Bull. Chem. Soc. Jpn., *59*, *2785—2788 (1986)*

A Voltammetric Detection System for Measuring the Concentration of Chloride Ions in Fresh Concrete

Akifumi Yamada,* Kazunori Hodouchi, Koichi Katoh,† Nozomu Otsuga,††
Choichi Hashida,††† and Tetsuo Honda††††
Department of Materials Science and Technology, Technological University of Nagaoka,
Nagaoka 940-21
†Department of Applied Chemistry, Faculty of Engineering, Niigata University,
Ikarashi 2-No-Cho 8085, Niigata 950-21
††Department of Inorganic Materials, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152
†††Yoshikawa Sangyo Co., Kurosaki-machi, Niigata 950-11
††††Frontex Co., 1408 Ubagayama, Niigata 950
(Received April 25, 1986)

A voltammetric detection system for measuring the concentration of chloride ions in fresh concrete has been developed. A comparative determination using the Volhard titration method showed that the voltammetric system works as well in slushy concrete as in an aqueous chloride solution. No interference from the admixture was observed.

There is a growing trend to use sea sand instead of river sand for making concrete. However, sea sand is likely to contain a lot of chloride which can assist in the corrosion of reinforcing steel.[1,2] It is important, therefore, to determine the on-the-spot chloride content in fresh concrete in order to avoid exceeding the maximum limit. At present, various photoelectric, conductometric, and ion-selective detectors are available for measuring chloride ions in solution.[3] These detectors, however, present considerable technical difficulties when chloride-ion detection is attempted in fresh concrete.[3,4]

Preliminary studies[5,6] of a voltammetric method have shown that a voltammetric sensor has an excellent response to chloride in sea sand and fresh concrete samples. This paper reports the results of a study designed to develop a voltammetric system that seems to work as well in slushy concrete as in an aqueous solution.

Experimental

Instrumentation. A schematic diagram of the voltammetric detection system is shown in Fig. 1 together with the voltammetric sensor which consists of a small silver electrode (working electrode), a lead(II) sulfate/sodium sulfate electrode (reference electrode), and a stainless-steel electrode (counter electrode). Details regarding the voltammetric sensor have been previously described.[5]

The sensor was connected to a computer-controlled potentiostat consisting of an adder, a current-voltage converter(I/V), a sample-and-hold circuit(S/H), an analog-to-digital converter(A/D), display devices (LED, digital printer and x-y polotter), and a microcomputer. Bias and pulse voltages are applied to the adder through a summing resistor (omitted in Fig. 1), respectively. The pulse width of the pulse voltage is established by a pulse-time switch (digital). The start signal, initiated by depressing the start switch in the digital timing and control section, gates the pulse from the analog waveform generator to the potential

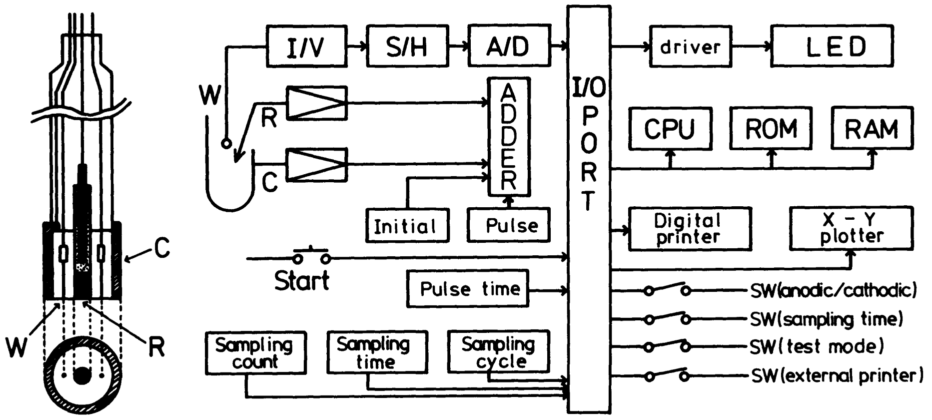

Fig. 1. Schematic diagram of the voltammetric sensor and the voltammetric detection system used for the determination of chloride ions in fresh concrete.
W: Working electrode, C: counter electrode, R: reference electrode, I/V: current-voltage converter, S/H: sample-and-hold, A/D: analog-to-digital converter, CPU: microcomputer, ROM: read-only memory, RAM: random-access memory.

control circuit and the cell. This also initiates a timing routine which controls the read signals to the analog-to-digital converter.

The current-monitoring sequence is accomplished by selecting three digital switches on a patchboard which controls the sampling count, sampling time and sampling cycle. The number of measurements and the interval of each run are controlled by a sampling-count switch and a sampling-cycle switch. A sample-and-hold circuit operates after the elapsed sampling time and the instantaneous current on chlonoamperogram is obtained. The analog-to-digital converter measures and converts the analog voltages from the current-measuring circuit. The digital information is stored in a random-access-memory unit. Upon completion of the measurements, the stored information can be recalled, then printed or plotted on an x–y plotter by operating a manual switch in the control section.

For a chloride determination, the electrolysis current is monitored only after the double-layer charging current has decayed. The working curve is stored in a read-only-memory unit and a fast determination of the chloride content is accomplished after comparing the current due to the chloride with a standard sample.

Procedure. During operation, the sensor is immersed in a concrete paste or paste filtrate with the working electrode held at 0.1 volt; at this potential silver chloride is reduced. Then, a 0.6-volt square-wave potential is applied to the working electrode and both the oxidation and reduction currents are monitored as a function of time. The electrode reaction is given by

$$\mathrm{Ag + Cl^- \longrightarrow AgCl + e} \quad \text{(anodic)} \tag{1}$$

and

$$\mathrm{AgCl + e \longrightarrow Ag + Cl^-} \quad \text{(cathodic).} \tag{2}$$

The results of the oxidation currents are mainly described in this paper. Usually, the following values are used for measurements: 10—15 for sampling count, 30—50 ms for sampling time, and 1 s for a sampling cycle. The current data correspond to the sampling count; an average of these data are printed out by a digital printer. Current-time curves can be plotted on an x–y plotter if necessary.

Materials. Fresh concrete was prepared by mixing ordinary portland cement (Asano, Onoda, Denka, and Kaihatsu), mineral aggregate, and water. It also contained some air and sometime air-entraining agents (Pozzolith No. 70, obtained from Pozorisu Bussan Co.). Reagent-grade sodium chloride was added to the mixing water to make a solution of the desired chloride concentration.

Reagent-grade silver nitrate, ammonium thiocyanate, ammonium iron(III) sulfate and nitrobenzene were used in Mohr[7] or Volhard[8] titration.

Results and Discussion

When portland cement is mixed with water, the cement particles become dispersed in the water. This suspension changes from the liquid state (slurry) to a plastic or a stiff paste with time. At the same time, a series of reactions occur between the two materials. These reactions are aggregately called the hydration of the cement and are frequently discussed in the literature:[9,10]

$$\mathrm{2(3CaO\cdot SiO_2) + 6H_2O \longrightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + 3Ca(OH)_2} \tag{3}$$

$$\mathrm{2(2CaO\cdot SiO_2) + 4H_2O \longrightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + Ca(OH)_2} \tag{4}$$

$$\mathrm{3CaO\cdot Al_2O_3 + 6H_2O \longrightarrow 3CaO\cdot Al_2O_3\cdot 6H_2O} \tag{5}$$

$$\mathrm{4CaO\cdot Al_2O_3\cdot Fe_2O_3 + 2Ca(OH)_2 + 10H_2O \longrightarrow 3CaO\cdot Al_2O_3\cdot 6H_2O + 3CaO\cdot Fe_2O_3\cdot 6H_2O} \tag{6}$$

Rapid hydration occurs primarily between the tricalcium aluminate of the cement and water. Simultaneously, the water becomes saturated mainly with calcium hydroxide, calcium aluminate, and gypsum; slurry-cement solutions exhibit remarkably strong alkaline nature.

It has been known that a number of insoluble complex salts such as $\mathrm{3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O}$ (Friedel salt), $\mathrm{3CaO\cdot Fe_2O_3\cdot CaCl_2\cdot 10H_2O}$, and $\mathrm{3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 32H_2O}$ are formed with chloride ions if chloride is present in the solution.[11] In fresh concrete, however, a major portion of the chloride is present as free chloride ions. The chloride determination was tested under various analytical conditions.

Working Curve in Chloride Solutions. The current-concentration characteristics of the voltammetric sensor were tested in chloride solutions with varying sodium chloride concentrations. The anodic current was measured at 50 ms after the beginning of electrolysis. Typical examples of the results are plotted in Fig. 2; a well-defined working curve was obtained in the range 0—1% NaCl (by weight).

The analyst usually wishes to measure the concentration of the chloride ions rather than their currents; thus concentration standards are necessary. When a sodium chloride solution is used for calibrating the electrode, the linearity in the standard seems to be excellent (Fig. 2). Thus, the working curve in the computer's memory was standardized before use.

Working Curve of Chloride in Cement Paste. A working curve for a cement paste which was prepared from different (Onoda, Denka, and Kaihatsu) commercially available cements was tested. Also 50 g of

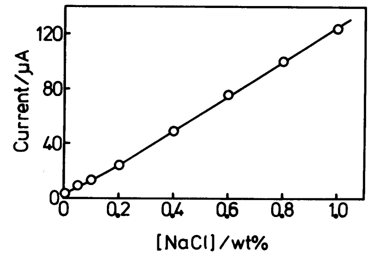

Fig. 2. Current-concentration characteristics of voltammetric sensor obtained in sodium chloride solutions (20 °C). sampling time=50 ms; sampling cycle=1 s.

portland cement was dissolved into 28 g of water containing various concentrations of sodium chloride. This cement paste was vigorously agitated in the thermostat(25 °C) for 20—30 min. Then, the sensor was immersed in a slushy paste and the current was measured fifteen times for a sampling time of 20 ms and a sampling cycle of 1 s. The average current for fifteen measurements was plotted against the chloride concentration after subtracting the background current.

The results are shown in Fig. 3. Although the background current due to the chloride-free-cement paste was somewhat different for each sample, a linear relation was found among those working curves: the slopes of the working curves were consistent with each other.

Reproducibility of Currents. The reproducibility of currents in a series of measurements was tested for a sodium chloride solution, a cement paste and fresh concrete. The composition of a cement paste is only cement and water, while fresh concrete contains water, cement, sand, gravel, and an air-entraining agent. The sensor was directly immerced in the solution, cement paste or mortar, and the current was measured every second with an appropriate sampling time (20—50 ms).

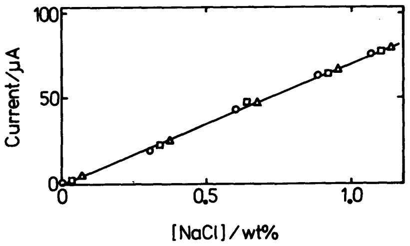

Fig. 3. Current-concentration characteristics of the voltammetric sensor obtained in cement pastes containing sodium chloride (25 °C).
Water/cement ratio=56%; sampling time=20 ms; sampling cycle=1 s.
○: Onoda cement, △: Denka cement, □: Kaihatsu cement.

Examples of raw-current data for ten runs are given in Table 1. Though the voltammetric sensor used in these measurements was not the same, a good reproducibility was seen for different media. The precision between runs varied from 1.5 to 5% over a range of 0.05 to 0.5% chloride. The last two columns are the currents for ten determinations, which involve ten runs in each measurement.

In general, the currents obtained in fresh concrete and cement paste were found to be smaller than those of a sodium chloride solution; this might be caused by a higher viscosity of the cement and by a bleeding phenomenon. When a concrete, after consolidation but still plastic, is allowed to stand unagitated, water usually appears at the surface. This autogeneous flow of mixing water within (or its emergence from freshly placed concrete, mortar or paste) is called bleeding, or water gain.[12]

Determination of Chloride in Fresh Concrete. Many different concretes are now being produced under different technical and economical conditions for a wide variety of purposes. Selections of concrete ingredients should be based on the construction conditions, the type of concrete structure, and the price and properies of the ingredients. In experiments, two types of fresh concretes with different consistencies were prepared; one was the normal concrete (slump=12 cm) and the other was hard concrete (slump=3 cm).

Fresh-concrete types were produced, according to JIS A 1138,[13] by mixing ordinary portland cement, natural sand, crushed stone, an air-entraining agent, and water. A proper amount of sodium chloride was

Table 1. Reproducibility of the Current Data Obtained in Fresh Concretes, Cement Pastes, and Sodium Chloride Solutions (25 °C)[a]

0.1 wt% NaCl solutions current/μA		Cement paste[b] containing 0.1 wt% NaCl current/μA		Fresh concrete[c] containing 0.2 wt% NaCl and admixtures			
				current/μA		current[d]/μA	
43.2	42.0	12.8	13.0	44.7	44.3	44.6	45.8
42.8	42.0	12.6	13.0	44.8	44.2	44.4	47.3
42.8	41.6	12.8	13.0	44.6	44.1	46.0	46.9
42.4	41.6	12.8	13.0	44.6	44.0	42.3	44.2
42.4	41.6	12.8	13.0	44.2	44.2	46.9	45.0
avg=42.3		avg=12.9		avg=44.4		avg=45.3	
σ=1.2%		σ=1.0%		σ=0.59		σ=3.2%	
t=50 ms		*t*=20 ms		*t*=50 ms		*t*=50 ms	

a) The sensor used for each measurement is different. Figures in the left column correspond to runs 1 through 5, and those in right column, to runs 6 through 10. σ represents the relative standard deviation of a single determination, and *t* is the sampling time. Sampling cycle is 1 s. b) Water/cement ratio=56%. c) Water/cement ratio=61%, Sand/aggregate ratio=50%. d) Data for ten determinations. A single determination gives an average of 10 runs.

Table 2. Proportioning of Test Concrete

No.	Max. size[a] mm	Slump cm	Entrapped air %	Water-cement ratio %	Sand-aggregate ratio %	Component in 1 m^3 of compacted concrete/kg					Chloride content[c] %
						Water	Cement	Fine[b] aggregate	Coarse aggregate	Admixture	
1											0
2	25	12	4.5	55.0	42.0	161	300	770 (757)	1069	0.750	0.02
3											0.05
4											0.10
5	25	2—3	4.5	47.7	43.6	140	300	825 (811)	1069	0.750	0.05

a) Maximum size of coase aggregate. b) The number in parentheses represents the weight of dry sand. c) Weight percent of NaCl for the weight of dry sand used.

Table 3. Determination of Chloride in Fresh-Concrete Samples

No.	Chloride content wt%	Slump cm	Entrapped air %	Chloride content found[a]/wt%		Difference[b] %
				Voltammetric method	Volhard method	
1	0	12.0	4.5	0.0075	0.0070	+7.1
2	0.02	11.0	4.5	0.0247	0.0236	+4.7
3	0.05	12.5	4.6	0.0538	0.0536	+0.4
4	0.10	12.0	4.6	0.103	0.104	−1.0
5	0.05	3.0	4.8	0.0532	0.0529	+0.6

a) Weight percent of NaCl for the weight of dry sand used. b) Difference between the voltammetric method and Volhard method.

added to the mixing water. The water/cement ratio was 48—55% and the sand/aggregate ratio was 42—44%. Table 2 summarizes the mix proportion used for the production of test concrete. The chloride concentration is usually expressed as the weight of sodium chloride divided by the weight of the small aggregate in a unit volume of concrete; this is the sodium chloride-sand ratio by weight.

The fresh-concrete types were filtered by an aspirator and the chloride content was measured by the voltammetric system. The chloride content was also determined by the Volhard method. Table 3 summarizes the results of the chloride content, slump and air content. The results show that the slump and air content agree with their target values; an adjustment of the batch weights for the test concrete was carried out satisfactory. Sample 1 (corresponding to no chloride content) showed a slight presence of chloride. This may have been caused by chloride contamination from the cement, air-entraining agent or water. However, it can be seen that the mutual relation between the voltammetric and Volhard methods was sufficiently estimated from the result of the measurements given in Table 3 (sample 1 through 4). The result of sample 5 shows that the voltammetric determination worked well for lower-water-content concrete; this method is applicable for concrete produced in general construction.

In conclusion, the convenience of this voltammetric system suggests that it could find on-the-spot applications in concrete manufacturing, in the construction industry, or for other consumers of concrete for a quality control of concrete.

The authors express their sincere thanks to Dr. Yoshikiyo Kato of Yamagata University for his continuous encouragements.

References

1) K. Kobayashi, T. Akaishi, K. Kishitani, M. Tokita, T. Fujii, Y. Kakegai, M. Kondou, Y. Nojiri, and H. Sawai, *Concrete Kougaku,* **22**, 2 (1984).

2) Proceedings of Japan National Council on Concrete, "Symposium on Effects of Chlorides in Reinforcing Concrete," Tokyo (1975).

3) A. Yamada and C. Hashida, *Denki Kagaku,* **52**, 728 (1984).

4) M. Tokita and H. Sakamoto, *Concrete J.,* **12**, 47 (1974).

5) A. Yamada and K. Hodouchi, *Denki Kagaku,* **52**, 633 (1984).

6) A. Yamada, K. Hodouchi, N. Otsuga, K. Ueda, and C. Hashida, *Chem. Lett.,* **1985**, 751.

7) "Shin-Jikken Kagaku Koza," ed by Chemical Society of Japan, Maruzen, Tokyo (1976), Vol. 9, p. 243.

8) Ref. 7, p. 244.

9) S. Popovics, "Concrete Making Materials," McGraw-Hill, New York (1979).

10) F. M. Lea, "The Chemistry of Cement and Concrete," 3rd ed, Chemical Publishing Company, New York (1971).

11) M. H. Roberts, *Mag. Concrete Res.,* **14**, 143 (1962).

12) S. Popovics, "Fundamentals of Portland Cement Concrete: A Quantitative Approach," John Wiley & Sons, New York (1982), Vol. 1.

13) Japanese Industrial Standard, "Method of Making Test Samples of Concrete in the Laboratory," Japanese Standards Association, Tokyo (1978).