Advanced Materials Research Vol. 687 (2013) pp 204-212
Online available since 2013/Apr/24 at www.scientific.net
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doi:10.4028/www.scientific.net/AMR.687.204

Properties of polymer modified concrete in fresh and hardened state

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Keywords: polyurethane; epoxy resins; fresh concrete; workability.

Abstract. It was carried out a study on the properties of polymer modified concrete (PCM) in fresh and hardened state. It was used three types of polymers: epoxy resins, polyurethane and methylcellulose in different percentages and different water cement ratio.

The main objectives was to improve workability and rheological behavior of these mixtures in fresh state and mechanical strength tests on hard concrete. Has been investigated the polymer influence on compression strength and flexural strength and analyzing the time evolution of these strengths and participation of polymer in the microstructure formation.

Introduction

Polymer modified concrete is mainly obtained by incorporating various polymeric materials in fresh concrete mixtures. The combination of mortar or concrete with polymers or polymer based materials may find out useful properties of both components, giving excellent strength, durability and better flow properties. A number of thermoplastic or thermo-type polymers are used in various forms, such as liquid resins, powder and latex redispersibile, water soluble polymers or copolymers to change concrete and mortar [1].

Concrete and polymer concrete are visco-elastic-plastic systems that can be characterized in terms of rheological through the following parameters: yield stress and plastic viscosity. The study of Yield stress may provide information about the workability.

Polymer modified concrete improves also the mechanical strength and durability of constructions made out of such a material. This type of materials are used to form waterproof coatings, reduce water infiltration, thin layers used in masonry repairs or resistance of building structures [2]. But the builders are skeptical about use of these types of materials either the small number of research carried out on these materials or due to their higher costs.

In Japan, the most used materials for repairs and finishing are polymer modified mortars and polymer concrete is rarely used due to high cost ratio - performance [3]. However, polymer modified concrete is widely used in the United States for coatings bridges. The first and the only impediment to use these types of materials are high costs but they offer high properties, high durability and so, consequently, they will not require frequent maintenance [4].

Reactions between polymers and cement particles in PCC have a grate influence on their performance and they have been extensively studied in recent years, such as concrete with vinyl polymers [5], concrete with polyvinyl chloride [6], polystyrene [7], or phenolic resins [8].The properties of polymer-concrete are influenced by the chemical nature, the type, and the ratio used for the polymer.

In this paper, we will study different types of concrete polymer microstructures, their flow and mechanical properties.

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Materials

The type of the cement used was Portland 42.5 R according to DIN EN 196-1. Methylcellulose - MC, epoxy resin and polyurethane, added to fresh concrete mixtures. Polymer solubility in water is mainly determined by the viscosity of the solution. They are dissolved in water according to the dosage recommended by the manufacturer. It was found that at room temperature all solutions of polymers form transparent and stable films.

It has been established as standard samples of cement paste to have the ratio w/ c = 0.4 Polymers were added in the following proportions:

- Methylcellulose - 0.2% and 0.6% by weight of cement,
- Epoxy resin - 1%, 5% and 10% by weight of cement,
- Polyurethane - 10% by weight of cement.

Were made also investigations on both micro and polymer compositions containing the standard composition.

Results and discussion

In this study were made the slump test for PMC and ordinary concrete to establish the influence of polymer additives used on its workability.

Table 1 reports slump for ordinary cement concrete with various water cement ratio and it was also established the influence of amount of water on workability. These tests were performed in order to choose a composition that shows poor flow properties and workability. Thus, we can determine the influence of polymer on these properties.

From the above results we conclude that concrete with water cement ratio w/c = 0.4 and 0.43 cannot be included in any class of workability, which shows that a large mechanical work is necessary to poor this materials.

Table 1 : Slump test for ordinary cement concrete

Water/cement ratio	Slump, mm
0.5	34
0.47	31
0.45	18
0.43	6
0.4	4.5

In case of the compositions containing polymeric additives, the slump varies depending on the amount of polymer used and their type

Table 2. Slump test for polymer cement concrete with water / cement ratio = 0.4

Mixtures	The additives proportion	Slump for PMC with w/c ratio = 0.4
PMC with epoxy	1%	5 mm
PMC with epoxy	5%	8 mm
PMC with epoxy	10%	67 mm
PMC with Methylcellulose	0.2 %	36 mm
PMC with Methylcellulose	0.6%	58 mm
PMC with Polyurethane	10%	7 mm

From these data we can notice that an epoxy resin quantity below or by 5% do not improve the workability, and the polyurethane is not recommended to be used for concrete mixtures. The mixes without polyurethane within their composition are more viscous than those ordinary ones.

Figure 2 presents graphical processing for values of slump test presented in table 2, reports for mixture studied properly w/c equal to 0.4.

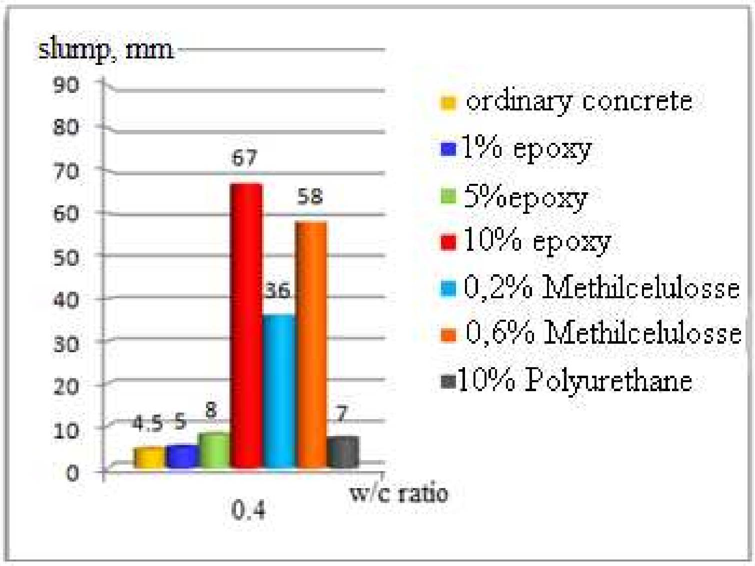

Fig. 2 Comparative analysis of conventional concrete and polymer concrete

The epoxy resin has the greatest influence on workability. Fig. 2 shows that the best results for slump were obtained with methylcellulose and 10% epoxy resin, which suggests that the wotk with PCC containing such polymer is easy, does not require a long vibration and we can cast into complex shapes.

We made also tests to determine the flow properties of these materials. It was determined cement paste flow through the hole of Marsh cone and with rheometer were made rheological tests for provide a better accuracy for yield stress values obtained .

Figure 3 shows the flow times of cement paste in different proportions of epoxy resin at different times from the water addition, as well as ordinary concrete - without resin.

Water cement ratio for all tests performed in this study remained 0.4. It has been made flow tests at different time intervals (3, 10, 20, 30 and 60 minutes after water addition) only for mixtures containing epoxy resin in proportions of 5 and 10%. Both standard and cemet paste containing 1% polymer is very high, thus making the work difficult and could not perform flow tests at different time intervals.

It can be seen that by adding epoxy resin in proportions greater or equal to 5%, the flow times have values in the range 11-36 seconds, which indicates that the polymer has a beneficial effect on the workability of concrete. They have done tests at all times set, the results are satisfying. The point of interest was the material flow at 30 minutes after water addition. There has been a decrease in flow time due probably latent period of development of hydration reactions when the newly formed hydration products covers unhydrated particle and prevents water penetration to the particle surface.

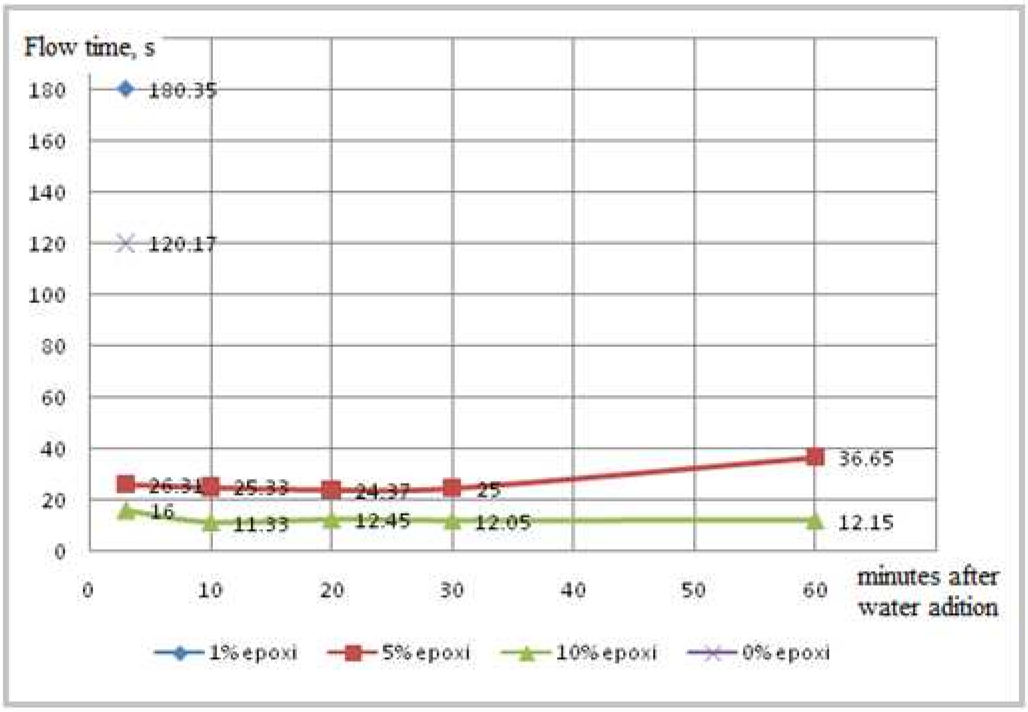

Fig. 3. Flow for diffrent cement pastes

The major difference during the flow is shown at 30 minutes after water addition, the flow of paste containing polymer is lower than the time obtained at 3 minutes after water addition thus establishing that one of the actions polymer is to slow down the hydration of cement.

The polymer covers the cement particle surface which begins to hydrate, forming a matrix of interconnected etringit and polymers, thus preventing water to reach the particle.

As the water penetrates the the matrix and reach the surface of unhydrated cement particle, new reactions take been, new products appear which cause cracking in polymer and etringit matrix and the hydration of mineralogical compounds with hydraulic activity from cement grain (calcium silicates) is carried out.

Because of this latent period it was decided that the yield stress determination to be made at 30 minutes after water addition.

In case of mixtures containing polyurethane and methylcellulose could not be determined the flow of material through Marsh cone, because in the presence of these types of polymer, a large amount of air is entrained into the paste.

It is considered valid that the rheological properties of concrete can be determined by studying cement paste with rheometer because of rheometer geometry is not possible to due the introduction of aggregates in cement paste.

Figure 4 shows the yield stress of studied mixtures at 30 minutes after water addition. Thus, for ordinary concrete without polymer (marked on the figure with the symbol OC - ordinary concrete) that has a w / c ratio equal to 0.4 yield stress value, this is 486 Pa, an unsatisfactory value for a high performance concrete, because a high yield stress leads to concrete segregation due to insufficient water. In such conditions, the material becomes viscous and it is possible that the cement hydration not be complete.

Determinations made on regular concrete highlight that an insufficient amount of water produced difficulties in implementing and adversely affect on strength, due to incomplete hydration and, consequently, the development of porous structures to strengthen. By contrast, the yield stress on the composition containning a ratio of 10% polymer has the lowest value, because of the improving workability of fresh material as well as due to dispersant action of the polymers on cement particles. Polymer action is seen by the formation of a thin layer of electrical charges on the surface of the cement particle, and thus particles will be rejected. This rejection produces a better flow, a lower yield stress and provides a longer period to put material into work and casting of special shapes.

Mixtures containing methylcellulose shows a higher yield stress than the reference concrete so it is not recommended to obtain a high performance concrete using this polymer. This negative effect is reflected on strength, as we will see below.

Polyurethane demonstrates the highest value of yield stress. Besides, flow tests, slump and strength was unsatisfactory. It is not recommended the usage of this type of polymer for obtaining a high performance concrete, due to the impossibility to cast in shape. On the other side, this polymer has the capacity to achieve rapid hardening. It is possible that it works very well when concrete is obtained at high water cement ratio, which may be used for manufacturing floors, concrete requiring fast setting and floors which in service are not subjected to very high loads.

In Table 3 are presented compressive strength of reference samples containing no polymer and have water / cement ratio equal to 0.4. It can be seen that over time compressive strength increases.

It can be seen that the compressive strength for concrete sample that has a water cement ratio equal with 0.4 are small, because such water / the ratio cannot achieve good compaction of materials, this material are viscous and there is a large air content within these compositions.

There have been also attempts experimantal tests on some concrete compositions with polymers in various proportions to determine their influence on both workability and hardening structure formation and development strength, table 3.

As described above, the maximum compressive strength of concrete without polymer is 47.8 MPa, obtained at 28 days after casting. In case of polymer concretes were kept the same water / cement ratio (0.4).

It was chosen three proportions of epoxy resin because it was obtained the best results in tests for workability with this resin. The first studied resin ratio was 1% by weight of cement, and were obtained compressive strength approximately equal to that of standard concrete. Hence, it can be concluded that such a proportion of polymer is insufficient to obtain significant improvement in resistance but increased the cost of production of concrete. The maximum value obtained for compressive strength was 52.8 MPa. Also in this case compressive strength values increase in time. In case of a proportion of 5% polymer it is obtained a higher mechanical strength, much higher than the values obtained for ordinary concrete as well as for concrete with 1% polymer. There is an increase in time, and at 28 days from casting it is obtained a maximum of 56.3 MPa. But this composition do not develop either adequate strength to high performance concrete class. The best results for compression strength are obtained in composition 10% epoxy resin. This composition can be cought in this class of high performance concrete obtaining a maximum of 77.4 MPa and also it can see an increase in time resistance. This mixture has also shown both good workability and high flow values.

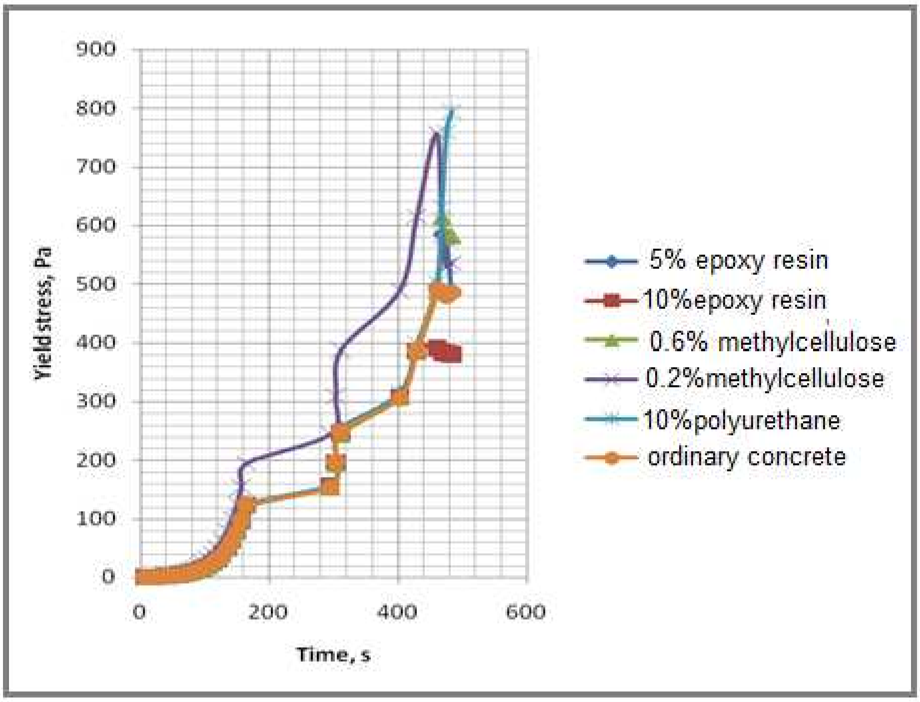

Fig. 4 Yield stress of mixtures studied at 30 minutes from addition of water.

Methylcellulose tends to become gel and because of this in concrete structure is involved a substantial amount of air, which is the main cause of the existence of structural holes. Hence, the existence of the modest mechanical resistance value, even if the workability of material is improved. The results show that the resistance develops in the range 40-50 MPa, comparable to those of concrete without polymer. The only benefit of using methylcellulose is to improve workability.

In the case of mixtures containing 10% polyurethane resistance is lower than those obtained by the above mixtures. Workability of material is difficult, it is also a fast polymerization.

Table 4 presents the flexural strength, where it is found that polymer concrete develop greater values of resistance than concrete without polymer, the polymer has the tendency to make flexible points between concrete components. The best strength was obtained, as expected, in the case of mixtures with epoxy because it shows a specific trendency to form elastic bridges between concrete components, which is also supported by microscopic investigations conducted.

Methylcellulose and polyurethane tend to fill air gaps existing in the structure of new formation products appeared in this context. Higher flexural strength concrete was superior to ordinary concrete for all the PMC mixtures, resulting that the polymer, by its nature, improves the elasticity of material.

In the following figures are shown the microstructures of reference concrete, as well as those with polymer. Figure 5 presents the usual concrete where it can be seen the products of hydration overgrown and how they include the aggregate particles. No elastic formation is observed, but the way in which the new hydration products cover both aggregate and cement particule. Figure 6 shows a concrete structure containing epoxy resin. The structure is more uniform and epoxy resin tends to form elastic bridges between concrete constituents, leading to increased mechanical strength. Products of hydration are less developed due to the tendency of the polymer to produce a thin layer of cement particle surface, thus slowing hydration reactions. When polymerization starts, the polymer is placed between particles, improving especially the flexural strength of the material.

Table 3 Compresive strength of concrete

Mixture, w/c ratio	1day [Mpa]	3days [Mpa]	7days [Mpa]	28days [Mpa]
Ordinary concrete, w/c = 0.4	17.32	31.50	26.60	42.00
	18.26	27.10	38.00	47.20
	19.28	34.10	45.40	46.90
	20.4	35.80	42.20	47.80
	17.86	33.20	44.20	45.80
	16.54	36.70	42.00	43.90
PMC with 1% epoxy resin , w/c = 0.4	16.32	31.80	26.60	42.00
	17.28	25.10	38.00	46.20
	19.28	34.10	39.40	40.90
	18.4	35.80	38.20	44.80
	17.86	33.20	34.20	52.08
	16.54	36.70	42.00	44.20
PMC with 5% epoxy resin , w/c = 0.4	16.18	31.70	40.92	50.00
	17.92	36.00	44.48	52.30
	18.51	35.20	39.88	56.00
	16.41	36.40	42.68	55.40
	17.63	27.40	42.36	56.40
	17.99	27.30	44.12	56.30
PMC with 1% epoxy resin , w/c = 0.4	12.97	31.50	54.48	75.20
	13.22	28.80	49.90	78.20
	13.66	29.80	48.8	74.50
	12.99	28.20	57.70	76.20
	12.60	29.40	47.50	77.60
	12.96	29.40	56.80	75.20
PMC with 0.6% Methylcellulose, w/c = 0.4	11.52	27.90	28.60	33.40
	10.65	28.50	32.20	48.90
	10.54	27.60	36.50	49.50
	10.90	26.30	36.20	50.20
	10.60	28.40	33.50	48.70
	9.99	26.60	36.40	51.40
PMC with 0.2% Methylcellulose, w/c = 0.4	12.34	27.80	27.30	43.40
	11.26	26.50	35.20	38.50
	10.54	29.60	36.20	49.50
	9.95	28.30	32.90	49.20
	11.40	25.40	35.50	50.70
	9.89	29.60	36.90	50.80
PMC with 10% Polyurethane, w/c = 0.4	6.80	17.90	22.50	39.50
	12.65	16.50	24.60	40.20
	10.90	14.60	19.80	35.60
	11.00	19.80	25.60	42.50
	7.90	20.00	22.30	42.90
	8.50	19.70	23.50	42.10

Table 4 Flexural strength of concrete

Type of concrete	The additives proportion (%)	Flexural strength (Mpa)	
		7days	28 days
PMC with epoxy	1	3.7	16,8
	5	4,5	22,45
	10	7,2	27,96
PMC with Methylcellulose	0.6	2,9	23,56
	0.2	5,7	22,23
PMC with Polyurethane	10	3.6	17,4
Ordinary concrete	0	3.0	15,9

Figure 7 shows the structure of a concrete composition with methylcellulose. Because it tends to involve air with foam formed in addition, the material becomes more porous, weak points apear in the structure, while the tendency of methylcellulose is to polymerize inside these holes, but without filling them completely.

Figure 8 shows the microstructures of mixtures containing polyurethane. In these mixtures, it can also be seen a large number of air voids. Polyurethane tends, like methylcellulose, to polymerize inside these goals. All microstructures were performed at 28 days of hydration.

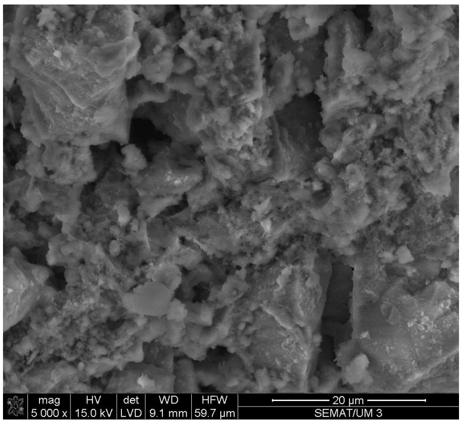

Fig. 5 Ordinary concrete 5000x

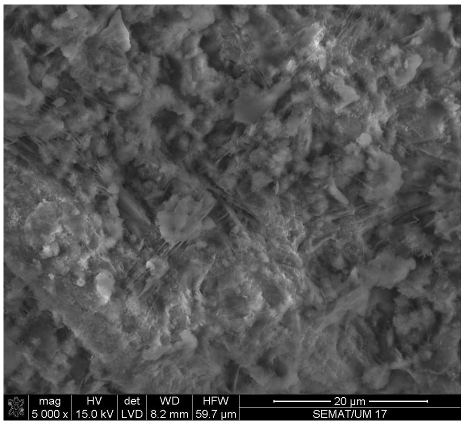

Fig.6 PCC with epoxy 5000x

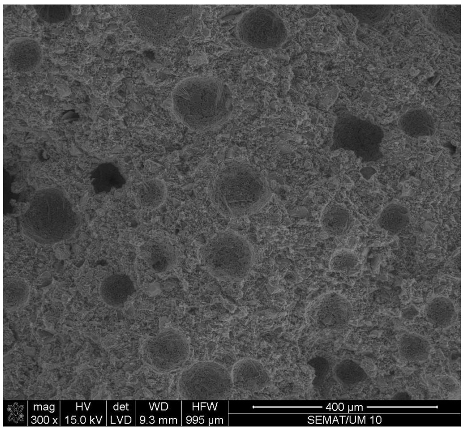

Fig. 7 PCC with Methylcellulose, mag 300x

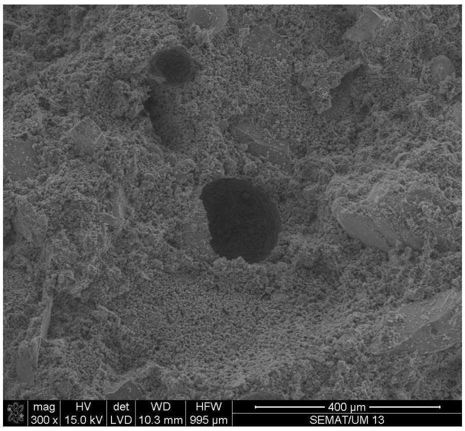

Fig. 8 PCC with Polyurethane, mag 300x

Conclusions

Composition containing 10% epoxy resin is characterized by improved workability, obtaining the best value for the slump test. At lower proportions of polymer addition, important effects are not visible in this context. Polyurethane is not recommended to be used in concrete compositions. Mixtures containing methylcellulose show a satisfying workability, but do not get mechanical resistance, as expected.

Methylcellulose and polyurethane do not lead to spectacular development of hardened concrete compressive resistance. The same conclusion can be drawn also from microscopic investigations of this mixture.

Higher flexural strength concrete was superior to ordinary concrete for all the PMC mixtures, resulting that the polymer, by its nature, improves the elasticity of material.

Acknowledgement

This work was partly financed by the European Social Fund through the POSDRU/CPP107/DMI1.5/S/77497 Program for PhD. Student
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10.4028/www.scientific.net/AMR.687

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