- Technical Paper -

THE EFFECT OF DIFFERENT ELECTROLYZED WATER ON PROPERTIES AND HYDRATION REACTION OF MORTAR

Liang WANG[*1], Kimitaka UJI[*2], Hisashi MOROZUMI[*3] and Minoru UEMURA[*4]

ABSTRACT

In this study, the effect of electrolyzed cathode water on the properties and hydration promotion of mortar was investigated by using two kinds of different electrolyzed water and ordinary tap water. The results showed that the single K^+ electrolyzed water in mortar can promote and stimulate the cement hydration to produce more $Ca(OH)_2$ amount, leading to a higher strength of mortar than ordinary tap water mortar. In contrast, the compound Na^+-K^+ electrolyzed water had a bad effect on cement hydration reaction and strength improvement of mortar for the long-term age.

Key words: compressive strength, $Ca(OH)_2$ amount, electrolyzed cathode water, hydration, mortar

1. INTRODUCTION

When a small amount of electrolyte is added into the water, the strong acid and alkaline electrolytic water would be generated at the anode and cathode side at the same time by electrical decomposition in a diaphragm type electrolytic cell. In addition, the electrolytic hypochlorite water would be generated by electrolytic decomposition in the electrolytic cell without diaphragm. When many kinds of electrolytes are added into the water to carry out electrolysis at the same time, the ionic environments of electrolyzed water produced at both sides of the anode and cathode will be more complicated. Taking advantage of the characteristics and functions of different kinds of electrolyzed water, the electrolyzed water has been widely used in food hygiene, environmental cleaning, medical and agricultural industries and so on. For example, the electrolyzed strong acid water has good sterilization effect, and the alkaline electrolyzed cathode water has a good rust decontamination ability on the lathe, metal, glass. So far, many researchers focused on the aspects about the sterilization and disinfection of electrolyzed water [1] [2].etc, but there are few researches about application in concrete industry to improve the properties of concrete. Sun, B. Q. [3] researched that the the total porosity of concrete mixing alkaline redox potential water decreased by 20%, and the carbonation depth of concrete at 28d decreased by 16% than that of normal concrete. If the electrolyzed water can be effectively used in the concrete industry, it can reduce the content of cement and save the construction cost, which has a good economic benefit and environmental benefit.

For different electrolyte solutions, the products of the cathode and the anode will be also different. In this study, in order to compare the effect of the electrolyzed waters produced from single electrolyte solution and compound electrolyte solution on the properties of mortar, two kinds of different electrolyzed cathode water and ordinary tap water were used, including K_2CO_3 electrolyzed cathode water and a kind of Potassium-Sodium compound electrolyzed cathode water. Because the hydration products of cement in mortar are mainly C-S-H gels and $Ca(OH)_2$, in this experiment, the degree of hydration reaction can be objectively characterized by $Ca(OH)_2$ amount. By the results of the strength and $Ca(OH)_2$ amount, the effect of electrolyzed cathode water on the properties of mortar and internal reaction mechanism would be determined. Fig. 1 shows the principle of electrolysis of K_2CO_3 single eletrolyte solution. It can be seen that, KOH is generated on the cathode, the water is decomposed into hydrogen and hydroxyl ions, it is a slightly alkaline solution; meanwhile, carbonic acid is generated on the anode, the water (H_2O) is decomposed into oxygen and hydrogen ions, it is a slightly acid solution.

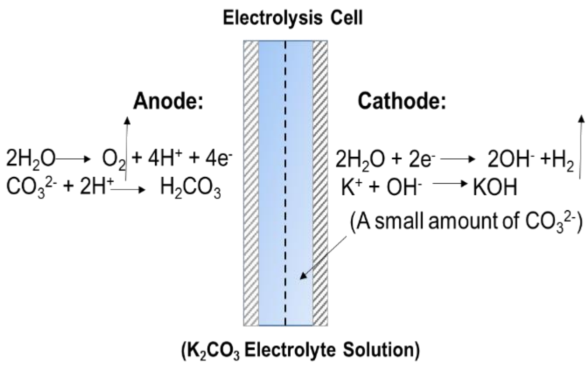


Fig.1 Schematic of principle of electrolysis

*1 Ph.D., Dept. of Civil Engineering, University of Tokyo Metropolitan University, JCI Student Member

*2 Prof., Dept. of Civil Engineering, University of Tokyo Metropolitan University, JCI Member

*3 Dept. of Electrolyzed Water Sales, AMANO Maintenance Engineering Co., Ltd, JAPAN

*4 Representative Director, UEXX Co., Ltd, JAPAN

2. EXPERIMENT PROGRAMS

2.1 Experimental Materials

An Ordinary Portland cement, which met the requirements of Japanese Industrial Standard (JIS) R5210 :2003 “Portland Cement”, was used in this study. The standard sand was used as fine aggregate. The water reducing admixture (WRA) which was diluted by 4 times and air entraining admixture (AE) which was diluted by 100 times in accordance with Japanese Industrial Standard for Chemical Admixtures for Concrete (JIS) A 6204 were used in this study to control the flow and air contents of different mortar.

Besides the ordinary tap water, two kinds of electrolyzed cathode water were both used in this study, which are the potassium (K^+) alkaline electrolyzed water (K_2CO_3 electrolyte solution) and Sodium-Potassium (Na^+-K^+) compound alkaline electrolyzed cathode water (Sodium salt and K_2CO_3 compound electrolyte solution). The water quality characteristics about the PH and ORP values of different water and admixtures were presented in Table 1. The “ORP” is short for Oxidation-Reduction Potential, which typifies the relative degree of oxidation or reduction of the medium as a comprehensive indicator. The PH and ORP meters were shown in Fig.2.

a) PH meter b) ORP meter

Fig.2 PH and ORP meter for water

2.2 Storage of electrolyzed water

From Fig.3, it can be seen that the PH value of electrolyzed water has a continuous declination with days under the condition of no cover, which would lead to the performance failure of electrolyzed water eventually; while the PH value of water with cover in tightly sealed container unchanged basically. Therefore, the electrolyzed water should be long-term stored in a sealed container.

Table 1 Characteristics of waters and admixtures

Type	Measured PH	Measured ORP	Mark
Tap water	7.51	343	TW
Electrolyzed water 1	9.74	179	KW
Electrolyzed water 2	9.68	224	NW
Water reducer	9.6	32	WRA
Air entraining	7.77	204	AE

* TW means the tap water from Hachioji city, Tokyo
* KW means the potassium alkaline electrolyzed water
* NW means Sodium-Potassium compound electrolyzed water

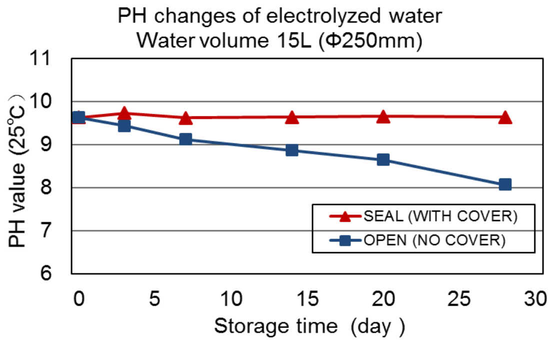


Fig.3 PH changes of electrolyzed water with days

2.3 Mix proportions

Table 2 presented the detailed mix proportions used in this study. The volume ratio of paste and sand in mortar was determined as 1: 1 in order to emphasize the changes of paste. The water to cement ratio (W/C) of 0.5 was used to prepare the specimens throughout the experimental program. Taking into consideration that the chemical characteristics of admixtures may have a certain effect on the performance of electrolyzed water mortar, the mortars were made in two series. Series 1 mortars TW-1, KW-1, and NW-1 were made as blank control group to be compared and analyzed, and without water-reducing and air entraining admixture. The flow and air content values of different mortar were also recorded. Series 2 mortars TW-2, KW-2, and NW-2 were made under the same condition of flow and air content in the main (The flow is 225±5mm ,the air content is 4±0.5%), with water-reducing admixture and air entraining admixture. Therefore, the effects of electrolyzed water and admixtures on the mixtures could be researched and determined.

Table 2 Mix proportions of mortar

Type	Mark	Water-Cement Ratio (%)	Unit Dosage(kg/m^3) Water	Cement	Sand	WRA (%) (*Cm)	AE (%) (*Cm)	Flow (mm)	Air content (%)
Series 1	TW-1	50	306	612	1315	0	0	–	–
	KW-1		306	612	1315	0	0	–	–
	NW-1		306	612	1315	0	0	–	–
Series 2	TW-2		304	612	1315	0.25%	0.50%	225±5	4±0.5
	KW-2		305	612	1315	0	0.50%	225±5	4±0.5
	NW-2		305	612	1315	0	0.50%	225±5	4±0.5

2.4 Experimental method

The specimens of mortar were made into Φ50×100mm cylinders, three identical specimens were made for each specimen design. The specimens were demolded 1 day later after pouring the mortar into mold. The specimens after demolding were placed in a water bath at 23±2℃ to start the curing. Based on JSCE-G 505, the tests for the compressive strength of mortar were conducted at 14, 28 and 91d, respectively.

Differential thermal analysis (TG/DTA) was used to measure the amounts of $Ca(OH)_2$ and combined water of different mortars. The center part of mortar specimen was cut off by a cutting machine ,broken into 2.5mm~5.0mm small particles with a long flat nose pliers, the hydration reaction of specimen particle has stopped after soaking in acetone for 24 hours, and the particles were put in a vacuum chamber for drying and preservation after evaporation of acetone. Then the particles were ground into powder by contusion mortar, the powder through 40μm sieve has been collected as the samples for test. The amount of $Ca(OH)_2$ in mortar was generated approximately at 460 ~510℃ by dehydration reaction, the decrement of the dehydration region can be read from the peak of DTA value[4]. More than 600℃, decomposition reaction of calcium carbonate would occur, so the amount of reduction before 600℃ was seemed as the amount of combined water. The range of testing temperature is Room Temperature ~ 1000℃. The speed of temperature increase in the analysis is 20℃/min. The processing method of specimens and device for TG/DTA test were shown in Fig.4 and 5, respectively.

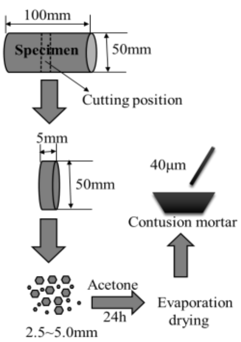


Fig.4 Processing method

Fig.5 TG/DTA device

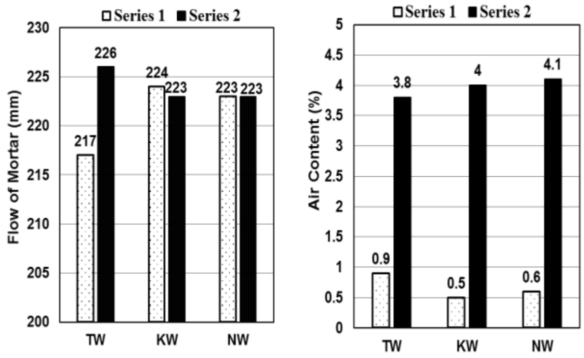
3. RESULTS AND DISCUSSIONS

3.1 Flow and air content

Fig.6 shows that the flow and air content values of different mortar in Series 2 were both basically controlled under the same conditions by adding the water-reducing and AE admixture. In contrast, the flow values of two kinds of electrolyzed water mortar in Series 1 were both higher than that of tap water mortar, but the air contents of all of mortars were very low and little difference, without the air entraining admixture.

3.2 Compressive strength of mortars

From Fig.7, it can be seen that under the condition



(a) Flow (b) Air content

Fig.6 The flow and air content of mortars

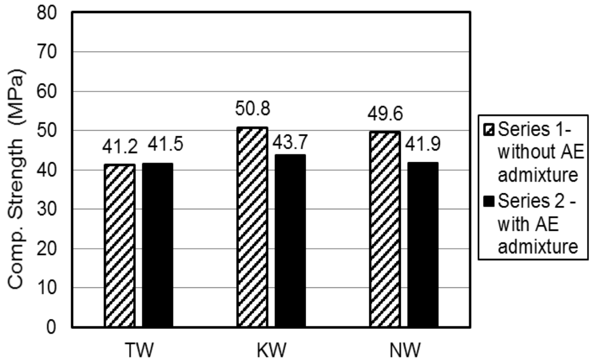


Fig.7 Compressive strength of mortar at 14 days

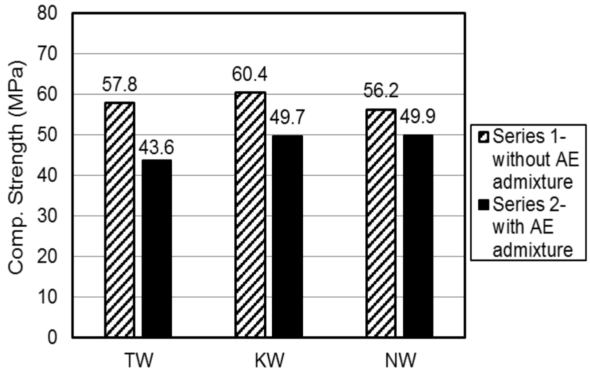


Fig.8 Compressive strength of mortar at 28 days

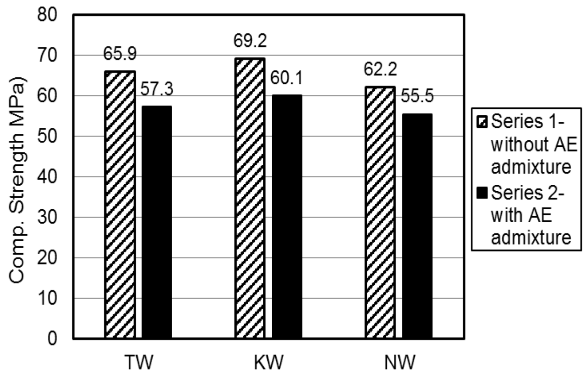


Fig.9 Compressive strength of mortar at 91 days

of Series 1 without AE admixture, the strengths of KW and NW electrolyzed cathode water mortar at 14d were both higher than that of tap water mortar, increased by

23.3% and 20.4% respectively. It revealed that the electrolyzed cathode water could stimulate the cement hydration of mortar at the early age, leading to the increase of strength. However, under the condition of Series 2 with AE admixture, although the strengths of KW and NW electrolyzed water mortar were also higher than that of tap water mortar, the growth ratio was relatively much lower. This showed that the addition of admixtures has some impeditive or delayed effect on the role of electrolyzed water in mortar because of their dispersity probably, leading to a worse growth ratio at the early age.

From Fig.8, at 28d, the effect of electrolyzed water in mortar was wearing off, the difference in strengths between electrolyzed water mortar and tap water mortar of Series 1 was narrowed; However, for the mortar of Series 2, the limiting effect of AE admixture on the role of electrolyzed water was also wearing off, the electrolyzed water in mortar at this stage could play a role to stimulate the cement hydration and improve the strength, the difference in strength was obviously increased. This also showed that at the early age, it is likely that the priority of reaction between the admixtures and cement was higher than that between the electrolyzed water and cement.

Fig.9 shows that, for the long-term strength of mortar, because of additions of air entraining admixture, the higher air content resulted in the increase of internal porosity of mortar, the strength of Series 2 mortar was lower than that of Series 1 mortar. No matter whether the AE admixture was used or not, the strength of K^+ electrolyzed water mortar (KW) was higher than that of TW mortar, increased by about 6%; but the strength of Na^+-K^+ compound electrolyzed water mortar (NW) was lower than TW mortar unexpectedly, decreased by about 5% at 91d. Therefore, it can be drawn a conclusion that the single K^+ electrolyzed cathode water can improve the strength of mortar more effectively than Na^+-K^+ compound electrolyzed water.

3.3 Amount of Combined water of mortar

From Fig.10, we can see that under the condition of Series 1 without admixture, with the increase of curing age, the amount of combined water in mortar was increased at the early age, and the increase gradually slowed down at the long-term age. The amounts of combined water in electrolyzed water mortar were both slightly higher than that of tap water mortar, while the combined water amount of KW mortar was the highest, the combined water amount of TW mortar was lowest.

From Fig.11, under the condition of Series 2 with AE admixture, there was little difference among the combined water amount of three kinds of mortar at 28d; but at 91d, the combined water amount of NW mortar was the lowest. The above results basically agreed with that of compressive strength of mortar.

3.4 $Ca(OH)_2$ amount and hydration of mortar

The hydration reaction of cement in mortar was shown in the equation (1) and (2). The degree of hydration reaction can be objectively characterized by $Ca(OH)_2$ amount.

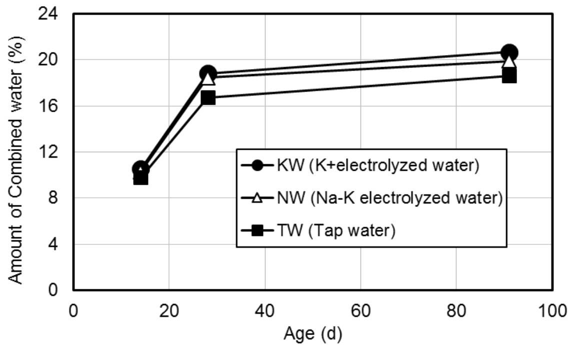


Fig.10 Amount of Combined water without AE admixture

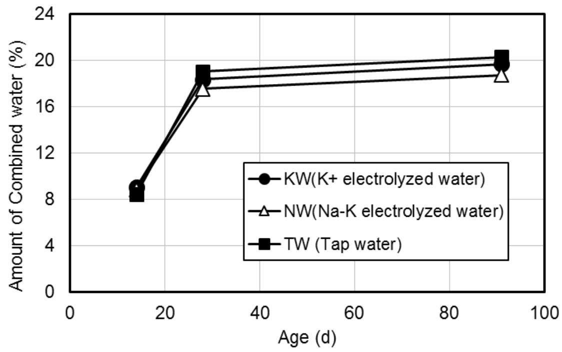


Fig.11 Amount of Combined water with AE admixture

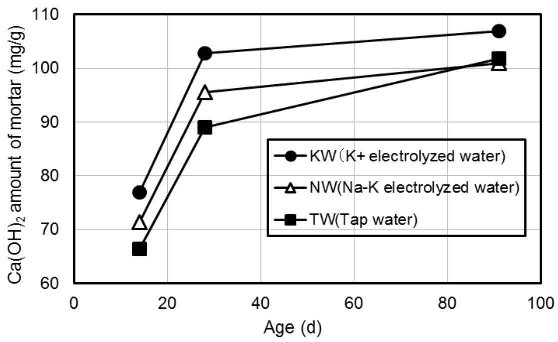


Fig.12 $Ca(OH)_2$ amount of mortar without AE admixture

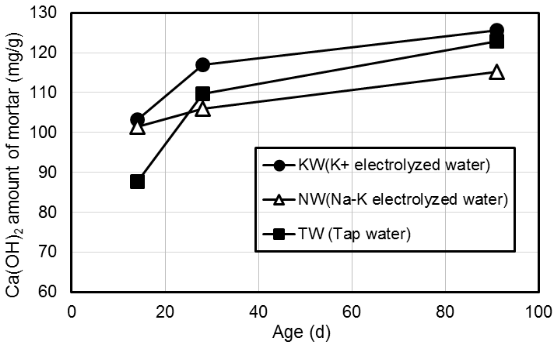


Fig.13 $Ca(OH)_2$ amount of mortar with AE admixture

$$3CaO\cdot SiO_2+nH_2O =xCaO\cdot SiO_2\cdot yH_2O+ (3-x)Ca(OH)_2 \quad (1)$$

$$2CaO\cdot SiO_2+nH_2O =xCaO\cdot SiO_2\cdot yH_2O+ (2-x)Ca(OH)_2 \quad (2)$$

Fig.12 showed the $Ca(OH)_2$ amount of mortar under the condition of no addition of admixture. The $Ca(OH)_2$ amount of KW electrolyzed water mortar was the highest at each age, much higher than that of tap water mortar at 14d and 28d, the difference in $Ca(OH)_2$ amount was narrowed at 91d. On the one hand, at the early age, there were many absorption positions with positive charge on the surface of cement particles (C_3A, C_3S.etc) [5], the highly active electrolyzed water with a strong negative charge (a large number of functional groups -OH, CO_3^{2-}) could be fully absorbed and covered on the surface of cement particles, the ion distribution of diffused double layer was formed on the surface [6], the double layer structure can make the particles evenly disperse because of electrostatic repulsion, the accumulation and flocculation of particles was slowed down, the combined water in mortar was released and more, which would stimulate and promote the cement hydration and connection among particles, leading to the production of more $Ca(OH)_2$ amount. The flow ability of mortar was relatively increased. The total porosity of mortar decreased and the strength increased. However, at the long-term age, the absorption positions on the surface of cement particles has reached the saturated condition, and the cement hydration was also relatively sufficient, the activity and electrostatic repulsion of electrolyzed water decreased, the difference in $Ca(OH)_2$ amounts of different mortar became smaller. This mechanism is a little similar to that of water reducing admixture in mortar [7]. The illustration of absorption on the surface of cement particles was shown in Fig.14.

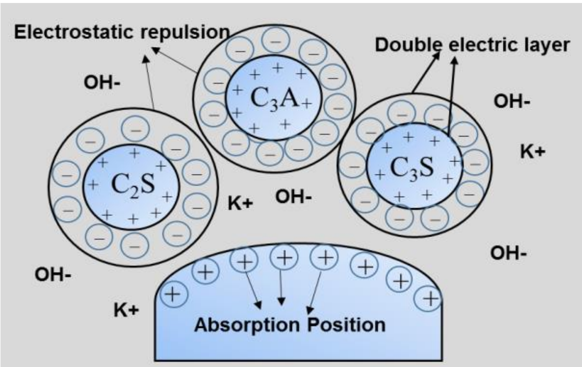


Fig.14 The ions absorption on the surface of cement particles in electrolyzed water mortar

On the other hand, at the early age, a certain concentration of KOH or NaOH in electrolyzed water (alkaline environment) was likely to react with the unhydrated $CaO{\cdot}Al_2O_3$ in cement to produce a small amount of the potassium aluminate (a kind of condensation promoter) and calcium hydroxide, as shown in the equation (3) and (4), which could promote the hydration rate and setting speed of cement at early age. This might be another reason why the CH amount and strength of KW mortar were increased than that of tap water mortar.

$$CaO{\cdot}Al_2O_3+6KOH=3K_2O{\cdot}Al_2O_3+3Ca(OH)_2 \quad (3)$$
$$CaO{\cdot}Al_2O_3+6NaOH=3Na_2O{\cdot}Al_2O_3+3Ca(OH)_2 \quad (4)$$

Similarly, the $Ca(OH)_2$ amount of NW mortar was higher than that of tap water mortar because of ion absorption at the early age, but the $Ca(OH)_2$ amount was lower than that of KW mortar and close to that of tap water mortar at 91d. It showed that the hydration of Na-K compound electrolyzed water mortar was far below the other two kinds of mortar at the long-term age. The reason may be that the free negative ion in the single K^+ electrolyzed water was much more than that in Sodium-Potassium compound electrolyzed water, which would more effectively stimulate the hydration reaction. In addition, the dependence of K^+ ion on negative ion is weaker than Na^+ ion, the complex ion environment could lead to the uneven absorption on the surface of cement particles, the absorption positions on the surface of cement particles has reached the saturated condition more earlier, leading to a slow hydration reaction at the long-term age. The growth ratio of $Ca(OH)_2$ amount in mortar at 91d was very low. The detailed reason and evaluation needs further study by other multiple methods.

From Fig.13, due to the AE water-reducer in tap water mortar, the hydration reaction of tap water mortar was accelerated and $Ca(OH)_2$ amount was increased obviously than that of NW mortar. Therefore, the admixture has a certain effect on the strength and $Ca(OH)_2$ amount of electrolyzed water mortar at early age, little effect on that at the long-term age. No matter whether the admixtures was used or not, the $Ca(OH)_2$ amount and hydration reaction of single K^+ electrolyzed water mortar were greater than that of tap water mortar, but lower than that of tap water mortar for Na^+-K^+ compound electrolyzed water mortar.

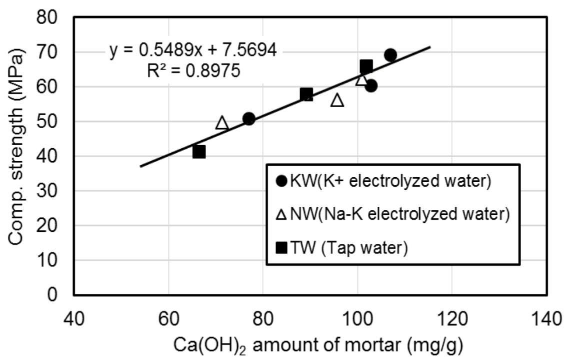


Fig.15 Relationship between $Ca(OH)_2$ amount and strength of mortar without AE admixture

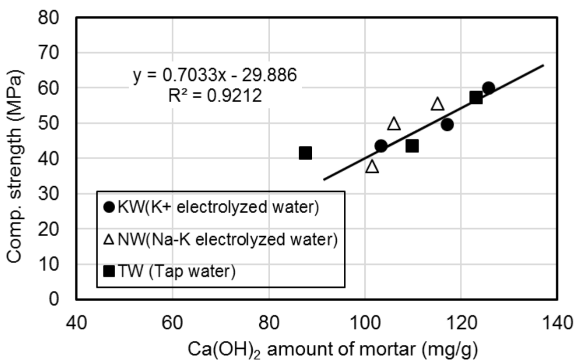


Fig.16 Relationship between $Ca(OH)_2$ amount and strength of mortar with AE admixture

Fig.15 and 16 showed the relationship between $Ca(OH)_2$ amount of mortar and compressive strength under the different conditions. It can be seen that no matter whether the admixture was used or not, the $Ca(OH)_2$ amount and strength of mortar possessed a direct proportional linear correlation, but the curve with AE admixture dispersed widely. This also revealed that the more $Ca(OH)_2$ amount of mortar, the hydration reaction of cement in mortar was more sufficient, and the strength was higher. The degree of cement hydration of mortar can be judged by the $Ca(OH)_2$ amount.

Because the electrolyzed water can effectively promote the cement hydration to produce more $Ca(OH)_2$ amount, the crystal structure of interface can be more complete and solid, the defects of interface are less. Therefore, if the electrolyzed water can be used to produce concrete, the bonding strength between cement and coarse aggregate could increase probably, the growth ratio of strength of concrete may will be greater than that of mortar.

4. CONCLUSIONS

Through a comprehensive analysis, the following results were obtained in this study:

(1) No matter whether the admixture was used or not, the strengths of electrolyzed cathode water mortar were both much higher than that of tap water mortar at the early age; however, the strength of single K^+ electrolyzed water mortar was still higher than that of tap water mortar, increased by about 6% at 91d; the strength of Na^+ and K^+ compound electrolyzed water mortar was lower than tap water mortar, decreased by about 5%.

(2) The $Ca(OH)_2$ amount of K+ electrolyzed water mortar at 91d was the highest among the three kinds of mortar, which of Na^+- K^+ compound electrolyzed water mortar was the worst. Because the $Ca(OH)_2$ amount and strength of mortar possessed a direct proportional linear correlation in this study, the degree of cement hydration of mortar also can be judged by the $Ca(OH)_2$ amount.

(3) Because of many absorption positions with positive charge on the surface of cement particles, the electrolyzed cathode water with a strong negative charge could be fully absorbed on the surface to form the ion distribution of diffused double layer, which would promote the cement hydration to produce more $Ca(OH)_2$ amount.

(4) A certain concentration of strong alkalinity (KOH or NaOH) in electrolyzed water may react with the unhydrated $CaO{\cdot}Al_2O_3$ in cement clinker to produce the soluble aluminate, which could promote the hydration rate and setting speed of cement at the early age.

(5) The compound electrolyzed water used in this study had a bad effect on cement hydration reaction and strength improvement of mortar, probably because of complex ion environment and mutual interference. The improvement action of single electrolyte electrolyzed water in mortar was more obvious and effective.

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REFERENCES

[1] Ahmad, R. M., Charles, N. T.,"Combined effects of slightly acidic electrolyzed water and fumaric acid on the reduction of foodborne pathogens and shelf life extension of fresh pork," Journal of Food Control, Vol. 47, Jan. 2015, pp. 277-284.

[2] Mahmoudreza, O., Hamzah M. A., Shyam, S. S.," Efficacy of acidic and alkaline electrolyzed water for inactivating Escherichia coli O104:H4, Listeria monocytogenes,Campylobacter jejuni, Aeromonas hydrophila, and Vibrio parahaemolyticus in cell suspensions," Journal of Food Control, Vol. 53, Jul. 2015, pp. 117-123.

[3] Sun, B. Q., Wang, L. J.,"Study on the Properties of Concrete Mixed with Alkaline Redox Potential Water," Journal of Building Materials, Vol. 12, No.1, Feb. 2015, pp. 112-115.

[4] Vedalakshmi, R., Raj, S. A., Srinivasan, S., Babu, G. K.,"Quantification of hydrated cement products of blended cements in low and medium strength concrete using TG and DTA technique," Journal of Thermochimica Acta, Vol. 407, Issues 1-2, Dec. 2003, pp. 49-60.

[5] Yoshioka, K.,"Adsorption characteristics of superplasticizers on cement component minerals, " Journal of Cement and Concrete Research, Vol. 32, Issue 10, Oct. 2002, pp. 1507-1513.

[6] Jolicoeur, C.,"Chemical admixture cement interactions: phenomenology and physic-chemical concepts," Journal of Cement and Concrete Composites, Vol. 20, Mar. 1998, pp. 87-101.

[7] Sugamata, T., Edamasu, Y,"Quantitative evaluation on the dispersing retention effect of a superplasticizer," Jounal of Transactions of the Japan Concrete Institute, Vol. 22, No.2, Jun. 2000, pp. 1-8.

[8] Li, M. C., Ma, C. A.,"Preparation of ionic water by electrolysis," Journal of Chemical World, Vol. 8, No.1, Jan. 2002, pp. 406-409.