33	1.13	0.51	—	—	96.48
Liquefied residue	—	47.21	30.80	14.34	3.78	1.18	0.08	0.05	1.28	98.72
Carbonaceous shale 1	2.17	56.66	22.79	7.44	5.18	2.22	1.47	0.31	1.99	100.25
Carbonaceous shale 2	1.02	55.20	30.18	5.81	2.44	1.33	1.62	0.18	2.31	100.15
Siliceous residue	6.93	65.63	22.60	1.81	1.01	0.43	1.76	0.18	0.23	100.13
Spent oil shale 1	1.85	60.53	23.24	9.46	1.11	1.26	0.63	0.64	1.14	99.86
Spent oil shale 2	4.02	57.43	24.60	9.35	1.13	0.70	—	—	—	97.43
Burnt clay	3.37	68.24	14.14	5.70	3.72	0.78	0.40	0.53	2.45	99.63
Burnt clay	4.25	66.35	20.47	5.70	1.25	0.54	trace	0.72	1.42	100.20

Table 2. Internal surface area of pozzolanas

Pozzolanas	Internal surface area, m^2/g
diatomaceous earth	135.7
zeolite	84.6
red shale	10.1
liquefied residue	4.9
fly ash	4.6

It is known that the larger the surface area is, the higher the surface energy, i.e. the greater the chemical reaction is. But in the mean time, the requirement for water increases. Therefore, the internal surface area of pozzolanas considerably affects the properties of cement.
In the past, many researchers put emphasis on the hydrated products made during the reaction between pozzolanas and clinker or $Ca(oH)_2$, neglecting the effect of the structure of those materials on the properties of cement. This approach is more or less one-sided, for the reason that a series of macroscopic be-havious of cement concrete depends on not only the hydrates, but more on the paste structure in connection with the pore distribution and the solid phase (1). The structure of the material itself affects the structure of the cement stone. Most pozzolanas possess a large number of micro pores which absorb water easily. Therefore, when concrete is mixed the requirement of pozzolanic cement for water is much greater than that of cement clinker during hydration. Because of extra water, a lot of pores were left after the hardening of concrete. This brings a bad effect on concrete. On the contrary, fly ash is formed into a large number of spherical particles, because coal burns at high temperature in the boiler until it melts, (Fig. 1). These spherical particles in the mortar or concrete act as ball-bearings, thus reducing the requirement of mortar or concrete for water and greatly improving the technical properties of concrete.

Fig. 1. Sphrical particles in fly ash

3. Meneralogical characteristics

Pozzolanas differ in mineral constituents, such difference is caused by their original formation and subseqent changes. Natural pozzolanas are mainly vitreous, the glass content being 40 - 50% or still higher. In addition to glass, they contain a small amount of $CaCO_3$, quartz and magnetite etc.. The trass formed by depositing, compacting and coagulating from volcanic ash contains more varieties of mineral constituents, such as quartz, feldspar, mica, montmorillonite and kaolinite etc.. Under the reaction by the alkali-rich solution, a part of the trass changes into zeolite. This process is what is known as the gradual conversion into very fine mineral crystalline.

Fly ash and liquefied residue are mostly vitreous, the glass content being above 50% or even up to 80%. They contain a small amount of

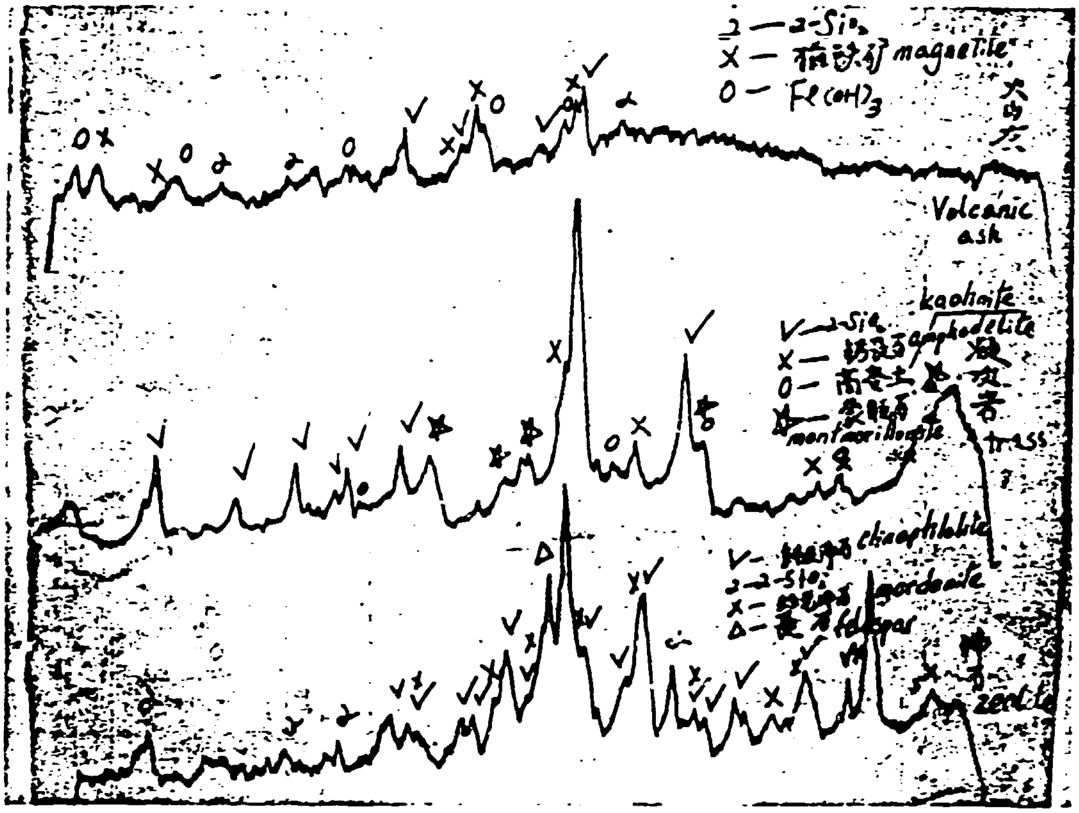

Volcanic ash
kaolinite
montmorillonite
trass
clinoptilolite
mordenite
feldspar
zeolite

Fig. 2-1

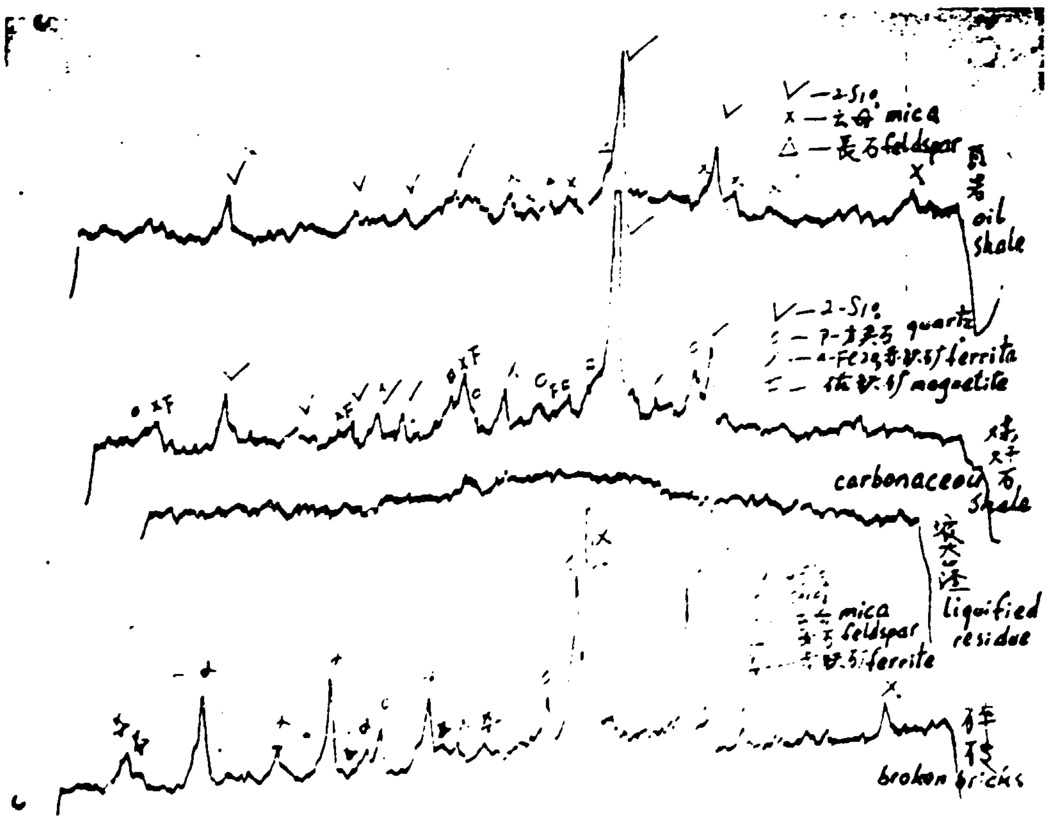

mica
feldspar
oil shale
quartz
ferrite
magnetite
carbonaceous shale
mica
feldspar
ferrite
liquified residue
broken bricks

Fig. 2-2

mullite and quartz. According to the calculation of their chemical composition, most fly ash and liquefied residue are located in the zone of A_3S_2 in the phase diagram, away from the zone of Portland cement, high alumina cement and blast-furnace slag. Only some coal ash whose calcium content is high may contain a small amount of β-C_2S and have a weak cementing property.

Carbonaceous shale and spent oil shale which fall into the category of burnt clays contain mainly quartz, feldspar, mica and ferrite etc.. The X-ray diffraction pattern of the materials mentioned above is shown in Fig.2.

Fig. 2 X-ray diffraction pattern

4. Resources and application of pozzolanas in China

China is a vast country rich in natural resources. Materials which come under the category of pozzolanas in other countries are also available in China. Table 1 shows merely some of the typical samples of such materials in this country.

True, China does not have so long a history as other countries in the use of pozzolanas, but she puts a high value on it. Research work on pozzolanas and their application in cement production and construction date back to the early years following the founding of new China. In the meantime, national standards for cement and materials related to pozzolanas were set. In China the purpose of using pozzolanas in cement production is to improve cment behaviors in order to meet the different needs involved in construction engineering as well as to save clinker and energy for the production of more cement. Now pozzolanic cement has become one of the most important cement sorts in China, because of their widespread use in cement production.

Pozzolanas in China have the following special features:
(1). It is revealed after years' investigations [2. 3] and production practice that natural pozzolanas available in areas easily accessible, such as pozzolan and trass, generally possess low pozzolanic activity and that their application in cement production is unsatisfactory. Diatomaceous earth, in spite of its good activity, has never been used in production because of its considerable requirement for water.

Recently, as a result of the efforts made by the geological and the building material departments, abundant zeolite resources have been discovered in China. It is proved in practice that the addition of zeolite in the course of shaft kiln cement production has achieved remarkable results in improving the soundness and the development of strength of cement, stabilizing the quality of cement. The drawbacks are that low strength at the early ages and considerable requirement for water. About 40 alterations of zeolite are available in nature. Among them, clinoptiloite and mordenite are proved to be the most ideal materials to be used in cement industry. And it happens that they are in abundant supply in our country, Therefore zeolite has a wide prospect for application in cement production in China.

(2). At present, such artificial pozzolanas as carbonaceous shale, spent oil shale and fly ash are widely used in China. Our country is a developing country whose industry is developing rapidly. Large amounts of waste residue are produced each year. So application of industrial resdue in cement and building materials is of immense importance; since it can not only eliminate industrial pollution and protect the environment, but also increase cement output and save energy. Besides, in China, the pozzolanic activity of these materials is usually higher then that of natural pozzolanas.

Properties of cement containing pozzolanas

1. Pozzolanic cement in China

China has a history of about 30 years in using pozzolanas for the production of a multiple variety of cement sorts and of cement with different grades.

As mentioned above, in China pozzolanic cement is produced to improve cement properties and save energy, and meanwhile, to adjust cement grade by changing the proportion of pozzolanas. In convection with this, national standards have been defined (Table 3).

Apart from limiting the proportion of pozzolanas, standards also involve other quality indices, such as soundness, SO_3 and MgO etc.

In addition to standards for cement, there are corresponding standards or technical specifications for pozzolanas in China, for instance, " Pozzolanas Used in Cement Production" and " Specification for Fly Ash Used in Cement Production and Concrete". These specifications set technical requirement for these materials in two respects, first in activity, which means the pozzolanic activity indices that pozzolanas have to attain are defined, as expressed mainly in terms of cement strength in China, and second, in the restriction of harmful substance contained in pozzolanic materials, such as SO_3 and unburnt substance in artificial pozzolanas so as to ensure the quality of cement right from the original materilas.

Table 3. Limitation of proportion of pozzolanas in cement

Cement	Designation number	Proportion of pozzolanas allowed in cement	Strength grade
ordinary Portland cement	GB 175-77	≤ 15%	225, 275, 325 425, 525, 625
pozzolanic Portland cement	GB 1344-77	20-50%	225, 275, 325 425, 525
fly ash Portland cement	GB 1344-77	20-40%	"
blast-furnace slag portland cement	GB 1344-77	≤15% and $\frac{1}{3}$ less than amount of slag	"

2. Properties of pozzolanic cement

The proerties of cement from pozzolanas have been described at length in various scientific literature. [2.5.6.7]

They can be summarized into the following points: high increasing rate of strength at long ages, low heat of hydration, high resistance to sulfate, good impermeability and good water retaining property etc. The drawbacks are low strength at the early ages, considerable water requirement and dry shrinkage as well as poor performance under low temperatures. Pozzolanic cement can be turned to good account provided that its behaviors are better understood so that strong points are made good use of and weak points avoided. The properties of some pozzolanic cements are shown

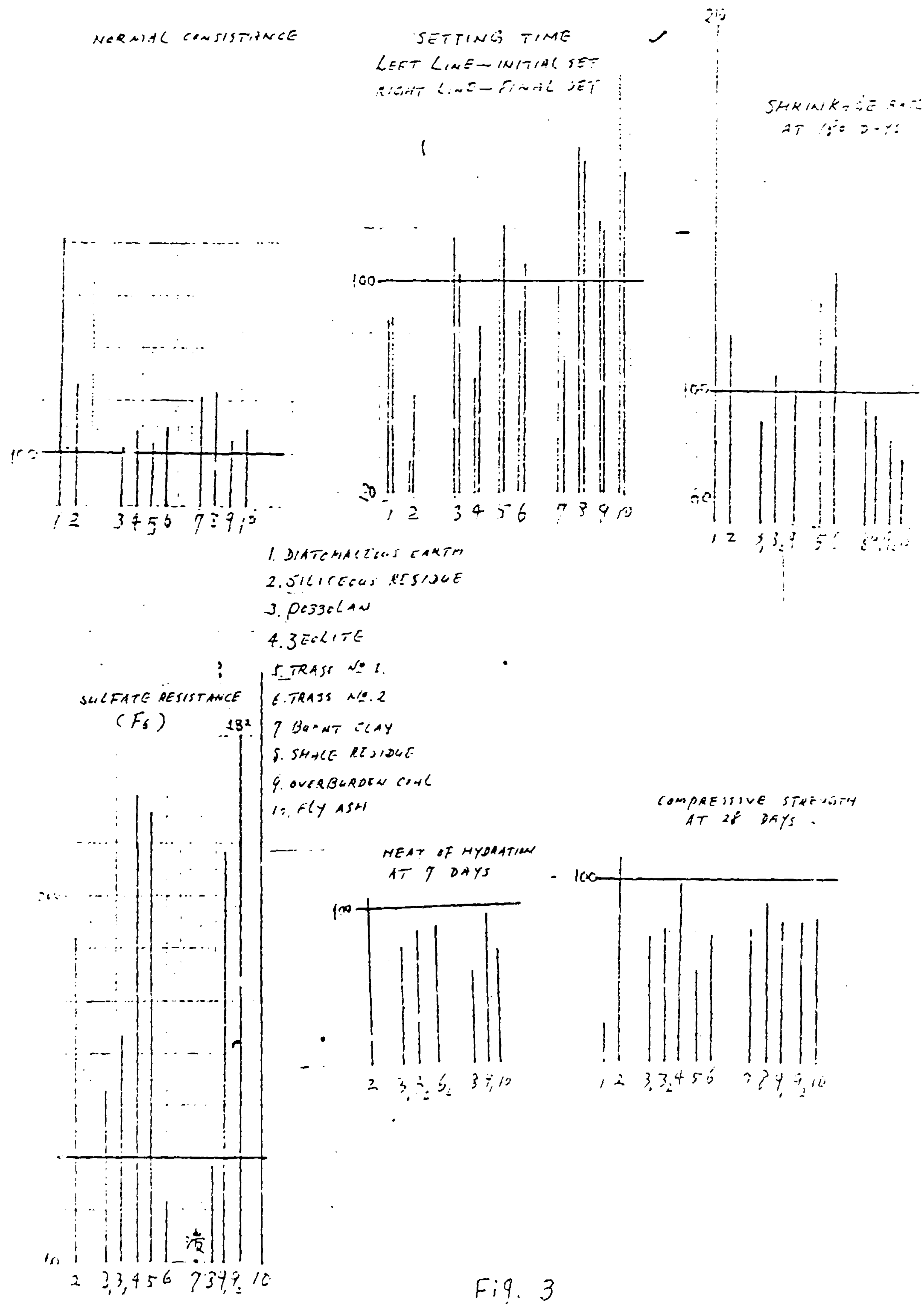

NORMAL CONSISTANCE
SETTING TIME
LEFT LINE—INITIAL SET
RIGHT LINE—FINAL SET
SHRINKAGE
100
1. DIATOMACEOUS EARTH
2. SILICEOUS RESIDUE
3. POZZOLAN
4. ZEOLITE
5. TRASS No 1.
6. TRASS No. 2
7 BURNT CLAY
8. SHALE RESIDUE
9. OVERBURDEN COAL
10. FLY ASH
SULFATE RESISTANCE
(F6)
HEAT OF HYDRATION
AT 7 DAYS
COMPRESSIVE STRENGTH
AT 28 DAYS

Fig. 3

graphically in Figure 3. Table 4 shows the mean strength values of mortars and concretes and illustrates the effects of different proportions of six pozzolanas (broken brick, spent oil shale, carbonaceous shale, burnt clay, volcanic ash and trass) on the properties of cement. It can be seen in Table 3 that according to Chinese classicification, hydrous siliceous materials themselves reqiure considerable amounts of water so the cemant made from those materials also reqiures much water. This group of materials have a certain effect on the acceleration of the set, but considerable reqiurement for water is unfavorable to strength and causes considerable dry shrinkage. And yet they have a good effect on the resistance to sulfate, because those materials possess high chemical activity and a very large internal surface area which can absorb a large amount of $Ca(OH)_2$. Nevertheless, difficulty arises in using these materials because of large water reqiurement. Volcanic glassy materials and burnt clays also reqiure much water, but they do not need as much water as hydrous siliceous ones. Meantime, these two groups of materials have effect on the retarding of the set. So far as strength is concerned, burnt clays are a little better than volcanic glassy materials. The compressive strength of pozzolanic cement made from volcanic glassy materials at 28 days is about 80% that of the base Portland cement while the cement made with burnt clays is about 84%. There is no obvious difference in sulfate resistance between these two groups of materials. As far as heat of hydration is concerned, the dilute action is considered to be predominant because of the short ages. If pozzolanas are added, the reduced percentage of heat of hydration at 3 days is the same as that at 7 days. However, as for hydrous siliceous materials, there is no indication of reduction of heat of hydration. It may be assumed that during cement hydration strong absorption occurs on these materials and heat of absorption is released.

The figures in Table 4 show that the strength of cement mortar concrete drops as the proportion of pozzolanas in cement increases. As the method of testing the strength of mortar in China has been changed from earth dry mortar to plastic mortar and the amounts of water used to make specimen increases, plastic mortar show a greater decrease in strength than earth dry mortars. In the case of concrete, the strength of concrete with a high water and cement ratio decreases more than that of concrete with a low water and cement ratio. At low temperatures, the strength of cement mortar containing more pozzolanas also decreases considerably. The bleeding rate quickly drops and water-retaining property improves as the proportion of pozzolanas increases.

It ought to be pointed out that good quality pozzolanas, especially natural ones were not discovered in large quantities in China in the past. Recently, natural zeolites have been found in China. It has been proved that natural zeolites are good pozzolanas. The greatest of its merits is that they can effectively improve the soundness of cement produced by shaft kiln, even more effectively than blast-furnace slags and other pozzolanas. (Table 5. Clinker as indicated in Table 5 contains 3.89% free lime and fails in the soundness experiment). They can also improve the strength of cement mortar at 28 days (Table 6). At the same proportion of 30%, cement containing zeolite has the highest strength of 93% and cement containing other materials 70-80%, although the strength of the former at early ages is relatively low, lower than that of cement containing slag or even other pozzolanic materials.

Table 4.

Item			proportion of pozzolanas (percentage)				
			0	15	20	30	40
EARTH-DRY MORTAR	COMPRESSIVE STRENGTH	3 days	342/100	286/84	272/80	226/67	170/50
		7 days	445/100	389/87	363/82	314/70	248/56
		28 days	581/100	530/91	512/88	476/82	393/68
	TENSILE STRENGTH	3 days	26.1/100	23.1/89	22.7/87	19.6/75	16.1/62
		7 days	29.2/100	26.9/92	26.3/90	23.6/81	21.1/72
		28 days	34.3/100	33.5/98	32.9/96	31.2/91	29.6/86
PLASTIC MORTAR	COMPRESSIVE STRENGTH	3 days	273/100	224/82	176/64	146/53	114/42
		7 days	361/100	290/80	241/67	201/56	158/44
		28 days	486/100	425/88	356/73	308/64	261/52
	BENDING STRENGTH	3 days	55.1/100	46.3/84	39.2/71	33.5/61	25.1/46
		7 days	65.6/100	55.8/85	49.2/75	43.2/66	35.7/54
		28 days	78.1/100	71.2/91	64.4/83	59.1/76	52.2/67
COMPRESSIVE STRENGTH OF CONCRETE	W/C=0.55	7 days	156/100	135/87	133/85	109/70	89/57
		28 days	250/100	217/87	231/92	190/76	151/61
	W/C=0.70	7 days	126/100	100/79	89/71	70/55	64/51
		28 days	183/100	150/82	138/75	117/64	101/55
CEMENT STRENGTH UNDER LOW TEMPERATURE (12°C)	COMPRESSIVE STRENGTH	3 days	236/100	195/82	161/67	-	-
		7 days	366/100	316/86	267/73	-	-
	BENDING STRENGTH	3 days	56.7/100	48.9/86	44.2/78	-	-
		7 days	69.3/100	61.4/88	58.6/85	-	-
Bleeding rate%			33.6	26.3	24.5	17.4	11.6

Note: Numerator is the strength value determined, demominator is the relative value (with the strength of the Portland cement without pozzolanas as 100%).

Table 5. Soundness of cement containing different blended materials

material / proportion	zeolite 1	zeolite 2	slag	carbonaceous shale	standard sand
10	fail	fail	fail	fail	-
20	OK	OK	fail	fail	fail
30	OK	OK	fail	fail	-

Table 6. Effect of blended materials and their proportion on the strength of cement

Age	Blended material	Proportion of blended materials (%) 0%	15	30
	slag	100	85/90	50/64
3 days	volcanic ash	100	82/88	53/64
	fly ash	100	-	51/58
	zeolite	100	64/83	53/61
	slag	100	87/92	58/71
7 days	volcanic ash	100	86/88	58/68
	fly ash	100	-	52/65
	zeolite	100	80/88	60/73
	slag	100	96/95	77/82
28 days	volcanic ash	100	89/92	65/77
	fly ash	100	-	66/70
	zeolite	100	110/103	93/93

Note: The numerator is the percentage of compressive strength and the denominator is the percentage of bending strength (with the strength of cement without pozzolanas as 100%).

3. Research on the action of pozzolanas in cement stone

The action of pozzolanas in the cement stone can be analysed from three aspects--chemical, physical and physico-chemical.

(1) Chemical action

The characteristic of pozzolanas is that when they mix with $Ca(OH)_2$ at ordinary temperature in the presence of water, hydrates having cementing property can be formed. Therefore, there is a secondary hydration process during the hydration of pozzolanic cement. As we know, the preliminary hydration is the process in which the hydration of clinker minerals takes place and preliminary hydrates are formed. By the secondary hydration is meant that the process in which preliminary hydrates react with the active SiO_2 and Al_2O_3 in pozzolanas to form secondary hydrates. These two processes take place alternatively.

(A) Combination of pozzolanas

Pozzolanas, like natural zeolite, have a strong ability to absorb $Ca(OH)_2$ during the hydration process. In order to determine whether such absorption is mainly physical absorption or chemical combination, we made an experiment as follows: The residues of the natural zeolite and ground quartz sand which had absorbed lime were boiled for 6 hours in the saturated NaCl solution and then they were filtered. Next, the filtrate was drawn out and the CaO content titrated. The result of this experiment showed that only 23.8% of the CaO absorbed by zeolite had been replaced by NaCl, which means that most of the CaO absorbed had undergone chemical action. On the contrary, most of the CaO absorbed by ground quartz sand was in the state of absorption and consequently had been easily replaced (Table 7).

Table 7

material	After 5 treatments with lime at $40^{\circ}c$ in ten days (mg CaO/g)	CaO in solution which has been treated by NaCl solution (mg CaO/g)
zeolite	138.8	33/23.8%
ground quartz sand	14.6	9/66.2%

X-ray diffraction analysis showed that the characteristic peak of zeolite mineral had undergone great changes after the material was treated

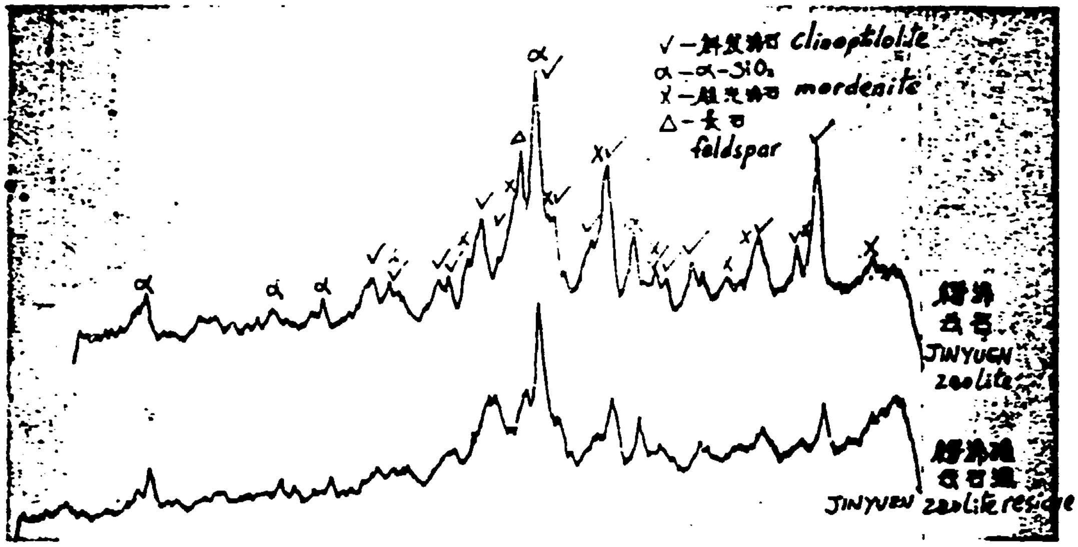

clinoptilolite
α-SiO_2
mordenite
feldspar
JINYUEN zeolite
JINYUEN zeolite residue

Fig. 4-1

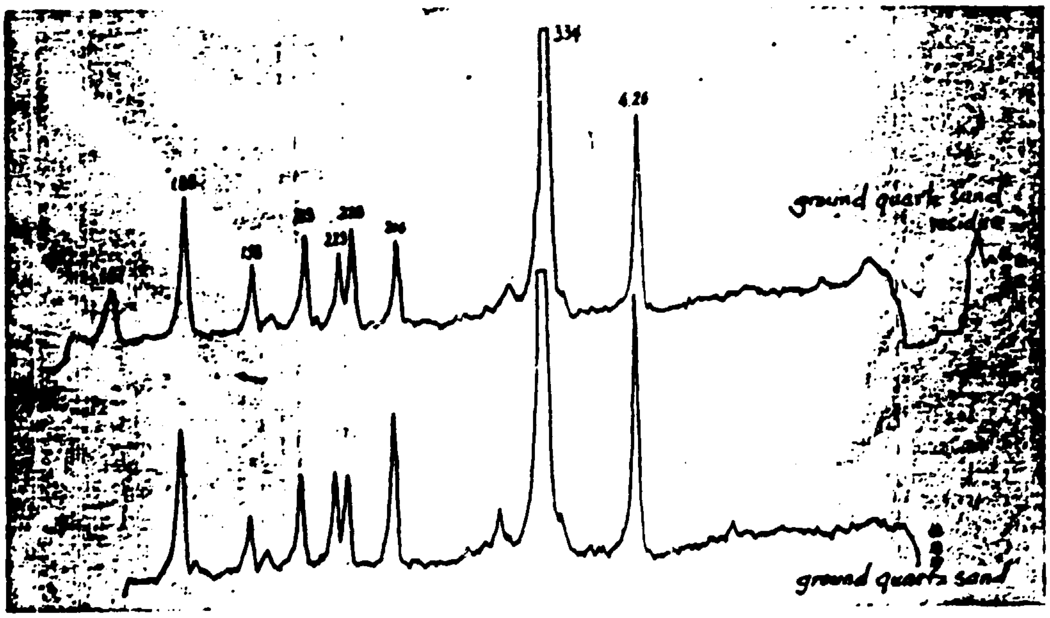

3.34
4.26
ground quartz sand residue
ground quartz sand

Fig. 4-2

five times with lime at 40^{o}c in ten days, while the X-ray diffraction pattern of ground quartz sand after treatment remained unchanged.(Fig. 4) This again proved that chemical combination between zeolite and Ca(OH) had taken place.

Fig. 4.

(B). Water of combination and $Ca(oH)_2$ content

The hydration process of cement can be shown by the change of the combined water and $Ca(oH)_2$ content in the cement stone. The theoretical value of the combined water required for the complete hydration of cement without any blended materials is 22.7%. But in fact, the complete hydration of clinker can not be achieved for varions reasons. Therefore, the amount of combined water is usually lower than the thoretical value. However, the value can reflect the degree of hydration. As pozzolanas have been added to cement, the corresponding amount of clinker decreases. So the amount of combined water of pozzolanic cement is smaller than that of the base Portland cement. If we deduct the amount of blended materials and calculate just the unit weight of clinker in cement, the combined water of pozzolanic cement will be greater than that of cement without blended materials (Table 8).

Table 8

Cement and proportion of blended materials	Amount of combined water(%) 7 days	28 days	180 days	$Ca(OH)$ content(%) 7 days	28 days	180 days
Base Portland cement	11.39/9.96	12.64/8.99	14.03/9.52	10.75/7.33	12.30/8.41	13.63/9.44
Cement with 30% zeolite	10.10	11.79	13.63	8.25	9.29	8.51
Cement with 30% fly ash	9.79	11.80	14.58	9.15	10.14	8.16
Cement with 30% ground sand	9.51	11.46	13.29	9.37	11.66	12.10

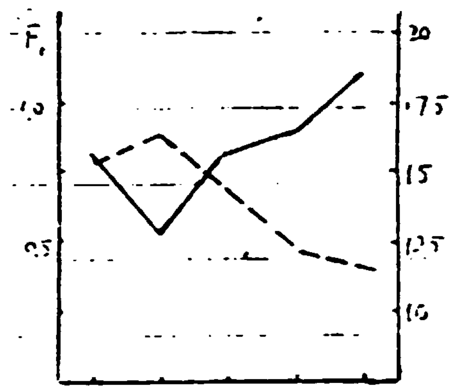
This can be attributed to two reasons: first, the addition of blended material increases the water and clinker ratio and accelerates the hydration of clinker; and second, pozzolanas react with $Ca(OH)_2$ released during hydration of clinker. The reaction also accelerates hydration. This effect is also reflected by the change of the $Ca(OH)_2$ content in cement stone..The $Ca(OH)_2$ content in cement stone grows as the age increases in the first 28-day period, but after 6months, the $Ca(OH)_2$ content in pozzolanic cement stone is reduced while the $Ca(OH)_2$ content of the cement containing inert material like ground sand rock keeps increasing in the same condition. This demonstrates that pozzolanic materials keep reacting with $Ca(OH)_2$ released during hydration of clinker, only the speed of $Ca(OH)_2$ absorption by pozzolanas at early ages is slower than the speed of $Ca(OH)_2$ release from clinker. But at long ages, the speed of absorption is greater than the speed of release. This expains why pozzolanic cement has low strength at short ages, high strength at long ages and good sulfate resistance.

(2). Physical action

The macroscopic performance of cement concrete depends on hydrated products, but more on the paste structure in connection with pore distribution and solid phase products [1].

Table 9.

Material	Thecontent of proes larger than 15 m %	Corrosion resistance coefficient (F1)
base cement	15.3	0.81
with 20% zeolite	11.5	1.11
with 20% fly ash	12.3	0.90
with 20% shale residue	14.6	0.82
with 20% ground sand	16.4	0.53



Base cement, with ground sand, with shale resisdue, with fly ash, with zeolitic

Fig. 5.

Table 10.

Material	Internal surface	Relative value of tensile strength			Relative value of dry shrinkage
	Area(M^2/g)	7 days	28 days	90 days	28 days
Base cement	-	1.00	1.00	1.00	1.00
with 30% zeolite	84.6	0.86	1.08	1.17	1.65
with 30% shale residue	10.1	0.80	0.96	0.97	1.47
with 30% liquified residue	4.9	0.70	0.91	0.96	0.86
with 30% fly ash	4.6	0.68	0.83	0.82	0.77

We investigated the physical action of pozzolanas from the aspect of pore structure. By means of the low pressure mercury pyrometer, we determined the content of pores with size >15 μm in cement mortar specimen. Pores of this range have an important effect on cement performance, because to start with, corrosion resistance, frost resistance and permeability are all affected by these pores. It can be seen in Table 9 that the content of pores in pozzolanic cement mortar (larger than 15 μm) is less than that of the base Portland cement mortar. Fig. 5 shows the good relation between the corrosion resistance coefficient (one month) and porosity of mortar (larger than 15 μm). This relationship is certainly not accidental. The high corrosion resistance coefficient results, on the one hand, from the decrease of the $Ca(OH)_2$ content due to chemical reaction of pozzolanas, and, on the other hand from the entry of no corrosive medium due to reduced pores in mortar.

(3). Physicochemical action

Generally speaking, pozzolanas has quite a large internal surface area and consequently, large surface energy and good absorption ability. For this reason, cement performance is affected. For instance, by adding pozzolanas the adhesive power between cement paste and sand is raised. In this way the resistance ability of the specimen to rupture, as shown in tensile strength, improves (Table 10).

If pozzolanas had no such effect on cement stone, the tensile strength of cement with 30% pozzolanas would be about 0.70 that of cement stone without pozzolanas. As a matter of fact, the relative value of the tensile strength is above 0.70 even at the short age (7 days). The value increases with the increase of the internal surface area. Of course, the large internal surface area causes an increase in absorption ability and water requirement. This may bring about an increase in the shrinkage of specimen, affect frost resistance and result in other unfavorable effects.

Undoubtedly, pozzolanas by no means have only one action in cement stone, but three existing simultaneously. The problem is which action is decisive. It can be assumed that at short ages physical action and physicochemical action play a more important role, while at long ages chemi. .l one is more important.

Evaluation of the quality of pozzolanas

1. Brief introduction to standards in different countries:

Main items required for the quality of pozzolana by the specifications of about ten countries are shown in Table 11. It can be seen that they vary greatly from one another. Some of the specifications such as those of ISO and France etc. are rather simple. pozzolanic property being determined only by one experiment while some of them are quite complicated, such as those of ASTM,. which require several items.

Pozzolanas differ from slags in how to evaluate the quality, which means that each country has its own crieterion. However, nearly all the slag specifications of various countries determine quality by chemical composition. This proves that no unanimous opinion has been reached on the method for evaluating the quality of pozzolanas. The reason is perhaps that pozzolanas have an extensive source and a great variety unlike slag; moreover, there is no proper method of evaluation. However, in spite of that, requirements for pozzolanas are defined in all specifications in two respects, one is to limit the content of harmful substances, mainly ignition loss (especially for artificial material),

TABLE 11. Fig. 11.

COUNTRY OR ORGANIZATION	DESIGNATION NOS.	REQUIREMENT FOR CHEMICAL COMPOSITION					TESTING METHOD FOR ACTIVITY				
		SiO_2	L.O.I	SO_3	CaO		LIME ABSORB METHOD	ISO METHOD	LIME MORTAR STRENGTH	CEMENT MORTAR STRENGTH	SETTING TIME FOR WATER RESISTANCE
ISO	ISO R863-68							Δ			
CHINA	DEPARTMENTAL SPECIF. 103-56		Δ	Δ			Δ		Δ		
	GB1596-79		Δ	Δ						Δ	
UNITED STATES	ASTM C618-78	Δ	Δ	Δ					Δ	Δ	
	SS-C-2086(52)									Δ	
CANADA	CSA A 363-76		Δ	Δ					Δ	Δ	
WEST GERMANY	DIN 51023-79	Δ	Δ	Δ					Δ		
SOVIET UNION	ГОСТ 6269-63	Δ	Δ	Δ			Δ				Δ
FRANCE	FD P11'15-A13-64							Δ			
BRITISH	BS 3892-1965		Δ	Δ				Δ			
	BS 4550-1970							Δ			
AUSTRIA	ÖNORM B3320(60)	Δ		Δ	Δ				Δ		Δ
	ÖNORM B3319(62)		Δ	Δ						Δ	
JAPAN	JIS A6201(78)	Δ	Δ	Δ						Δ	
HOLLAND	N 488 (1932)								Δ		
ROMANIA	STAS 2241-68	Δ									
AUSTRALIA	AS1129-1971		Δ	Δ							
CZECHOSLOVAKIA	ČSN 72-1120(1978)						Δ	Δ	Δ	Δ	
BULGARIA	БДС 166-72		Δ	Δ			Δ				
TURKEY	T.S 639-68	Δ	Δ	Δ	Δ					Δ	
INDIA	IS 3812(1966)	Δ	Δ	Δ					Δ	Δ	

NOTE: ГОСТ 6269-63 was replaced by СТ 21-9-74.

the SO_3 content and soluble alkali (in some of the specifications). The other is to estimate the active constituents in pozzolanas. Harmful substances in excess such as SO_3 and soluble alkali are limited to prevent the expansion they may incur. This problem may as well be solved by physical test. Requirements for such a test have been defined in some specifications, such as ASTM, CSA and IS. However, physical test takes time and therefore it is not so convenient and quick as chemical test.

Since the high value of ignition loss brings a bad effect on the durability of the concrete, ignition loss of fly ash is limited in all countries. which differ in the value, though.

The methods for testing the activity of pozzolanas vary from country to country and even the same method used by some countries differ in requirement. The methods can be divided into two groups. The first group is the chemical method as employed by ISO, France, the Soviet Union and Bulgaria etc.. The principle is that the CaO content in the solution is determined and by the change of the CaO content the activity is evaluated. The second group is the physical method. The activity is evaluated by the value of mechanical strength whether it is lime mortar strength or cement mortar strength. In very few countries, it is evaluated by the "Final setting time" and "Water resistance" of the pozzolana-hydrated lime paste. To test the activity of pozzolanas, most countries tend to use the physical method, especially the strength method, because it is more apparent and convenient, advantageous to production and application. Its drawback is the long length of time. In general, it takes 28 days and over to obtain the result. The chemical method usually obtains a different result from the strength method. Suppose the lime absorption method is employed, material having a high absorption value does not necessarily have high strength. On the contrary, material with a low absorption value may have high strength. There is a significant tendency in the use of chemical method, i.e. the method suggested by Fratini after being improved and recommanded by ISO in 1968, was adopted by Italy in 1968. Britain in 1970 and Czechoslovak in 1978 as the standard method. The main point of this method is to determine whether the solution in contact with the set cement is saturated with calcium hydroxide or not.

We have tried this method and found that this method saves time. It takes only 7 days to get the result because of using accelerated curing. It is accurate enough to distinguish between active and non-active materials. The method is simple and convenient, easy to use. However, as mentioned above, its drawbacks is that the result sometimes disagrees with that obtained by the strength method. It can not be applied to fly ash with a high Cao content. Test procedures also remain to be improved. In short, this method needs further study.

(2) Specification in China

As shown in Table 11, China has two specifications for pozzolanas: " Pozzolanas Used in Building Material" (103-56), a specification at the ministry level,"Fly Ash Used in Cement and Concrete" (GB 1596-79), a national standard.

By research we find that excessive So_3 content in pozzolanas, especially artificial pozzolanas, may cause steel corrosion and ettringite expansion which reduce the durability of the building. We have such records. Too much ignition loss in fly ash will reduce the frost resistance of concrete. If ignition loss is below 12%, strength is hardly affected.

Therefore, as in most specifications in the world, the amount of SO_3 and ignition loss are limited in these two chinese standards. The content of soluble alkali remains undefined in the Chinese specification, because pozzolanas are mainly used as blended materials in cement production in China, while the national cement standard has defined the maximum proportion of pozzolanas in cement at 50%, but in practice, the proportion usually is about 30%. When converted to the alkali content in cement, the figure is quite low.

The chemical composition of SiO_2 is not defined in China's specification, because there is no fixed relation between the SiO_2 content and pozzolana quality.

We have done some research work on the method of testing activity, and discovered that the lime absorption method defined in the ministerial specification 103 - 56 can not determine the actual activity of pozzolanzs. For instance, the lime absorption value of fly ash is much below the value defined in the specification, but the performance of cement made from such fly ash is good, as it has high strength at long ages and good resistance to sulfate. Similarly, cement performance has nothing to do with the content of soluble SiO_2, soluble Al_2O_3 and insoluble residue in pozzolanas. So it is nor advisable to use them as criteria for evaluation of pozzolanas activity. The ISO method and the method used by the Soviet Union can only evaluate qualitatively whether pozzolanas are active or not, but can not give the quantitative value. The result achieved by the lime mortar strength method quite agrees with that achieved by the cement mortar strength method. However, the lime pozzolana mortar strength method has its shortcomings. First, the strength value of plastic lime mortar is low, which comes to only 10-30

kg/cm^2 at 7 days and 30-50 kg/cm^2 at 28 days (that of cement containing zeolite is higher, 50-100 kg/cm^2 at 7 days and 140-180 kg/cm^2 at 28 days). Second, it has a considerable test error. Third, the test method is imperfect. For instance, the amount of water used is not easy to be fixed. As the flow table is used to control the flow value in the range of 120-130 mm, the water and mixture ratio of lime mortar for various pozzolanas can be changed from 0.46 to 0.65 so that it is difficult to compare the strength value. Besides, the requirement for the quality of hydrated lime is so high that it is not easy to meet. Through the above comparison, we find that the cement mortar strength method is much better than the lime mortar method in determining the activity of pozzolanas. This method is linked directly with cement production, advantageous to application in practice. Therefore, it has been accepted by the Chinese specification as the standard method for testing activity of fly ash. We are planning to use the same method for the revision of pozzolana specification being carried on now. Of course, it is necessary to conduct other research work in order to find an accurate, quick and simple method of evaluating the activity of pozzolanas.

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