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Development and Application of Rapid Measuring Method for Chloride Ion Content in Hardened Concrete

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ABSTRACT

On the maintenance of the reinforced or prestressed concrete structures, measurement of chloride ion content in concrete is one of the important issue. Generally the amount of chloride ion content is measured in the laboratories according to JIS A 1154 or JCI-SC5 or ASTM C1152 etc. In most cases, acid-soluble chloride is equivalent to total chloride. In this paper, a developed rapid method using drilled powder of concrete is described. The amount of chloride using the rapid method is approximately equal to acid-soluble chloride. In the method, chloride ion is eluted with hot distilled water and auxiliaries, then chloride ion content is measured by the potable chloride ion meter (Coulometric titration method). So the method can be carried out on the site and get a result in about 15 minutes. Case studies applied to bridges are also described in the paper

Keywords. chloride content, acid-soluble chloride, rapid method, drilled powder, on sit test

INRODUCTION

Concrete structures in Japan often exposed to the environment where chloride penetration can be occur. Near the sea area chlorides brought from sea water and in the inland chlorides brought from deicer salts. And in 1970's sea sand without enough desatlting was used for concrete mainly in western Japan. Chloride attack is one of a leading cause of the deterioration of concrete structures inducing corrosion of reinforcement.

In health monitoring and rehabilitation of the concrete structures, measurement of chloride amount is required. Then cores are taken from the structure and sliced into 10 to 20mm thick discs. Each disc is crushed and the chloride content of each layer is determined. Recently a sampling by drilling is increasing in number. The amount of chloride ion content is generally measured in the laboratories according to JIS A 1154 or JCI-SC5 or ASTM C1152 etc. When the analysis is ordered to a private laboratory, it takes 2 weeks to a month to get the results depending on number of samples and a cost for it tend to increase.

Especially in repair work, the extent and the depth to remove the contaminated concrete is determined by measured chloride content. So, rapid test methods assist the work by providing a fast and reasonable approximation of the chloride in concrete. Coarse aggregate that contain chloride is not used in Japan, so prediction of chloride penetration or diffusion is done by using total chloride content in concrete. So, rapid test method obtaining good approximation of chloride ion content in concrete has been expected.

In the paper an idea for the rapid test method and the developed method is described. Applied case studies are also described.

DEVELOPED RAPID METHOD

Idea for a rapid method. Chloride ion is thought to exist in concrete as a free ion in pore water and fixed in hydrate of cement. Typical hydrate of cement which fixes chloride is known as Friedel's salt. Test methods analysing chloride ion content in hardened concrete are the tests for acid-soluble chlorides and water soluble chlorides. It is often observed that acid-soluble and water-soluble chloride contents in carbonated part of a concrete show almost the same value. If carbonation of concrete sample can be achieved in analysing process, a chloride content that has a good approximation thought to get with a similar method for water-soluble chloride contents. A carbonation of concrete sample in short time may be achieved by adding some carbonates on elution process of chloride ion.

Basic investigations to confirm the idea. To confirm the idea, some investigations are carried out (Goto2010, Kondo2010). They are trial tests with ground concrete samples which have already finished measuring acid-soluble chloride and cured cement pastes adding deferent amount of salt. Used samples are shown in Table1.

Table 1. Samples used in basic investigations

	Concrete obtained from a structure			Hardened cement paste (w/c=45%, cured 28 days in ϕ 5x10cm mold)					
				Ordinary portland cement			Blast furnace slug cement		
Symbol	C1	C2	C3	OP1	OP2	OP3	BF1	BF2	BF3
Acid-soluble Chloride (%)*	0.293	0.433	0.563	0.150	0.833	1.512	0.175	0.837	1.506

*acid-soluble chloride content by JIS A 1154; % by mass

Chloride content of samples are measured as follows,

(1) weight of sanple:10g
(2) weight of distilled water: 50g, Temperature of distilled water: 20, 50, >80℃
(3) duration time of elusion: 2 to 60 minutes
(4) measurement of chloride ion in distilled water: Potable coulometric titration meter
(5) Carbonate used: $NaCO_3$ and $NaHCO_3$, Dosage of carbonate: 0.5~10g for 10g of sample. A carbonate was added before pouring distilled water

Fig.1 shows test results using sample C2, carbonate used is $NaHCO_3$ and T express temperature of distilled water at pouring. This data shows that addition of carbonate and distilled water higher than 80 degree result in a good approximation to the acid-soluble chloride content.

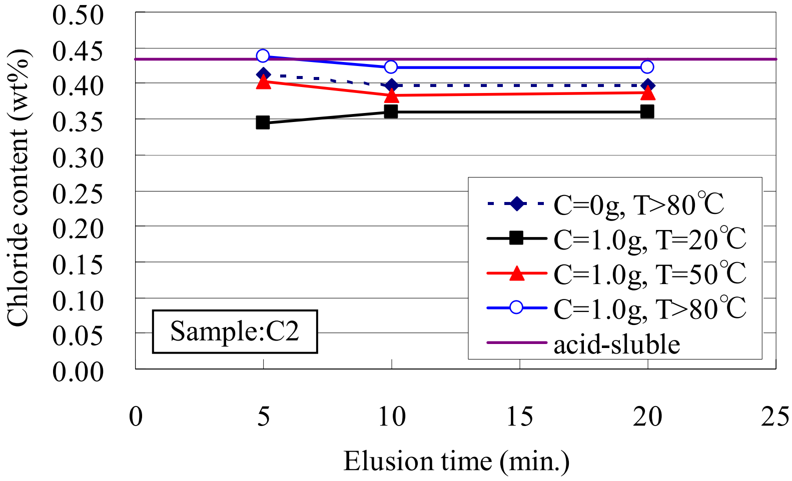

Figure 1. Chloride content in deferent elusion condition（Goto 2010）

Fig.2 shows test results using sample C3, in this test dosage of a carbonate was increased, temperature of distilled water is higher than 80 degree. This data shows that for sample C3 (0.633wt%, about 13kg/m^3 of concrete), dosage of carbonate should be more than 0.5g for 10g of concrete sample.

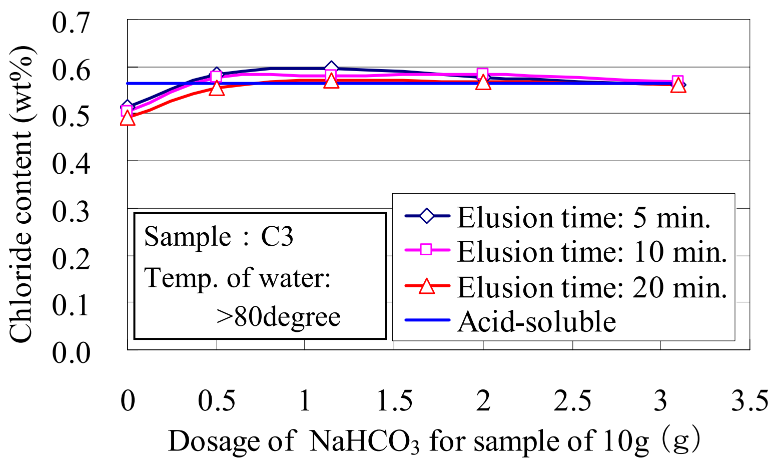

Figure 2. Dosage of carbonate and chloride content（Goto 2010）

Fig.3 shows test results using sample C1, in this test two carbonates are used. This result shows that addition of carbonate give better approximation to acid-soluble chloride content and $NaHCO_3$ is slightly effective than Na_2CO_3.

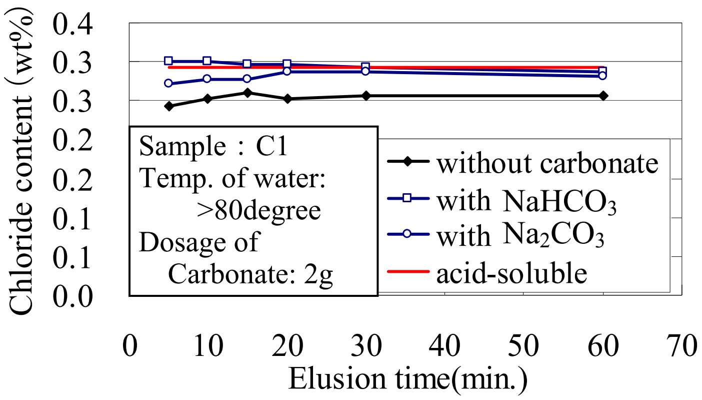

Figure 3. Effect of carbonates on chloride content（Goto 2010）

Results using cement pastes are shown in Fig.4. Used cement pastes are cured for 28 days and pulverized for measuring chloride content as passing 0.015mm sieve.

For ordinary portland cement paste, addition of carbonates gives higher chloride contents and difference of obtained values between added carbonates are small, but the values are lower than acid soluble values. Reasons of deference of the data are not clear, but chloride ion combined with some hydrates and the decomposition of hydrates may not occur completely with the elusion process and condition employed. For blast furnace slag cement pastes, addition of the carbonates also gives higher chloride contents than the cases without using them. But there are values which are higher than acid soluble chloride contents and the value for the same sample ranged widely. These phenomena seemed to be affected by existence of sulfide sulfur in blast furnace slag. Potable coulometric titration meter is interfered by the sulfides and electrodes are covered with silver surfied and become black.

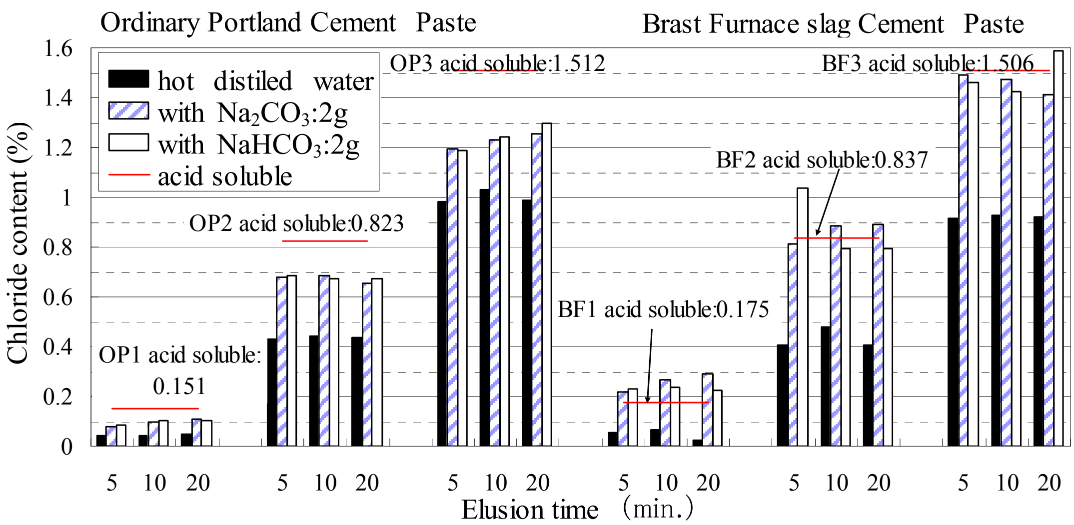

Figure 4. Results of the rapid method applied for cement paste（Kondo 2010）

Treatment with hydrogen peroxide is known to be used to eliminate such interference. Fig.5 shows measured results with and without using hydrogen peroxide of 2 ml. Used samples are 2, 5 and 10g and acid soluble chloride content of sample is 0.761% by mass. In the elusion process, treatment with hydrogen peroxide gives equivalent value to acid soluble value.

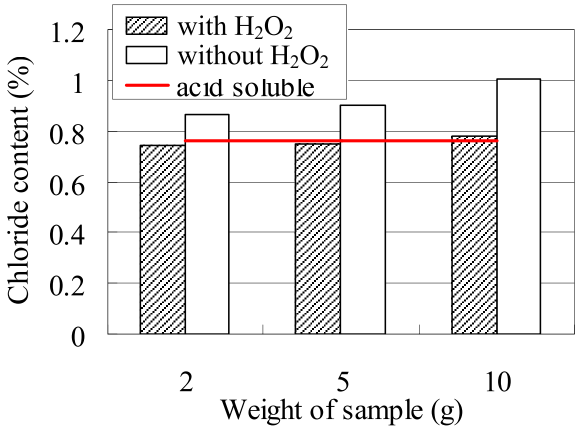

Figure 5. Results of the rapid method with and without hydrogen peroxide (Kondo 2010)

Fig.6 shows a part of X-ray diffraction chart of filtered and dried samples eluted with or without adding carbonate. A peak around angle of 11degree is a peak of Friedel's salt and the peak becomes small or almost disappears by addition of carbonate. This indicates that addition of the carbonate with hot distilled water causes a decomposition of Friedel's salt.

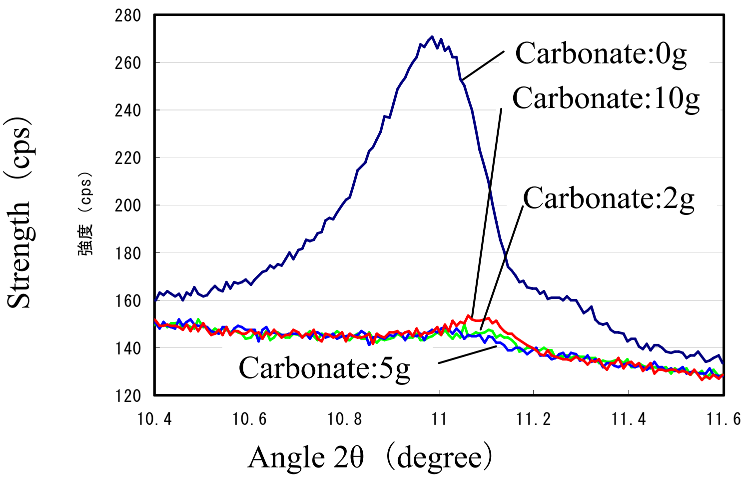

Figure 6. X-ray diffraction chart (Friedel's salt) of the samples obtained by filtration of sediments after elusion treatment with deferent amount of carbonate (Kondo 2010)

Basic investigations shows that adding carbonate with hot distilled water read to get higher chloride content, for concrete samples chloride content is equivalent to acid soluble chloride content. But for cement pastes cured for 28 days, there is still deference between results of the rapid method and acid soluble chloride content.

Standardization of the rapid method. On the basis of the basic investigations, the procedure of the rapid method fixed as follows,

1) Prepare drilled powder or pulverized powder and mix well
2) Weigh concrete powder of 10g, put into a 100ml polypropylene bottle. Record the weight to the nearest 0.1g.

3) Open a seat of aid（carbonate）2g and add to the polypropylene bottle.
4) Pour boiled and stored distilled water (>80℃）about 50g to the bottle and weigh to the nearest 0.1g and record it.
5) Close the cap tightly and shake by hand 5 times in one minutes and repeat up to 10 minutes.
6) Input a weight of sample, a weight of added distilled water and unit weight of concrete(often supposed as 2,300kg/m^3 in Japan) to the SALMATE, chloride ion meter (Coulometric titration method)
7) Take supernatant liquid (0.2ml) and measure a chloride ion content by the meter.
8) Calculated result of the chloride content（C:kg/m^3）by equation (1) is printed.

$$C = \frac{W_W \times S}{W_S \times 100} \times \gamma_c \qquad (1)$$

where, W_W : weight of added hot distilled water (g)
W_S : weight of concrete powder (g)
S : chloride（Cl^-）content of liquid (%)
γc: unit weight of concrete （kg/m^3）

SITE INVESTIGATIONS

For concrete samples obtained from structures, rapid method gives the good results in basic investigations. Site investigations are carried out to confirm the effectiveness of the rapid method. One is the application for elevated highway piers and the other is elevated railway structures.

Coastal highway piers. (Niitani 2010) Sampling of the drilled powder was carried out from ten piers of the highway constructed along the beach. Samples were obtained from 5 different depths, every 2 cm, of four drilling holes and samples of same depths were mixed together. One core was sampled from each pier. Sampling and analysis of drilled powders were done in two days by three members. Measurement of chloride content for fifty samples was carried out in the car at the site on the second day. Drilled samples analysed by JIS A 1154 in the laboratory, and the results were compared with those of the rapid method. Cores were sliced into 20mm thick discs and pulverized, and chloride content was measured by the rapid method and JIS A 1154.

Fig.7 shows the results of the drilled powder. For the rapid method, drilled powder was used without pulverized. There is some deference between the data by two methods but as a whole nearly equal chloride content can be obtained by two methods.

Fig.8 shows the results for pulverized core discs, chloride content obtained by two methods are considered almost equal.

Railway structures. (Yoshida 2010) Samples were obtained from railway structures, those structures were constructed using concrete with sea sand in which some salt was left. Sampling was done by drilling form deferent depth. Drilled samples were ground with a mortar then tested by the rapid method and JCI-SC5, one of the methods obtaining acid soluble chloride content.

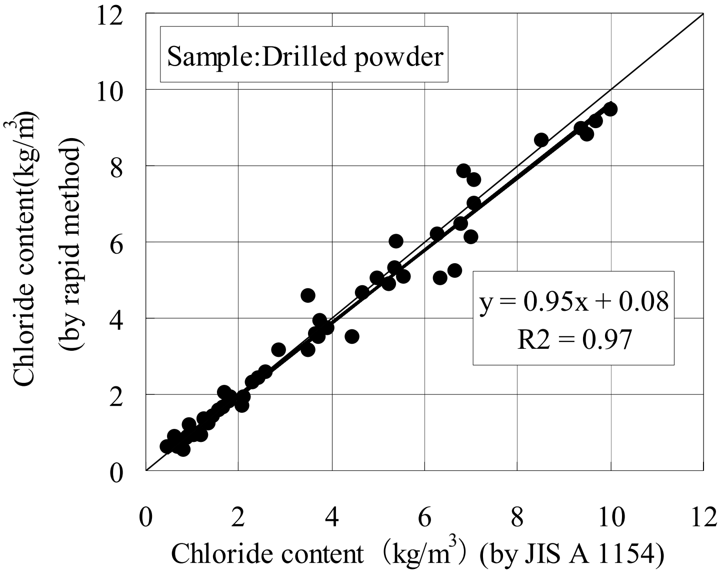

Figure 7.　Relationship between chloride contents obtained by JIS A 1154 and developed rapid method（Goto 2010）

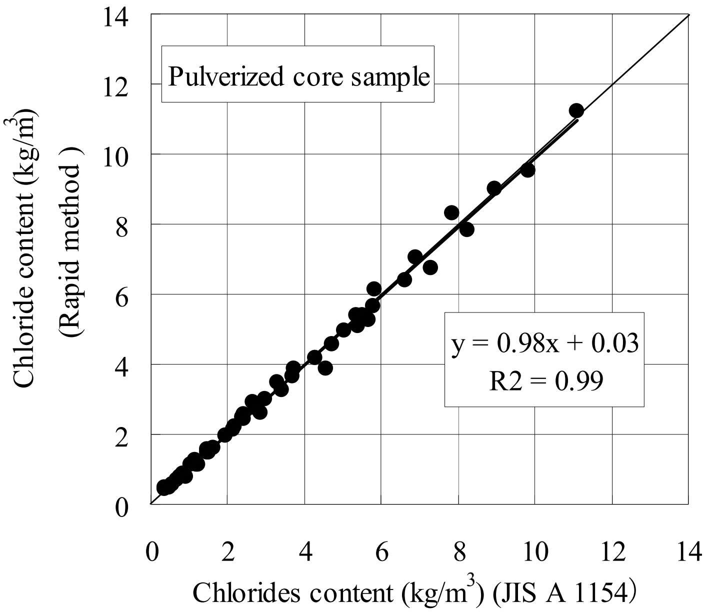

Figure 8.　Relationship between chloride contents obtained by JIS A 1154 and developed rapid method（Goto 2010）

Fig.9 shows relationship between the results of two methods. For chloride contents lower than 0.5 kg/m^3, results which were measured by the rapid method show higher values than those by JCI –SC5 method. In this case the data may be interfered by the ions such as sulfide sulfer etc., but it is not confirmed.

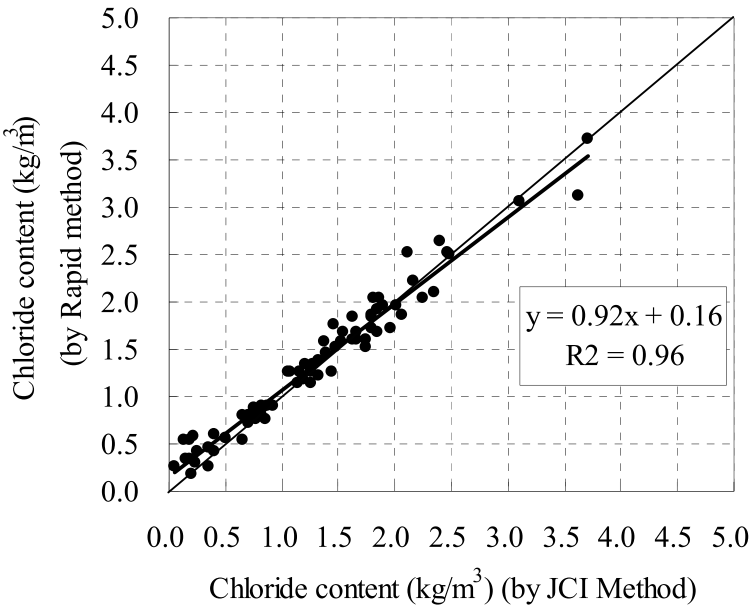

Figure 9. Relationship between chloride contents obtained by JCI-SC5 and developed rapid method（Yoshida 2010）

Site investigations show that the developed rapid method measuring chloride content in hardened concrete provides good approximation with standardized methods. Measured results may be affected by sulphide sulphur or there ions, but a treatment with hydrogen peroxide contributed to get better approximation.

APRICATIONS TO SITE INVESTIGATIONS

High rise coastal bridge inspection. The bridge named “Hamana-ohashi Bridge”, total length of 1,437m, is PC box girder type and located near the coast, and was completed in 1976. Renewal work to increase earthquake resistance was done in 2009, and investigation to evaluate the soundness was carried out in that occasion. Investigations include measurement of depth of cover and carbonation of concrete, chloride content in concrete, half-cell potential test and inspection of grouting state of PC cables.

To determine chloride content, sampling by drilling were done at the points ① to ⑥ in sections marked ▲, and sampling by coring were done at the points ① to ④ in the sections marked △ in Fig.10. Sampling depths were 0 to 20mm, 20 to 40mm, and 40 to 70mm. Chloride content was measured by the rapid method for drilled samples in site office and the results were obtained in the day or the next day, and by JCI-SC5 (acid soluble) for cores in the laboratory.

Fig.11 shows the typical results of the investigations. Chloride contents decreased with depth at each point. At depth of 30 mm, near the reinforcements, chloride content is lower than 1kg/m^3 at most of the points. But at the Point ② of section P7-P8, chloride content is about 1.5 kg/m^3 and corrosion of reinforcement may start.

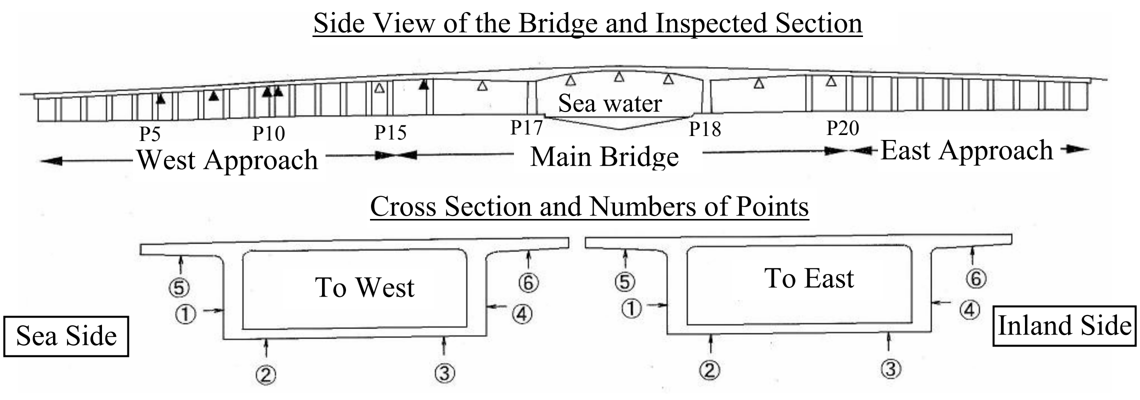

Figure 10. Sampling sections and points of Hamana-ohashi Bridge（Niitani 2010）

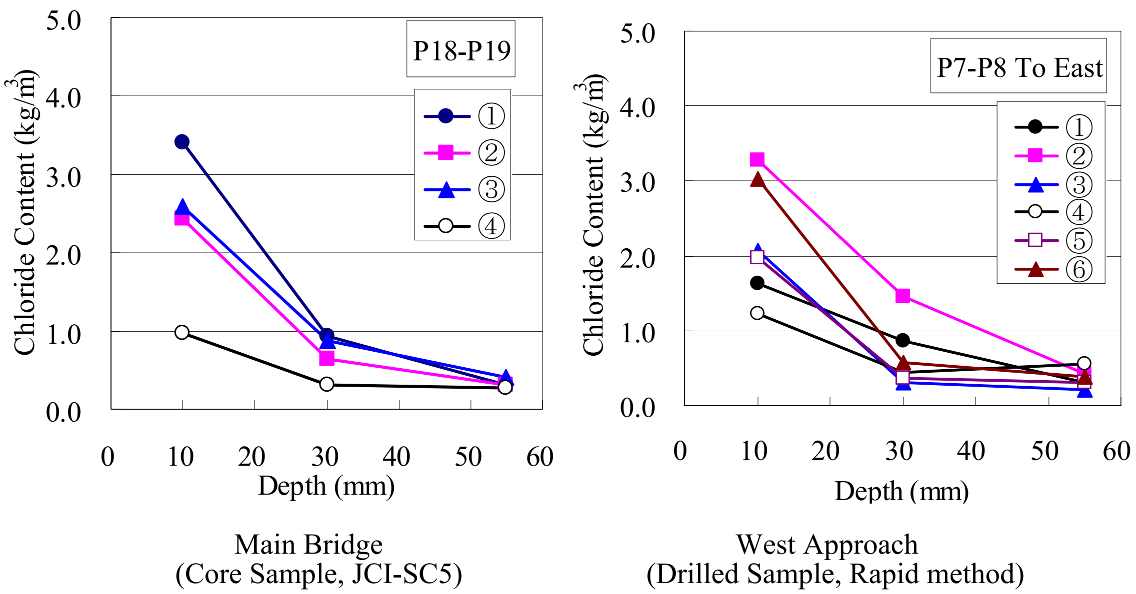

Figure 11. Chloride Content in Concrete（Niitani 2010）

Table 2 shows chloride content range of box girder concrete at a depth of 0 to 20mm. Minimum values of the west approach seems lower than that of main bridge over the sea water and maximum values are about the same.

Judging from the order of the chloride content and relation between content and depths, data obtained by the rapid method provide good approximation.

Table 2. Chloride Content in Concrete Box Girder

	Chloride content in concrete at the depth of 0-20mm (kg/m^3)											
	West Approach (by Rapid Method)					Main Bridge (by ICI-SC5)						
Section Pier No.	4-5	7-8	9-10	10-11	14-15	15-16	16-17	17-18	17-18	17-18	18-19	19-20
Min.	0.78	0.71	0.65	0.84	0.42	1.70	1.08	1.15	1.33	1.27	0.97	1.52
Max.	2.95	3.28	3.97	2.10	2.27	3.36	4.32	2.67	2.62	2.48	3.40	3.68

Inspection of the bridges affected by deicer. Deicer has been used in winter all over Japan, especially in northern part and high elevation aria. Deicer sometimes leaks with water from joints of bridges and leaches to an end of bridges. There is much reinforcement in bridge ends, so sampling by drilling and measurement of chloride content by the rapid method provide a good combination. Chloride content can be obtained by the rapid method at the site, it is suitable to specify the damaged extent for inspection and repair work.

Over sea project for inspection of the bridge. The Rapid method also applied to a project for inspection of the bridge in Africa. Investigations on the site include hammer test, cover survey, chipping and measurement of carbonation depth, core sampling and drill sampling for determination of chloride content, and half-cell potential test. Advantages to employ the rapid method for measuring chloride content were as follows,

a) Chloride contents of many bridge piers were obtained at the site,
b) Obtained data were used for deciding the points of core sampling and half-cell potential tests.

Chloride contents of surrounding soil were also measured by chloride ion meter.

CONCLUSION

The Rapid methods to measure chloride ion content in hardened concrete were developed and estimated to provide good approximation to the acid soluble data through site investigation. By the application to the site investigation project, many data can be obtained at a low cost on site and laboratory. So this method is thought to be very effective for site investigation and repair or renewal works. On the other hand, there are some themes to be improved, such as for cement paste there is difference between data obtained by the rapid method and that by the method using acid. At lower range of chloride content, the rapid method has a tendency to give higher value. Those are cased by elution process of chloride ion and coulometric titration chloride meter itself. We are going to make efforts to provide method having better approximation.

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