

office without being double checked by one of the partners who was not directly responsible for its preparation. This highly-commendable practice symbolizes GCC's careful, independent and efficient approach to corrosion problems, which has enabled the partnership to achieve its unparalleled position amongst those whose job it is

to combat the effects of corrosion wherever it occurs.

The assistance of the partners in GCC in the preparation of this review of their activities is gratefully acknowledged. Global Corrosion Consultants can be contacted on 0952-462777 (fax no: 0952-462903).

# The influence of clay addition on the electrochemical corrosion behaviour of mild steel in concrete

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*THE CORROSION BEHAVIOUR of mild steel embedded in concrete containing various proportions of clay and partially immersed in sea water, sodium chloride and sodium sulphite solutions respectively, has been studied in this investigation by potential measurements using a digital voltmeter and a Cu/CuSO<sub>4</sub> electrode. A reduction in corrosion behaviour in all the corrosive test media was obtained when increasing proportions of the total concrete mix (Portland cement) were being replaced with increasing percentages of clay additions. This has been attributed to the reduction in porosity of the concrete matrix due to the addition of fine clay, which hinders the mobility of chloride, sulphide, sulphate and other ions in the sea water. The clay additions also provide increasing bonding strength and causes a reduction in the carbonation process. Corrosion reactions in sea water were found to be more than in NaCl solution, and sodium sulphide solution has the lowest tendency towards corrosion. The addition of clay to the concrete mix was found to be beneficial to an extent towards corrosion prevention or control.*

## Introduction

The desire to gain more knowledge about corrosion phenomena and their prevention or control in steel reinforced concrete structures has been of utmost concern and interest, in particular to corrosion scientists and engineers, for quite some time. The prevention of metallic corrosion in structures, and the consideration of its effects in initial design and fabrication or later during in-service inspection and retrofit, is vital in ensuring the expected longevity of the structure. A consideration of the ramifications of corrosion and its prevention in different types of structures such as modern high-rise buildings, multi-storey car parks, stadia, bridges and other specialized structures has been mentioned[1].

Various means have been derived to control corrosion in structures. Among these means are cathodic protection, applying barrier coatings on the embedded steel to resist corrosion, and application of similar barriers to the concrete surface to resist penetration of the constituents contributing to corrosion. It is believed that addition of other fine mineral particles or dusts to concrete mixes could protect or aggravate corrosion by either enhancing the passivity of the embedded

steel or by contributing to its breakdown. Therefore, an investigation has been carried out to determine the effects of addition of micro-silica or condensed silica fume to cement pastes on the durability of reinforcing steel in concrete, particularly under circumstances in which chloride-contaminated concreting materials are liable to be encountered[2].

The objective of this current work is to look at the effect of fine clay particle additions to cement paste on the corrosion behaviour of embedded steel in concretes. In addition to other factors, the results obtained will help to determine the suitability of clay as an addition to a concrete mix.

The general term 'clay' refers to a group of minerals in which the chief constituent is hydrated silicate of alumina. This group occurs as aggregates of minute flakes, the chemical structures of which consist of sheets of atoms, the nature and detailed arrangements of which determines their bonding characteristics[3]. The two major forms of clay are kaolinite (Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>.2H<sub>2</sub>O) and bentonite (with a general formula Al<sub>2</sub>O<sub>3</sub>.4SiO<sub>2</sub>.xH<sub>2</sub>O). The clay used in this work consists more of kaolinite mineral than montmorillonite - the major mineral in the bentonites as observed from x-ray diffraction[4].

| Constituent          | Concentration |
|----------------------|---------------|
| K <sup>+</sup> ppm   | 300           |
| %                    | 0.03          |
| Na <sup>+</sup> ppm  | 1710          |
| %                    | 0.171         |
| Ca <sup>2+</sup> ppm | 1120          |
| %                    | 0.112         |
| Fe ppm               | 8080          |
| %                    | 0.808         |

Table 1. Chemical composition of Igbokoda clay.

The clay was obtained from Igbokoda in Nigeria, where among its uses has been traditional house construction.

Sea water was used in this study to represent or simulate the marine environment, while sodium sulphite was used to simulate an industrial or chemical-industrial environment. Sodium chloride was used because of its aggressive corrosion reaction (due to the Cl<sup>-</sup> ion) in steel-reinforced concretes[5-7].

Concrete is a hard, dense material that consists of cement paste surrounding aggregate particles. The behaviour of steel in contact with concrete is generally governed by the properties of the Portland cement, which is an alkaline material resulting from the presence of Ca(OH)<sub>2</sub> and other soluble alkaline salts. The pH of a saturated Ca(OH)<sub>2</sub> solution is known to be approximately 12.5[1]. It is also known that under these circumstances and in the presence of moisture and oxygen, the steel will be in a passivated condition due to the formation of a thin film of oxide - generally considered to be FeOOH. However, the behaviour of steel in concrete as it is influenced by high pH can be drastically altered by two primary factors[1,8]. The first is carbonation, or the reaction of the Ca(OH)<sub>2</sub> with CO<sub>2</sub> from the air to form calcium carbonate (CaCO<sub>3</sub>) which lowers the pH of the concrete. Under these conditions, the steel is no longer passive, but can become active and corrode significantly. This is a process of carbonation which is a function of the porosity of the concrete, itself a function of other factors among which is the water/cement ratio. Corrosion of embedded steel

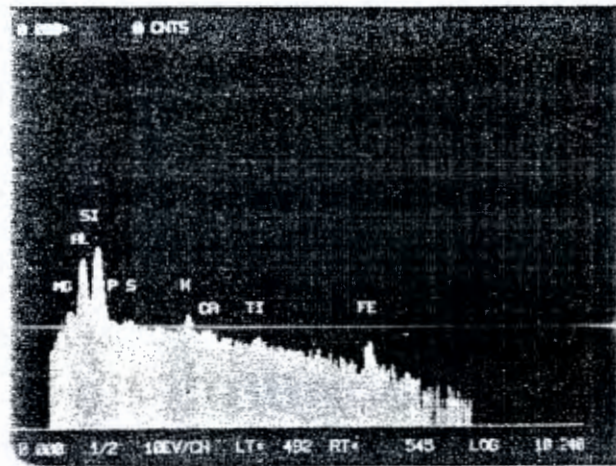


Fig.1. SEM/EDS qualitative analysis of Igbokoda clay.

due to carbonation is commonly prevented by using protective coatings on steel or using inherently corrosion-resistant materials such as stainless steel.

The influence of chloride is the second major factor to corrosion of embedded steel in concrete. In sufficient quantity, chloride prevents the formation of the initial protective oxide film on steel (if the chloride is present in the material mix during the curing process), or, if added later, breaks down the passive film and allows corrosion to proceed by a mechanism similar to the pitting of stainless steel passive films by chloride.

With reference to the above review, it is expected in this work that the addition of clay will have some modifying effect on the rate at which CO<sub>2</sub> from the air could penetrate the concrete to react with the Ca(OH)<sub>2</sub> due to the clay's finely-particulate nature, its bonding tendency, and the fact that it would alter the chemistry of the concrete composition. It is also expected that the carbonation process which is a function of the porosity of the concrete could be affected by the addition of clay; and also that the reaction and/or free movement of chloride ions within the concrete could be hindered.

## Experimental procedure

### Preparation of slab samples

The reinforced slabs used for the experiments contained cement, sand and gravel in the ratio 1:2:4, with varying amounts of clay particle addition as given below. Each slab was 160mm long, 100mm wide and 100mm thick: some were made with no clay addition, while others were made with 5%, 10% and 15% clay addition.

The type of cement used was Portland, while the Igbokoda clay had the chemical composition listed in Table 1.

After drying in the oven, the clay was ground into fine particles, and a water/cement ratio of 0.9 was

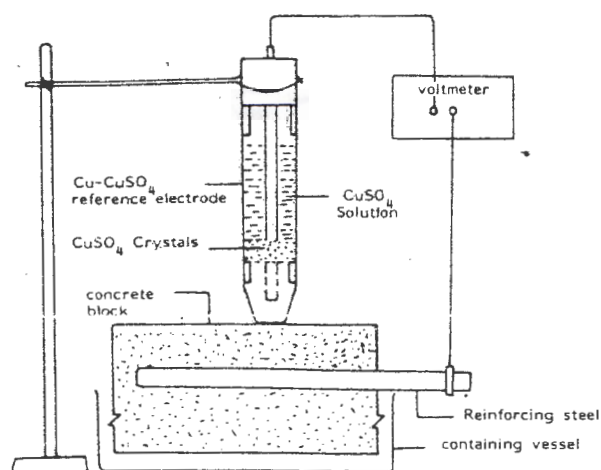


Fig.2. Schematic diagram of the experimental set up.

used for mixing the clay with the cement, sand and gravel.

The embedded cylindrical reinforcing steel bar used was of type ST-60 mild steel obtained from Oshogbo Steel Rolling Mill Co Ltd, Nigeria. It had a chemical composition of 0.35%C, 0.30%Si, 1.6%Mn, 0.04%P, 0.04%S, 0.25%Cu, 0.1%Cr, 0.1%Ni, 0.11%N, the remainder being Fe. The 120-mm diameter steel bars were each cut into 160-mm lengths.

Before embedding in the concrete, mill scale was removed using silicon carbide 120 and 240 abrasive paper; 140mm of each steel bar sample was embedded in each concrete, while the remaining 20-mm portion outside was used for electrical connection to a voltmeter. The outside portion, with the exception of the point of wire connection, was painted with epoxy paint to prevent its corrosion by moisture.

#### pH measurement

10gm of the fine clay particles were dissolved in 50ml of distilled water. Its pH was measured with a pH meter.

#### SEM analysis

A scanning electron microscope (SEM) equipped with energy dispersive spectrophotometer (EDS) was used qualitatively to analyse the chemical composition of the clay (Fig.1).

#### Test solutions

The solutions used as corrosive media in this work were:

- sea water;
- 1M NaCl solution;
- 0.3M Na<sub>2</sub>SO<sub>3</sub> solution.

#### Potential measurements

The experimental set up in this work (Fig.2) follows the same procedure as has been previously

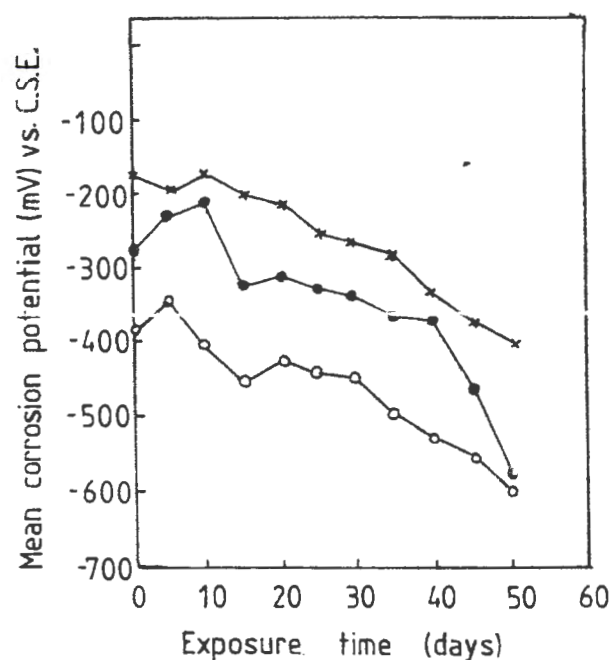


Fig.3. Variation of corrosion potential with time for mild steel in concrete without clay content. Note: x = 0.3M Na<sub>2</sub>SO<sub>3</sub> solution; • = 1M NaCl solution; o = sea water.

described[5]. Each of the steel-reinforced concrete slabs with and without different percentages of clay addition was placed, in turn, in a rectangular plastic vessel, and one of the three above test media added. A copper/copper sulphate electrode was then placed on the concrete slab and firmly clamped. The Cu/CuSO<sub>4</sub> electrode was connected to the voltmeter by an insulated flexible wire, and the voltmeter was similarly connected to the outside portion of the reinforcing steel bar to complete the circuit. Readings were taken at five-day intervals, and this procedure was repeated for every test medium used. The readings thus obtained were used to plot mean-corrosion-potential vs time-of-exposure curves.

#### Results and discussion

The clay's pH of 4.2 shows that it is acidic, indicating that its chemical composition is rather more influenced by calcium ions than sodium ions. At this pH value the clay was viscous due to the flocculation[9] of the clay platelets.

Though a previous chemical analysis has shown, in part, that the chemical composition of the clay was as shown in Table 1, the SEM/EDS analysis (Fig.1) did not indicate the presence of sodium ions.

#### 0% clay addition

Fig.3 shows the curves of mean corrosion potential vs time of exposure (in days) for the steel reinforced concrete slab specimens without clay addition, and partially immersed in sea water, sodium chloride and sodium sulphite solutions. The Na<sub>2</sub>SO<sub>3</sub> medium showed very little corrosion.



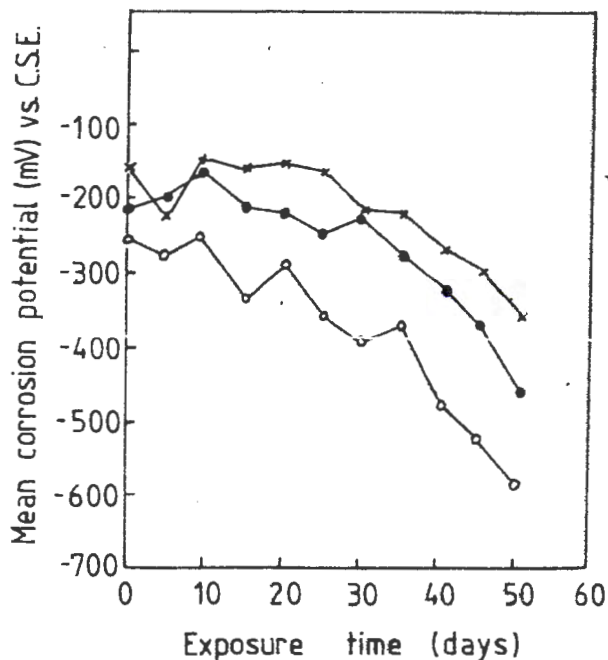
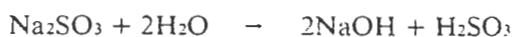


Fig.4. Variation of corrosion potential with time for mild steel in concrete with 5% clay content. Note: x = Na<sub>2</sub>SO<sub>3</sub> solution; • = 1M NaCl solution; ◊ = sea water.

Though the curve indicates an active corrosion reaction throughout the whole experimental period, corrosion did not start until about the 40th day of the experiment, when the potential was about 350mV. With reference to a Cu/CuSO<sub>4</sub> electrode, a potential within a range of 0-200mV indicates no corrosion occurrence and a passive corrosion reaction, and the range 200 to 350mV indicates an active or passive condition[8]. The modest corrosion reaction in Na<sub>2</sub>SO<sub>3</sub> is due to the weak nature of the sulphurous acid produced by the reaction of the solution with water:



which could not depassivate with ease the passive film on the embedded steel bar caused by the alkaline nature of the deposit.

In the first 10 days of the experiment, the NaCl solution has a passivating effect on the embedded steel in the concrete, as does the sea water in the first five days. The reacting ion species, particularly the Cl<sup>-</sup> ion, could not depassivate the hydroxyl passivating film on the steel bar within these periods. However, from the 10th day of the experiment, there was an increasing corrosion of the steel bar in the NaCl solution right up to the end of the experiment on the 50th day. It was observed, though, that very little corrosion occurred during the period between the 15th and 40th days, which was undoubtedly as a result of the 'stifling' nature of the corrosion deposits on the corrosion reactions. The sodium chloride solution was far more corroding than the Na<sub>2</sub>SO<sub>3</sub> solution due to

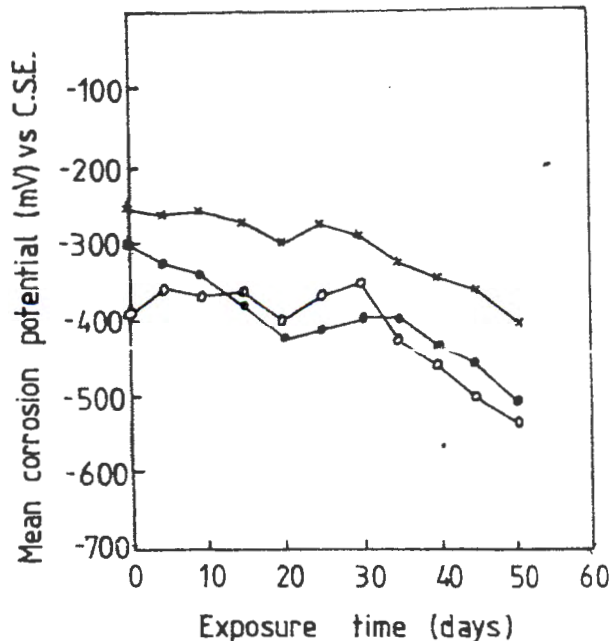


Fig.5. Variation of corrosion potential with time for mild steel in concrete with 10% clay content. Note: x = 0.3M Na<sub>2</sub>SO<sub>3</sub> solution; • = 1M NaCl solution; ◊ = sea water.

the chloride ions which could more easily penetrate the passivating film.

The sea water was the most corrosive of the three corrosive media. Though with little fluctuation between the 15th and 30th days, the medium showed active corrosion throughout the experimental period after the first five days. The corrosive nature of the sea water is not unexpected considering the various anions and cations it contained, including the aggressive Cl<sup>-</sup> ions. Further comments on the effect of the sea water will be given later in this discussion.

#### 5% clay addition

The addition of 5% clay to the concrete mixture caused some changes in the corrosion behaviour as shown in Fig.4. All the corrosion potentials recorded increased in the positive direction when compared with those of Fig.3, except for the sea water medium on the 50th day, which maintained the same potential of -600mV.

All the initial potentials increased; that is, they became more passivating when compared with those in Fig.3. The curve for the sodium sulphide medium, though showing an active corrosion reaction after the 25th day, did not reach the corrosion range until after the 45th day when the recorded potential fell below -300mV. Also, the active corrosion in NaCl solution started after the 30th day and continued to the end of the experiment, with a potential of -470mV compared with -575mV recorded for the specimen without clay addition. The sea water shows a fluctuating curve of active and passive corrosion reactions for

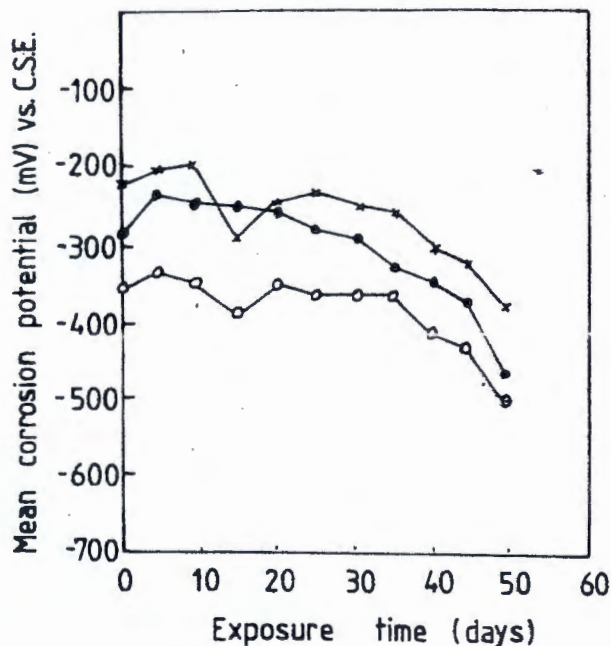


Fig. 6. Variation of corrosion potential with time for mild steel in concrete with 15% clay content. Note: x = 0.3M Na<sub>2</sub>SO<sub>3</sub> solution; • = 1M NaCl solution; o = sea water.

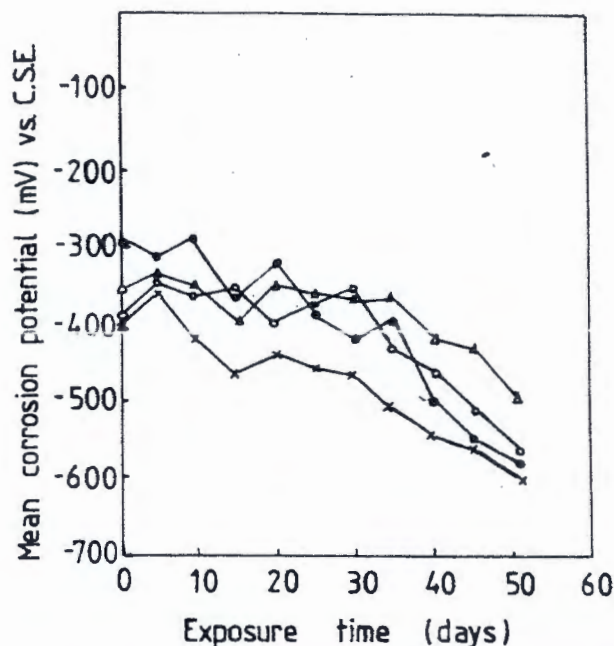


Fig. 7. Variation of corrosion potential with time for mild steel in concrete with various clay contents, partially immersed in sea water. Note: x = 0% clay; • = 5% clay; o = 10% clay; Δ = 15% clay.

the first 20 days of the experiment. before the predominant active corrosion set in and lasted until the end of the experiment.

The implication of these results is that 5% clay addition to the concrete mixture has either imparted some passivity onto the embedded steel which makes it difficult for the reacting species (ions) to penetrate the passivating film, or that the fine clay particles have produced very fine pores that make it difficult for the reacting ions to move freely to the steel bar. The chemistry of the concrete mixture might have also been changed, thereby causing less corrosion reactions; this will be further explained later. In Fig. 4, the order of the corrosion reactions' magnitude is: sea water > NaCl solution > Na<sub>2</sub>SO<sub>3</sub> solution, due to the same reasons given earlier.

#### 10% clay addition

Fig. 5 shows that there was a drastic diminishing of the active corrosion reaction of the embedded steel bar in the three different test media with the addition of 10% clay to the concrete mixture. Even with aggressive and corrosive sea water, all the recorded potentials were above -500mV except for on the 50th day (-515mV). The only well-defined active corrosion reactions recorded for the sea water started after the 30th day; the NaCl solution did not record any potential more negative than -500mV, and the Na<sub>2</sub>SO<sub>3</sub> solution maintained a very weak and slightly-active corrosion reaction only after the 30th day of the experiment.

It could thus be seen that an increase in the percentage of clay content of the concrete mixture

caused a further reduction in the corrosion reaction occurring at the interface of the embedded steel bar and the concrete matrix.

#### 15% clay addition

The trend of corrosion behaviour, in general, as shown in Fig. 6 with 15% clay content in the concrete mixture, is different from that of Fig. 5 in that the sea water maintained an almost steady-state corrosion behaviour up to the 35th day except for a slight change on the 15th day of the experiment. The most negative potential recorded was -500mV, and active corrosion started mainly after the 35th day. In the sodium chloride solution the embedded steel bar remained at potential values (between -200 and -300mV CSE) where corrosion did not occur (the passive condition) for the first 30 days of the experiment. The corrosion that occurred in the last 15 days could not be said to be much, as indicated by the potential values -310mV (at the 35th day) and -470mV (at the 50th day) of the experiment.

#### 20% clay addition

With 20% clay addition to the concrete matrix, the corrosion reactions and hence the corrosion of the embedded steel was very much further reduced. The increased clay content also further reduced the concrete porosity by blocking the pores and thereby considerably hindering the free movement of the chloride ions and other reacting species migrating to the steel/concrete interface. Furthermore, the steel bar seems to have been passivated to such an extent that the reacting ions found it difficult to penetrate.

A comparison of the corrosion behaviour of the specimens with differing clay contents was made in sea water (Fig.7). Sea water was chosen as it was the most aggressive media used; it also combines different reacting ions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Br}^-$ , etc. Sea salt is known to be particularly aggressive to steel, due to the fact that it contains substantial concentrations of magnesium chloride in addition to the chloride from its major constituent - sea salt, sodium chloride. The effect of  $\text{NaCl}$  on the conductivity of the liquid film and its destruction of protective corrosion films makes it deleterious to the corrosion behaviour of steel. In addition,  $\text{MgCl}_2$  acts to acidify the liquid film, and by its deliquescent action, to increase the time of wetness. The most negative potentials and hence the greatest corrosion of the embedded steel bar in concrete, were obtained in the order 0% clay > 5% clay > 10% clay > 15% clay additions. Except for the specimen that had no clay addition, the above order became very clear only after the 20th day. In addition to the above discussion, the decrease in corrosion reactions and in the corrosion of the embedded steel bar in concrete, as indicated by the potential values, can further be explained on the basis of the nature of the clay chemistry. A strong clay-water-silica-cement bond can be formed, in addition to the fine clay particles blocking the interstices, that could both hinder the free movement of chloride and sulphite ions, and the penetration and diffusion of atmospheric  $\text{CO}_2$  into the concrete matrix. This will limit the number of reacting ions getting to the steel, as well as the occurrence of carbonation resulting from  $\text{CO}_2$  penetration.

As mentioned above, the Ighokoda clay has a greater mineral kaolinite content than that of montmorillonite and others minerals, as shown in Fig.1 and Table I. The pH of the clay is 4.2, making it acidic and viscous. Clay particles, in general, possess a surface charge either due to rupture of the bonds (in kaolinite) or because of lack of electrical neutrality (in montmorillonite). In both cases, exchangeable ions such as  $\text{Na}^+$  may be adsorbed to provide neutrality[10]; this attracts water molecules either to the edge, as in kaolinite, or between the plates, as in sodium montmorillonite. Surface attraction also exists between water and quartz (sand) because of an unequal balance of charges at the fractured quartz surface. A linkage, quartz (sand)-water-clay- is therefore set up, and this in combination with cement will form a very strong bond.

The interaction of the sodium ion content of the sea water, the  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_3$  respectively could activate the clay and thereby replace its calcium content and, in part, the calcium content of the cement. This will lead to the precipitation of a calcium salt ( $\text{CaCl}_2$ ). When chloride is present in

the concrete mix, the tricalcium aluminate of the concrete can 'insolubilize' a certain portion of the chloride during the curing process[1]. This fact possibly accounts for the insoluble salt ( $\text{CaCl}_2/\text{NaCl}$ ) observed forming on top of the concrete after some time during the period of the experiment.  $\text{CaCl}_2$  has been known to be deliberately added to the concrete mixture (approx. 2% by weight of cement) to accelerate the set[1].

The acidic nature of the clay is an indication that excess  $\text{H}^+$  ions are bonded to the clay particles. The  $\text{Na}^+$  (from the  $\text{NaCl}$ , sea water, etc.) which 'activates' the clay by ion exchange/adsorption) will make the clay basic by replacing the excess  $\text{H}^+$ , in addition to the contribution from the very basic composition of the cement. As the pH changes towards the basic value, viscosity will also change[9], thereby enhancing optimum distribution of clay particles within the concrete mixture. A good distribution is expected in order to make a contribution to good bonding in the concrete, blocking the interstices and hence reducing porosity and free chloride movement. This will also hinder  $\text{CO}_2$  penetration into, and diffusion within, the concrete matrix. A combination of these factors should lead to a decrease of corrosion of the embedded steel bar in the concrete.

## Conclusions

1. The addition of clay to the concrete mixture reduces the corrosion of mild steel bar embedded in it. The greater the quantity of clay added, the less the corrosion reactions. This has been attributed to the bonding effect of the clay, and its blocking of the concrete interstices and consequent reduction in the porosity and hindering of the free movement of chloride and other ions. Blocking the interstices also reduces the penetration into and diffusion within the concrete matrix of the atmospheric  $\text{CO}_2$  which causes carbonation.
2. Sea water was found to be most corrosive, followed by the sodium chloride solution, with the sodium sulphite solution being the least corrosive.

## Acknowledgements

The authors acknowledge the co-operation of the Department of Metallurgical and Materials Engineering, Obafemi Awolowo University for making available the research facilities used in this work. The kind permission of the Department of Engineering Metals, Chalmers University of Technology, Gothenburg, Sweden, in the use of SEM/EDS equipment for qualitative clay analysis is also acknowledged.

See the top of page 109 for References

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# Galvanic corrosion of API N-80 carbon steel and high chromium steel in aqueous CO<sub>2</sub> environments and its inhibition — Part 2

by Chun-Chi Su

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*THE FIRST part of this paper was published in our February 1989 issue. In it, the author explained the philosophy behind his research, gave experimental details, and discussed the effect of temperature on galvanic corrosion between the steels examined. He noted that the galvanic effect was more significant at 70°C and 100°C in 0.03% NaCl solutions respectively. This concluding section reports on the effect of chloride ions and the efficiency of inhibitors on galvanic corrosion, and presents the author's overall conclusions.*

## 2. Effect of chloride ion

From the data given in Table 2, it is clear that the galvanic effect is more evident with the increase of sodium chloride concentration except at 70°C. At temperatures of 100°C and 150°C, the galvanic effect in 3% NaCl solution is more evident than that of the 0.03% NaCl solution in which galvanic corrosion almost does not occur.

The corrosion rate of N-80 carbon steel does not change noticeably when it couples to AISI 410 SS at high temperatures (>100°C), in 0.03% NaCl solution. Under this condition, a dense corrosion product deposits on the surface of the carbon steel as shown in Fig.5(a). As the concentration of sodium chloride was increased to 3%, the morphology of the corrosion product film is changed, as shown in Fig.5(b). The crystals of the corrosion product are layer-like and do not completely cover the metal surface; however, no apparent difference on the morphology of the corrosion product is found in 0.03% and 3% NaCl solution at 70°C, as shown in Fig.6. This explains

why the galvanic effect is more pronounced at 100°C and 150°C in 3% NaCl solution than that in 0.03% NaCl solution, and no apparent difference is found between 0.03% and 3% NaCl solution at 70°C.

The effect of temperature on galvanic corrosion in CO<sub>2</sub>-containing environments is affected by the chloride ion. It is proposed that the chloride ion plays the following role: (1) it causes a higher potential shift of N-80 carbon steel when it couples to AISI 410 SS, and therefore results in the damage of the protective film; (2) it changes the morphology and character of the corrosion product (FeCO<sub>3</sub>); and (3) it enhances the dissolution of iron (Fe — Fe<sup>2+</sup> + 2e<sup>-</sup>) due to the strong electron affinity. The above three reactions perhaps take place simultaneously and complement each other.

*Inhibition efficiency of corrosion inhibitor on galvanic corrosion*

Table 3 shows the corrosion rate of coupled and uncoupled N-80 carbon steel with inhibitor treatment and the protection percentage at different



strongly protected by the presence of  $\alpha$ -phase, compared to its uncoupled corrosion rates. SAF 2205 is thus found to have a much better corrosion resistance than corresponding austenitic stainless steels on this case. These tendencies are verified by the comparison of the active curves of SAF 2205,  $\alpha$ - and  $\gamma$ -alloys. Although these curves show real dissolution rates and are free from any influence from the cathodic reaction, their shape is influenced by the modifications of the specimens surface during the dissolution process of duplex steels.

► An examination of the variation of the anodic current of SAF 2205 with time within the active range shows a difference in the shape of the curves depending on whether one or two phases are involved in the dissolution process. A combined effect of surface alteration due to selective dissolution and the local variation of the solution composition is believed to be the reason for this behavior.

► A reduced dissolution rate at the corrosion potential of SAF 2205 has been achieved by increase of the anode/cathode area ratio through heat treatment. However, a secondary peak of very high dissolution rate appeared on the active curve, which was attributed to the above-mentioned local variations.

#### ACKNOWLEDGMENTS

The present work was carried out as a part of the basic research program of the Swedish Institute for Metals Research. Fi-

ancial support was provided by the Swedish Board for Technical Development, Sandvik Steel AB, Avesta AB, AST, Fagersta Stainless, APM.

The author is indebted to Bevis Hutchinson, SIMR for valuable discussions and critical reading of the manuscript. H. Eriksson, P. Hagenfeldt, P. Norberg, Sandvik Steel AB, S. Hertzman, SIMR, and members of the research committee are thanked for stimulating discussions and suggestions. H. Thoors is thanked for assistance with the SEM work.

All material used in this study was provided by Sandvik Steel AB.

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# Electrochemical Noise Generation during SCC of a High-Strength Carbon Steel ☆

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#### ABSTRACT

*Stress-corrosion cracking experiments have been performed on a high-strength carbon steel exposed to acidified sodium chloride solution poisoned with sodium sulfide. The electrochemical potential of the specimen was monitored during the experiment, and this paper reports the observed electrochemical noise. The analysis was performed using both the maximum entropy method and the discrete Fourier transform. A consistent noise behavior was observed throughout the experiment, with the only perturbation of any significance being associated with major transients that occurred when the specimen actually failed. The average noise power measured over a period of the same order as the duration of the transients has been found to be an effective method of detecting them, but it is expected that this will be much more difficult in service conditions.*

**KEY WORDS:** electrochemical, frequency, noise generation, power spectra, stress corrosion, time record.

#### INTRODUCTION

Noise is a general term used to describe the fluctuating behavior of a physical variable with time. For an electrochemical process one may measure either the voltage noise (i.e., the fluctuation in the electrochemical potential with time) or the current noise (e.g., the fluctuation of galvanic current flowing between two specimens or the fluctuation in applied current in a potentiostatic experiment). For this work the voltage noise has been studied, and this introduction will concentrate on this mode of measurement, although it will be appreciated that current noise measurements are similar in most respects.

The phenomenon of electrochemical noise and the information that it may provide on corrosion processes has received considerable attention in recent years.<sup>1-5</sup> The analysis of electrochemical noise is now considered to give useful information about the rate and nature of electrochemical processes taking place at the electrode, although the theoretical basis of much of the interpretation is somewhat limited. For a pure activation-controlled process the source of the noise is thought to be the stochastic fluctuation of the rates of the forward and reverse reactions. In the more common case (for corrosion) of reaction at filmed interfaces the source of the noise is somewhat less clear, but it tends to be attributed to the breakdown and repair of the film. Other processes

\* Submitted for publication October 1986; revised August 1988.

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that can be expected to give rise to noise are the unstable initiation and repassivation of pits, crevice corrosion, fluctuations in convective mass-transport, and the growth of a stress-corrosion crack. As the several mechanisms proposed for the growth of stress-corrosion cracks may be expected to have different electrochemical noise characteristics, it was felt to be useful to determine these characteristics for systems with reasonably well-understood mechanisms of crack growth.

In this work the electrochemical noise generated during the SCC of a high-strength carbon steel freely corroding in a deaerated, acidified NaCl solution has been studied, and the noise emitted correlated with the progress of the stress corrosion test. SCC in this metal-environment system is almost certainly due to hydrogen embrittlement, and it was expected that the cracking would occur by a discontinuous, essentially mechanical process, with the main source of noise being associated with the intermittent exposure of fresh surface to the solution.

## EXPERIMENTAL PROCEDURE

### Material

The material used for these tests was purchased as "gauge plate," mainly because this provided a good-quality high-carbon steel in the form of thin surface-ground sheet. The composition of the material was: 0.95C, 0.35Si, 1.27Mn, 0.019S, 0.018P, 0.16Ni, 0.06Cr, 0.08Mo, 0.12V, 0.02Co, 0.002Ti, 0.028Nb, 0.23Cu, 0.05Al, 0.04Sn and 0.017Pb. This was cut into blanks 120 mm long, 10 mm wide, and 1 mm thick. Preparation of the specimen involved heat treatment followed by polishing. Heat treatment consisted of austenitization in argon at 800°C for 2 hours, followed by oil quenching. The specimens were then tempered at 207°C for 1 hour. This heat treatment gave an ultimate tensile strength (UTS) of 2274 MPa and a Brinell Hardness of 680. The surfaces of the specimens were prepared by polishing with abrasive paper down to 1200 grit, followed by 3 and 1  $\mu\text{m}$  diamond.

### Sample Loading

The specimens were loaded in buckling using a simple bolt-loaded clamp which is shown in Figure 1. The main feature of this loading is the loading washer, which contains an annular groove into which the end of the specimen fits, thereby ensuring reasonably precise alignment. A large-diameter (20-mm) bolt was used to maximize the stiffness of the loading jig. The stress in the specimen was determined by measuring its curvature with a dial gauge mounted on a U-section stand, the stress in the outer fibers being calculated from the relationship:

$$S = \frac{4Et d}{l^2}$$

where

S = Stress in outer fiber

E = Young's modulus

d = Distance of center of arc to the chord

t = Specimen thickness

l = Length of chord

### Environment

The solution used was 3.5% sodium chloride solution, to which 500 ppm of sodium sulfide was added as a hydrogen recombination poison. Shortly before the experiment, the solution was acidified with  $\text{H}_2\text{SO}_4$  to a pH of 2. Additionally, the solution was deaerated with nitrogen in order to reduce the competitive effect of oxygen on the cathodic reaction. As a result of the low pH the sulfide would have been present predominantly in the form of  $\text{H}_2\text{S}$ , some of which will have been removed by the deaeration, but this still results in an environment with a very strong tendency to generate hydrogen, which dissolves in the steel.

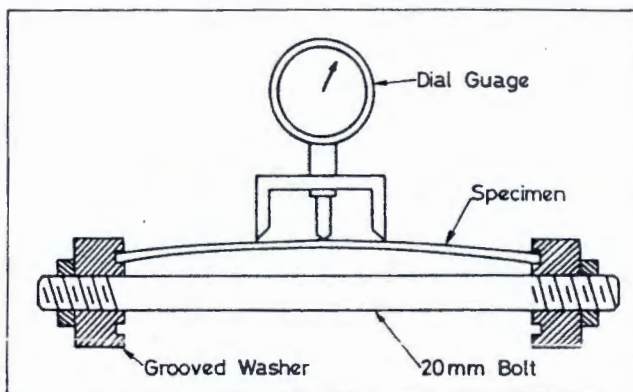


FIGURE 1. Specimen configuration and loading jig.

### Time-to-Failure Tests

In order to provide a baseline for the electrochemical noise measurements the time-to-failure was determined for specimens stressed to a range of values. The time to-failure was monitored visually, and by means of a record of the specimen potential. The results are shown in Figure 2. As might be expected for a very high-strength steel in an aggressive environment, failure occurs rapidly, even at relatively low stresses.

### Electrochemical Noise Measurement

For studies of electrochemical noise, the specimens were stressed to 796 MPa (35% of the yield stress), giving a time-to-failure of approximately 2½ hours. The loading jig was supported above the surface of the solution, so that only the stressed steel was exposed to the solution. The electrochemical potential of the specimen was measured with respect to a saturated calomel reference electrode. The measurement was made with a Solartron<sup>(1)</sup> 7055 digital voltmeter. This was controlled by a Hewlett Packard<sup>(2)</sup> HP85 desk-top computer, which also served to record the readings on magnetic tape. Time records consisted of blocks of 1024 readings taken at one second intervals. Allowing for a delay of about 3 minutes while the readings were written to tape at the end of the time record, each reading took approximately 20 minutes. Other than the delay in storing the data onto the tape, time records were taken continuously, hence about eight time records were taken over the duration of a typical test.

### Data Analysis

It is not clear that an optimum method has yet been developed for the presentation and interpretation of electrochemical noise data. The most common approach used is to transform the data from the time domain (i.e., the time record) to the frequency domain to give a spectrum of the power density present at any given frequency. This is a common technique in various fields of physical science, particularly communications engineering, and several algorithms have been developed to perform this transformation. Unfortunately, none of these are without difficulties when applied to typical corrosion time records, since they must all make assumptions about the properties of the variable being studied. In general the mathematically rigorous techniques assume that the variable is stationary, i.e., all its statistical properties such as mean and variance do not change with time. This tends to be a questionable assumption for corrosion processes; in particular the mean value of electrochemical potential is frequently observed to drift with time. The variance may well change with time as well, although this is more difficult to detect by inspection of the time record.

<sup>(1)</sup> Solartron Instrumentation Group, Sangamo Weston, Inc., Irvine, CA.

<sup>(2)</sup> Hewlett Packard Co., Precision Instruments, Palo Alto, CA.