CHEMISTRY LETTERS, pp. 751-754, 1985.

IN-SITU DETERMINATION OF CHLORIDE IONS IN FRESH CONCRETE BY VOLTAMMETRIC SENSORS

Akifumi YAMADA,* Kazunori HODOUCHI, Nozomu OTSUGA,†
Kazuyoshi UEDA,†† and Choichi HASHIDA†††
Department of Materials Science and Technology, Technological University of Nagaoka, Nagaoka 949-54
†Department of Inorganic Materials, Tokyo Institute of Technology, Ookayama, Tokyo 152
††Frontex Co., Ltd., 1408 Ubagayama, Niigata 950
†††Yoshikawa Sangyo Co., Kurosaki-machi, Niigata 950-11

The voltammetric sensor was applied to the analysis of chloride content in sea sand and fresh concrete samples. The oxidation and reduction currents at the silver electrode were monitored as a function of the time. Chloride recovery was found to be good from fresh concrete.

Concrete is a stone-like material obtained by allowing a carefully proportioned mixture of cement, sand and gravel (or other aggregate), and water to harden. Recently, a lot of sand obtained from the sea has been used instead of river sand. Sand from the sea, however, contains a higher concentration of chloride ions; these chloride ions assist in the corrosion of reinforcing steel.[1,2] It is important, therefore, to determine on-the-spot chloride content in fresh concrete to avoid exceeding the maximum limit. The maximum limit is now under consideration in the Ministry of Construction, but the value will be in the range of 0.17 - 170 mmol dm^{-3}.[3] At present various photoelectric, conductometric and ion selective detectors are available for the detection of chloride ions in solution.[3] These detectors, however, present considerable technical difficulties when chloride ions detection is attempted at fresh concrete.[3,4]

In this investigation we applied the voltammetric sensor to the analysis of chloride ions in sea sand and fresh concrete samples. The voltammetric sensor[5]

consists of a small silver electrode (working electrode), a lead sulfate/sodium sulfate electrode (reference electrode) and a stainless steel electrode (counter electrode) as shown in Fig. 1. It is not necessary that these three electrodes be situated together. The size of the working electrode can be reduced so that in-situ determination of chloride ions in fresh concrete is possible.

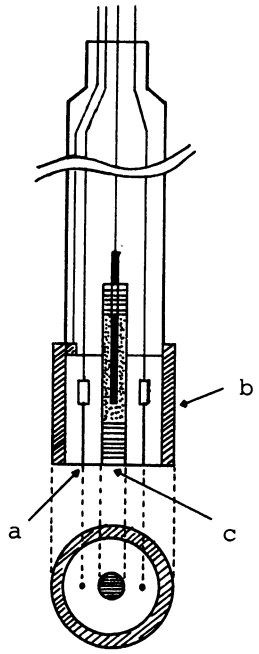

Fig. 1. Voltammetric sensor for detection of chloride ions in fresh concrete
a. silver
b. stainless steel
c. $Pb/PbSO_4/NaSO_4$

The sensor was connected to a computer-controlled potentiostat. The potentiostat consists of an adder, an analog-to-digital converter, display devices (LED, digital printer and X-Y plotter), and a microcomputer. The working curve is stored in read-only memory, and fast determination of chloride content was accomplished after comparing the current due to chloride with standard one.

Initially, the potential of the working electrode was held at the potential at which silver chloride is reduced (+0.1 V) and then the square wave potential (0.6 V) was applied to the working electrode. The electrode reaction is given by

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

and

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

Both the oxidation and the reduction currents at the silver electrode were monitored as a function of time.

The working curve of this sensor was tested both in basic solution (0.1 mol dm^{-3} NaOH) and in neutral solution (0.1 mol dm^{-3} $NaNO_3$) with varying chloride concentration. A well defined working curve was obtained in the range of 0 - 0.2 mol dm^{-3} Cl^-. The slope of the working curve obtained in the basic solution, however, was smaller than that obtained in the neutral solution. This may be due to the following reaction.

$$2Ag + 2OH^- \longrightarrow Ag_2O + H_2O + 2e^- \qquad (3)$$

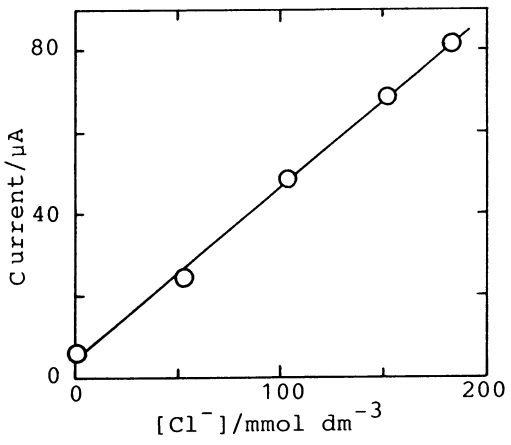

Fig. 2. Working curve for detection of chloride ions in fresh concrete
water/cement ratio = 28 : 50
temperature = 25 °C

Table 1. Examples of current data for detection of chloride ions in fresh concrete

Run	Current/μA	Run	Current/μA
1	18.4	9	21.6
2	19.6	10	22.0
3	20.4	11	22.0
4	20.8	12	22.0
5	20.8	13	22.0
6	21.2	14	22.4
7	21.2	15	22.4
8	21.6	average	21.2

Water/cement ratio is 28 : 50.
Concentration of Cl^- : 27 mmol dm^{-3}.
Temperature: 25 °C.

A dummy, fresh concrete (water/cement ratio = 28 : 50) paste was also used to test the function of the chloride sensor. The sensor was directly inserted into 78 g of paste made from portland cement and water (pH ca. 13.4). Sodium chloride was added to the concrete paste and the chloride content was checked both by the voltammetric sensor and by the Mohr's method. Chloride recovery was good from fresh concrete and resulted in a linear voltammetric response over a concentration range of 0.17 - 170 mmol dm^{-3} as shown in Fig. 2. A similar test was also done for samples of sea sand, and chloride recovery was found to be good. A particle size of sea sand did not affect the accuracy of measurements.

Examples of the current data obtained in fresh concrete (water/cement ratio = 28 : 50) containing 27 mmol dm^{-3} Cl^- are given in Table 1. The precision between runs varied from 1.5% to 5% for a concentration range of 10 - 100 mmol dm^{-3} Cl^-. The accuracy of chloride determination obtained at lower concentrations (0 - 5 mmol dm^{-3}) was not as good as that obtained at higher concentrations.

Fresh concrete was prepared by mixing cement, sand, gravel and air-entrapping agents by using water containing sodium chloride. The water/cement ratio was 61% and the results are given in Fig. 3. The chloride content was also determined by the Volhard's method. The results were in good agreement with that obtained by

the titration method as is shown in Fig. 3. It was also found that chloride content obtained in the upper part of the cement paste was larger than that in the bottom part. This may be due to phenomena of bleeding.

Other useful applications of this teqchnique include the direct analysis of chloride ions in foods without dilution. A well defined, but non-linear work curve was obtained up to 600 mmol dm^{-3} Cl^{-}.

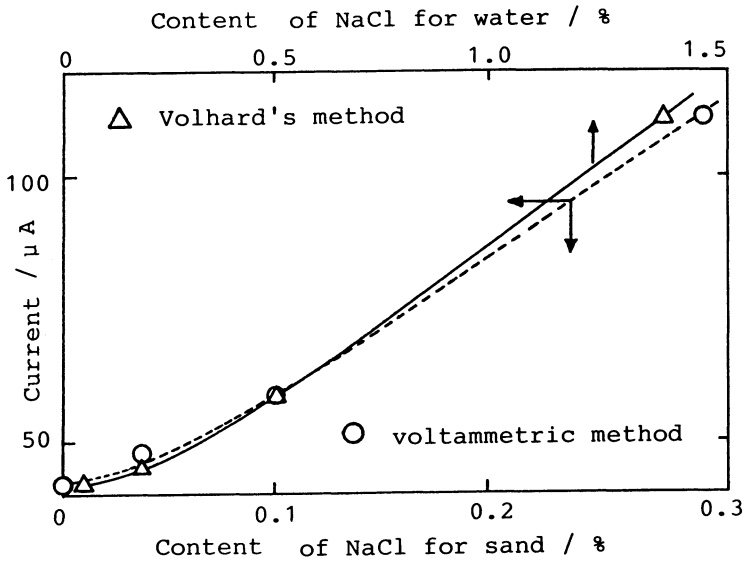

Fig. 3. Determination of chloride content in freshly prepared concrete by means of the voltammetric method and Volhard's method at room temperature.
water/cement ratio = 61%
sand/gravel ratio = 50%

The authors express their sincere thanks to Drs. Yoshikiyo Kato of Yamagata University and Koichi Katoh of Niigata University for their continuous encouragements.

References

1) K. Kobayashi, T. Akaishi, K. Kishitani, M. Tokita, T. Fjii, 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 Journal, 12, 47 (1974).
5) A. Yamada and K. Hodouchi, Denki Kagaku, 52, 633 (1984).

(Received March 25, 1985)