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Degradation of Epoxy Coating due to Aging Acceleration Effects

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This paper is to investigate feasibility on quantitative aging state of epoxy coating on concrete wall in containment structure under operation of nuclear power plants. For evaluating the physical characteristics of the epoxy coating, adhesion strengths of two kinds of degraded epoxy coating systems on both steel surfaces and concrete surfaces were measured via accelerated aging. Comparatively impedance data taken by ultrasonic test were also taken to relate with adhesion data. After aging, in case of concrete, from half of specimens, aging of epoxy coating was developed. As for steel, on 4th inspection day, adhesion force was failed. To improve reliability on quality degradation of epoxy, relationship between adhesion and impedance was analyzed. By tracing to co-respond to these data, it was possible to Fig. out physical state of as-built epoxy coating. The possibility to develop new methodology of time - dependent aging state on epoxy coating was found and discussed.

Keywords *: degradation, adhesion, epoxy, acceleration, aging, concrete, steel*

1. Introduction

The focus of this research is related to maintain functional coating for more than nineteen year old nuclear power plant structures. Nowadays some studies related to maintain NPP structures are under progress to prove quantitative methods such that structures have been working properly as intended functions. However any studies for evaluation of specially designed functional coating for NPP structures have not been performed in Korea. The goal of this study is to identify a possibility to develop the maintenance method to evaluate aging state of epoxy coating systems in power block structures. The management and maintenance of epoxy coating has been depended on visual inspection and on local destruction method such as measurement of adhesion strength. The adhesion is purposed not to evaluate physical property on degradation, but to assess adhesion between coating and main structure surface during annual overhaul period. Accordingly, it is brought to our attention that quantitative estimation of quality deterioration of epoxy coating is needed. A coating system for this experiment is epoxy-coating system applied to concrete surfaces, the other is epoxy system for steel surfaces. To make the aging state worse, after selecting aging parameters accelerated aging test is conducted for sixty four days. On expected measuring days, both impedance value using ultrasonic test and adhesion strength was taken from each specimen. Based on these results, a possibility of reliable quantitative evaluation has been suggested to be the same degradation lines as comparing with impedance and adhesion force.

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2. Acceleration experiment

2.1 Preparation of steel specimens

The dimension of specimens is 50 mm x 50 mm ASTM A36 steel plates with 3 mm thickness. The surface was blasted to be roughness as 1.5 to 3 mils according to SSPC SP-10. The coating system is composed of two coats. ; the first coat is XX 19Y, its thickness is 3 to 6 mils, the second coat is XX 56Y, its thickness is 3 to 5 mils, so total thickness is limited from 6 to 11 mils.

2.2 Preparation of concrete specimens

The specimens are 50 mm x 50 mm x 50 mm concrete cubes which made of 19 mm diameter aggregates and type

5 cements the same as applied to nuclear power plant structures. Concrete specimens were cured at 10 ℃ and 30 ℃ separately to simulate the winter and summer condition, respectively. The cured concrete specimens are grounded to remove surface defects like concavo-convex and laitance for surface preparation of coating. The epoxy coating, provided by a domestic company K qualified for nuclear power plant, is applied on the concrete specimens. When it was coated in accordance with specification requirements, the ambient temperature was over 18 ℃ and the water content ratio of concrete surface was limited within the range of 6%. The primer of concrete specimens was treated with sand filled epoxy grout to remove pin holes on concrete surfaces and to improve adhesion as well. After finishing this process, the first coat XX 112Y was applied. The concrete specimens before and after epoxy coating are shown in Fig. 1. For the second coat to the fifth coat layer, XX 514Y epoxy was applied. The thickness of each coat is 3-5 mils as requirements of specification. They had cured for minimum 3 days per each coat. Two kinds of specimens, one with standard coating thickness of 20-24 mils and the other with 1.5 times(30-36 mils) more thicker than the standard, were manufactured.

2.3 Plan of accelerated aging experiment

Water content and temperature are the factors that the coating may make its quality worse than design criteria. Based on these phenomena, the aging factors were selected as followings;

- 64 days immersion under clean water with 3 different temperatures of 100 ℃, 80 ℃, and 60 ℃ .
- 64 days of alternative salted water spray (12 hour spray under -20℃ and 12 hour spray under +60℃) on 1st, 8th, 16th, 32nd, 48th, and 64th days, the specimens were inspected under the above described aging conditions. The detailed aging conditions and numbers of specimens are shown on the Table 1.

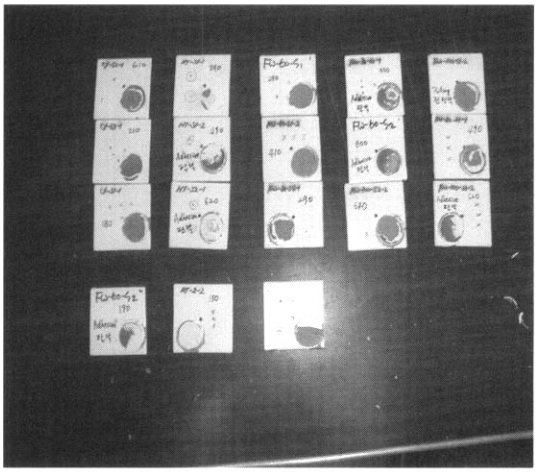
Table 1. Outline of accelerated aging experiment

Aging parameters \ days		Control	No. of specimens					
			1st	8th	16th	32th	48th	64th
Adhesion	Dolly Test	3	3		3	3	3	3
Immersion	Immersion at 60℃		3	3	3	3	3	3
	Immersion at 80℃		3	3	3	3	3	3
	Immersion at 100℃		3	3	3	3	3	3
Cyclic Test	From -20℃ for 12 hours +60℃ for 12 hours		3	3	3	3	3	3

2.4 Testing method

2.4.1 Adhesion test

Adhesion test of the aged specimens were conducted in accordance with ASTM D4541(dolly method). The Elcometer 106 Model was used for the first measurement. The second adhesion test was done by the Elcometer 110 Model to increase accuracy. The air pressure used for the Elcometer 110 model, was minimum 9 barometers of compressed oxygen. The dolly adhesive was used to mix up two component epoxy liquid. It was tested after minimum 24 hours of curing under normal temperature. The allowable tolerance of the adhesion testing equipment was ±5%. The design requirements of adhesion on concrete surface are as follow : In case that the specimens were exposed to Minimum Radiation dose rate of $2x10^9$ rads, the adhesion strength of specimens should be minimum 79.7 psi. In otherwise condition, the adhesion strength of specimens should be minimum 101.5 psi.



(a) steel

(b) concrete

Fig. 1. After adhesion test

Adhesion test was done by at least more than one at one side of each specimen, and additional test was done in cases of specimens partly failed in the adhesive layer or specimens showing the unusual high or low adhesive strength results. Moreover, in case of irregularly harsh aging phenomena, less damaged surface by visual inspection was selected for the adhesion test.

2.4.2 Impedance

A method to measure impedance from epoxy coating is to use ultra-sound. The reflection is produced by the difference of impedances of each epoxy coating when ultra-sound is projected on the new and old epoxy coated surfaces. The impedance is calculated by the measurement of the reflection wave. The Fig. below explains this principle. The level of reflected ultra-sound energy that is projected to the epoxy applied on concrete or steel, can be measured.

In case of epoxy coat film, the surface flatness does not vary largely due to measuring location. But because it is painted on the irregularly uneven concrete surface, not only the coating thickness varies a lot but also surface flexure does like coating thickness in the case of concrete lining as coating. To minimize this problem, it is required to minimize the ultra-sound beam projected on the coating material. To minimize the ultra-sound beam, the acoustic lenses may be used. When the acoustic lenses were used to measure the reflection factor, the focus of acoustic lenses must be kept consistent. This method is not appropriate as on-site testing because of surface flexure and the couplant between the lens and the coating material. On this experiment, with a special wedge of cone shape, the area of the ultra-sound beam being projected on the coating surface is decreased significantly as Fig. 3 shows the structure. The upper 15 mm part diameter of the wedge and lower 1 mm part diameter of the specimens were calculated.

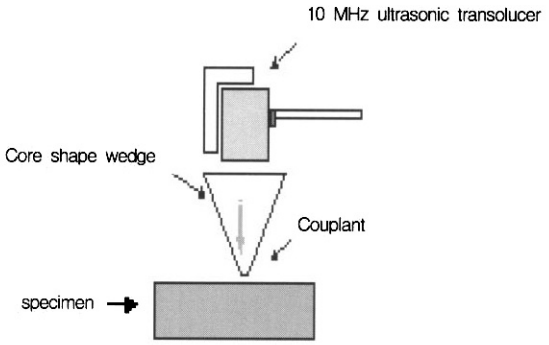
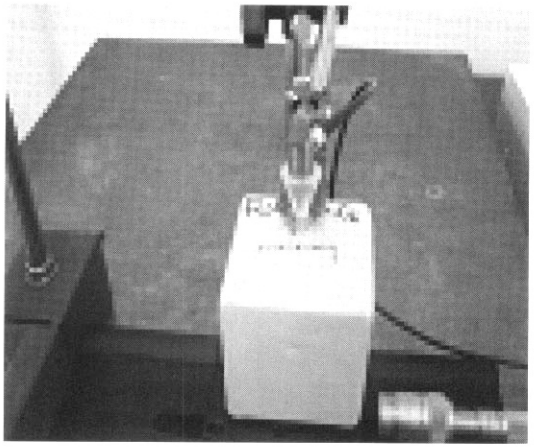
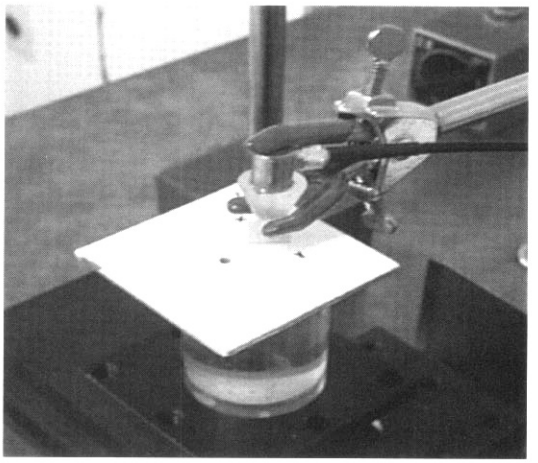


Fig. 3. Concept of measuring impedance



(a) concrete



(b) steel

Fig. 4. Impedance measurement

2.4.3 Analytical Method

By characteristics of polymer like epoxy, the property of material or adhesion can be affected differently by factors such as water contents, temperature. As for the aged specimens, degradation of adhesion and impedance were compared to parameters of accelerated aging agent ; immersion environment at 60, 80, 100 ℃, cyclic condition on hot/cold temperature and variation of coating thickness. The co-relation between adhesion and impedance was reviewed.

3. Analysis of test results

3.1 Epoxy coating system on steel surface

3.1.1 Adhesion strength

Specimens of immersion condition at 60 ℃ were degraded greatly from 640 psi to 100 psi than other speci-

Table 1. Adhesion Force on Steel Specimen

Parameter \ Day	2 (S1)	4 (S2)	8 (S3)	16 (S4)	32 (S5)	64 (S6)
Salt spray	410	150	100	120	190	110
Immersion at 60℃	640	480	480	420	190	100
Immersion at 80℃	410	350	330	250	180	140
Immersion at 100℃	410	120	190	180	180	140
Cyclic immersion 12Hr at-20℃ 12Hr at+60℃	380	500	400	330	200	190

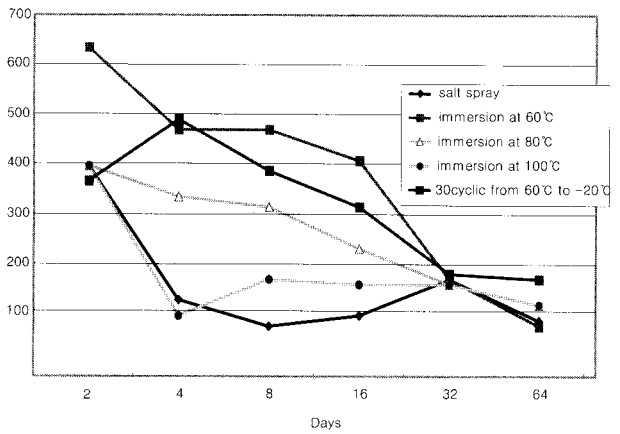


Fig. 5. Adhesion strength on Steel Specimen

mens. In case of salt spray condition and immersion condition at 100 ℃, from 2nd measuring step, severe degradation was investigated as follows. 410 psi at 1st measuring step was deeply fallen to 100 psi at 2nd measuring step. Generally both immersion condition at 60 ℃ and 80 ℃ has inclined to lines of similar degradation as Fig. 5 and Table 1.

The decline ratio of adhesion force is as follows: Immersion at 60 ℃ has decreased by 15% after finishing aging acceleration. Salt spray condition has decreased by 27%. Both immersion at 80 ℃ and at 100 ℃ has decreased by 34%. The worst case is cyclic immersion which was recorded by reduction of 50%. In case of Immersion at 80 ℃, adhesion force of the 4th inspection step, 16 days has decreased by terribly 66%. The 5th measuring stage, adhesion value of 32 days was recorded as one hundred ninety psi, but the permitted guideline of adhesion force is regulated as 200 psi. In this case, this value of 5th stage is meaningless because some blistering had been already torn out, and loosen its intended function, adhesion.

3.1.2 Impedance

The thickness of coating system on steel is much thinner than that of coating system on concrete. So, impedance

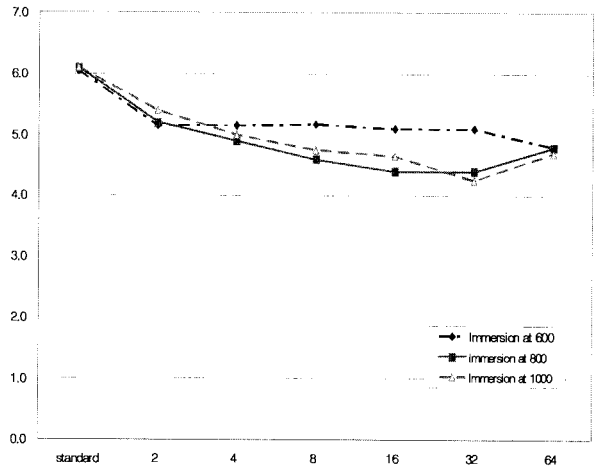


Fig. 6. Impedance of steel specimen

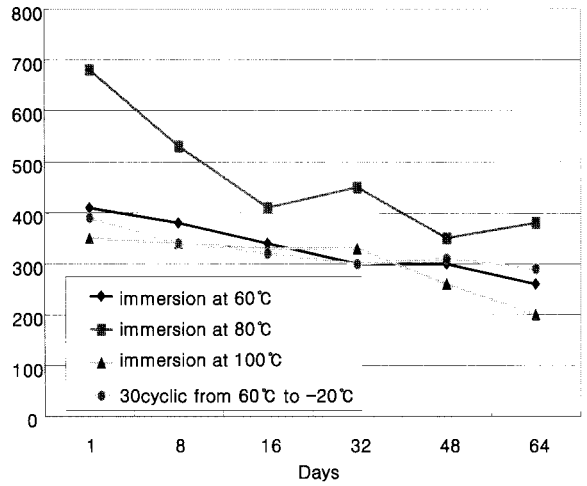
taken from thin film coating systems were fluctuated due to noise. For example, impedance in immersion condition at 60 ℃ was not reduced as specimens were degraded, in some cases, somewhat higher than that of control specimen. The reduction ratio of impedance is eight percent after sixty four days at immersion condition at 80 ℃. Comparatively, the reduction of immersion condition at 100 ℃ is twelve percent as Fig. 6.

3.2 Epoxy coating system on concrete

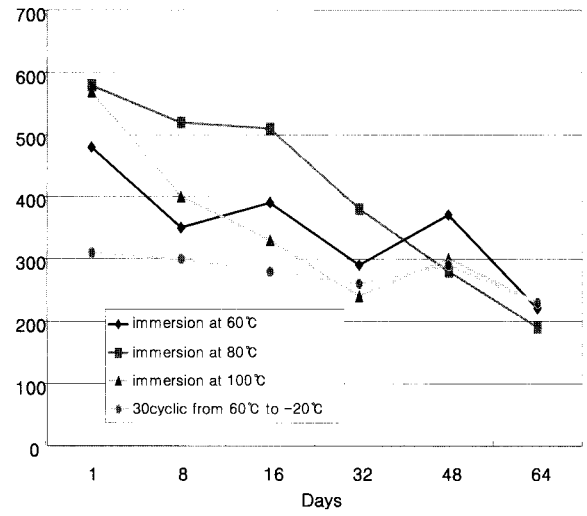
3.2.1 Adhesion strength

The adhesion test results of coating on specimens that concrete were cured at 10 ℃ are shown in Fig. 7. In accordance with the testing results in Fig. 7 (a), the condition that best described aging trend was appeared under immersion at 80 ℃. The decreasing ratio of adhesion strength compared to the beginning was appeared as 49% that is the largest value of other conditions. The least decreasing ratio of excessive thick coating specimens of which the concrete were cured at 10 ℃, measured under the cyclic immersion condition, was appeared as 26% shown in Fig. 7(b).

The adhesion test results of 1.5 times overcoat applied on the 10 ℃ cured concrete are shown in Fig. 7(b). As for the standard coating thickness of specimen that the 10 ℃ cured concrete, the most drastically degraded adhesion strength was recorded at the 6th inspection point, 64th days under immersion at 80 ℃. The decreasing ratio of adhesion strength was 67%. Under immersion at 100 ℃, the decreasing ratio of adhesion strength at 64th days compared to the 1st day was 60%, but degradation trend from 8th day to 64th day got relatively worse than under immersion at 80 ℃. In general, it was appeared that degradation trend of adhesion strength in standard coating



(a) standard coating thickness



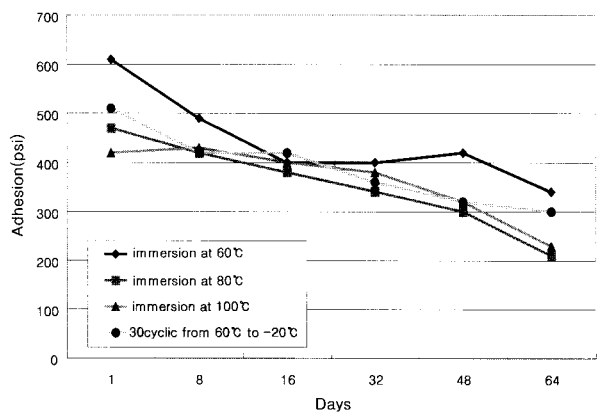
(b) 1.5 times coating thickness

Fig. 7. Adhesion degradation of concrete specimen under curing at 10 ℃

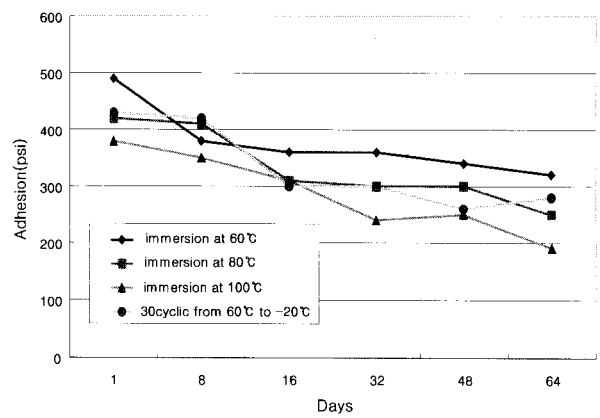
thickness was lower than in 1.5 times coating thickness regardless of immersion conditions. The adhesion test results of standard coating thickness on the 30 ℃ cured concrete are shown in Fig. 8(a).

The condition that described the harsh aging trend was under immersion at 80 ℃. The decreasing ratio of adhesion strength, among each environmental condition, was similar trends. At the beginning, the value of adhesion strength is appeared as max. 610 psi. to min. 420 psi. At the last measurement point after 64th day, its value is recorded from max. 340 psi. to min. 230 psi., relatively. The decreasing ratio of adhesion strength compared to the beginning was appeared as 40% to 50%. Based on visual inspection, from the 4th step, 32th days of one or two specimens, aging phenomena of epoxy coating such as blistering, pin hole was occurred. The diameter of blistering is about 5 to 10 mm.. The adhesion test results of 1.5 times overcoat thickness on specimens that concrete were cured at 30 ℃ are shown in Fig. 8(b). At the beginning, the value of adhesion strength is appeared as max. 490 psi. to min. 380 psi. At the last measurement point after 64th day, its value is recorded from max. 320 psi. to min. 190 psi., relatively. The decreasing ratio of adhesion strength compared to the beginning was appeared as 35% to 50%. coating films got thinner. This is why the less coating thickness has, the more it is influenced to the surface of coating film on concrete. The surface aging of thicker film was relatively more intensive than thinner one. In the standard film specimen shown in Fig. 9(a), the impedances are generally reduced, as the aging time goes longer. But at some section, it may be observed that this trend is not fit to decline or to rather increase. This is considered as noise signal. The impedance is relatively reduced as about 10-15% to the first stage.

As Fig. 9(b) shows the case of excessively thick films on specimen, it shows the degradation 60 ℃ conditions,



(a) standard coating thickness



(b) 1.5 times coating thickness

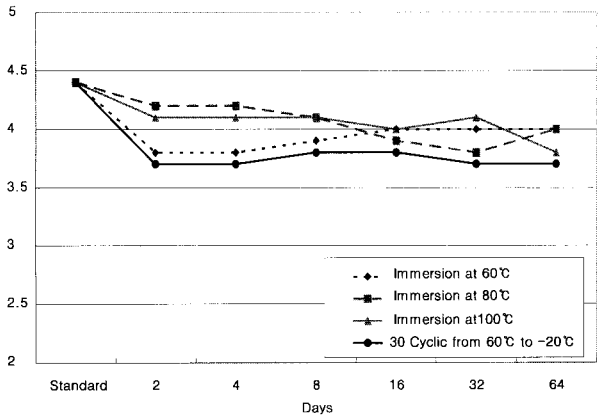
Fig. 8. Adhesion degradation of concrete specimen under curing at 30 ℃

reduction ratio of impedance is the largest as 20% compared to the first stage. In cyclic sequence of heat resistance of cold and hot environmental conditions, the reduction rate of impedance was relatively lower than it under immersion condition. This means that the conditions under immersion are contributed to epoxy aging more than cyclic condition does.

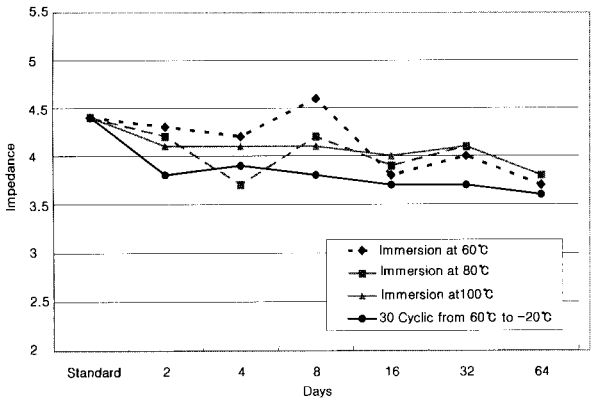
3.3 Adhesion-impedance relation due to aging.

To derive some certainty from results of co-relation between adhesion force and impedance, total sixteen aging parameters including environmental factors, seasonal factors were investigated and analyzed. However it is not clearly fit well to accommodate each result taken from experiments. For adhesion-impedance relation, the value of adhesion strength under immersion conditions was selected because these specimens were easily degraded. It is why the reduction ratio in this case was relatively higher than it under cyclic condition. In case that the decreasing range of adhesion strength is relatively small, in consideration of probability, data only measured under the conditions of relatively big degradation trends of adhesion strength were analyzed. For corresponding one data to one data co-relationship between adhesion strength and impedance, the value of impedance was focused on results of 1.5 times overcoat specimens.

As the aging state by variety of epoxy coating thickness was analyzed, more effective impedance value could be obtained from thicker film. The reduction ratio of adhesion strength was taken more severely from concrete specimens cured under 10℃. Moreover it was taken more than 50% for excessive thickness under immersion at 60, 80, 100 ℃. Instead, as to standard films, it showed less than 50% of reduction ratio under immersion at 60, 80, 100 ℃. It simply appeared that adhesion variations are more severe for excessive coating thickness by 20% to 40% than the standard films has variations of 10% to 20%. on the contrary, for impedance changing range, it was uncommon as about 0.7 of variations for standard thickness films, and about 0.4 to 0.3 of variations for excessive thickness films were shown.



(a) standard coating thickness



(b) 1.5 times coating thickness

Fig. 9. Impedance degradation of concrete specimen under curing at 10 ℃

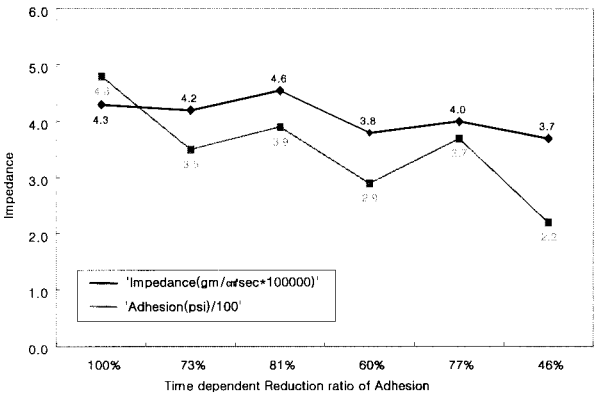


Fig. 10. Relation between adhesion strength and impedance on concrete

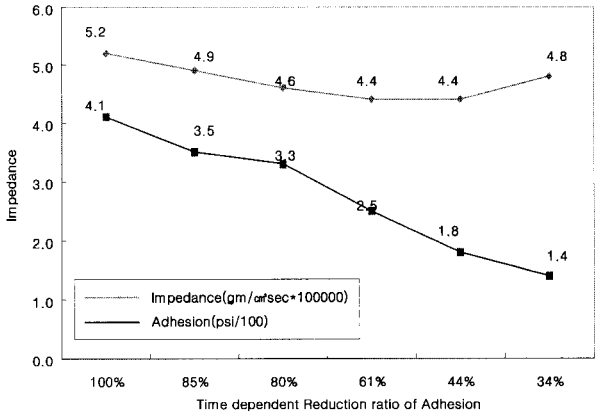


Fig. 11. Relation between adhesion strength and impedance on steel at immersion 80℃

In case of steel, the reduction rate of adhesion strength is much greater than that of impedance value. Based on Fig. 11, at the 5th and the 6th measuring step, adhesion strength was decreased, but impedance is rather reversed. However, as prescribed in adhesion analysis, at the 4th measuring step, some swollen blistering on steel surface were torn. So the effective data was limited by the 4th measuring step, at that time, the reduction rate of adhesion strength is 61 %. Relatively it is known that impedance is 4.4 before failure of normal degradation. Like the method described above, it is shown that similarity is existent in correlation between adhesion strength and impedance.

4. Conclusion

The test results were somewhat fluctuated as aging time passed because water contents, air dried condition of specimens were different. However this is understandable that the degradation of adhesion force and impedance is not linear trends, but similar trends due to characteristics of macromolecule such as epoxy coating unlike other common materials. The results of experiment on epoxy coating by accelerated aging parameters were learned by using the adhesion strength and the impedance as follow:

1) In case of coating system on steel specimen, when impedance value is taken as 4.4, this coating system does not have proper adhesion strength.

2) From adhesion test of concrete specimen, the results after aging acceleration were shown that it was reduced on average from 35% to 60% under several underwater conditions, and that excessive thickness films was degraded worse than standard films.

3) The reduction ratio of impedance of concrete was recorded as average 15% to 20%. In case of thicker coating and more homogeneous surface conditions of base material, more effective impedance value could be obtained.

Through this experimental study, it is confirmed that a quantitative aging evaluation may be possible if evaluation of epoxy coating's physical quality is added to adhesive evaluation, impedance, and visual inspections.

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