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Effect of $RuCl_3$ Concentration on the Lifespan of Insoluble Anode for Cathodic Protection on PCCP

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Prestressed Concrete steel Cylinder Pipe (PCCP) is extensively used as seawater pipes for cooling in nuclear power plants. The internal surface of PCCP is exposed to seawater, while the external surface is in direct contact with underground soil. Therefore, materials and strategies that would reduce the corrosion of its cylindrical steel body and external steel wiring need to be employed. To prevent against the failure of PCCP, operators provided a cathodic protection to the pre-stressing wires. The efficiency of cathodic protection is governed by the anodic performance of the system. A mixed metal oxide (MMO) electrode was developed to meet criteria of low over potential and high corrosion resistance. Increasing coating cycles improved the performance of the anode, but cycling should be minimized due to high materials cost. In this work, the effects of $RuCl_3$ concentration on the electrochemical properties and lifespan of MMO anode were evaluated. With increasing concentration of $RuCl_3$, the oxygen evolution potential lowered and polarization resistance were also reduced but demonstrated an increase in passive current density and oxygen evolution current density. To improve the electrochemical properties of the MMO anode, $RuCl_3$ concentration was increased. As a result, the number of required coating cycles were reduced substantially and the MMO anode achieved an excellent lifespan of over 80 years. Thus, we concluded that the relationship between $RuCl_3$ concentration and coating cycles can be summarized as follows: No. of coating cycle = $0.48*[RuCl_3 \text{ concentration, M}]^{-0.97}$.

Keywords : *cathodic protection, insoluble anode, MMO (Mixed Metal Oxide), lifespan, ruthenium chloride, PCCP (Prestressed Concrete steel Cylinder Pipe)*

1. Introduction

Various metallic structures have been buried in underground soil. These structures can be classified as buildings, basic piles of civil structure, tanks storing oil and gas, and pipes for transfer of various fluids etc. Among these buried structures, pipes hold special important in the field of corrosion engineering. On the other hand, the corrosion rate of piles is not so high in soil. Moreover, limited numbers of corrosion and pollution problems are associated with thanks. Thus, we can safely imply that piles and tanks do not undergo massive corrosion in soil as they occupy limited area. However, pipes laid underground in soil, extending over large areas both in terms of width and length. Therefore, underground pipes are susceptible to corrosion. In particular, scientists and engineers working are nuclear power plants have to devise a novel and effective strategy to control corrosion of pipes, else there could be leakage from corroded pipes in nuclear power plants and fossil fuel power station; since the plants may induce shutdown of energy utility, corrosion control strategy should be established.

Prestressed Concrete steel Cylinder Pipe (PCCP) has been fabricated according to AWWA C301 standard which clearly describes the mandatory requirements that need to be adhered to while fabricating underground pipes[1-3]. While developing PCCP, manufacturer includes steel wiring and prestressing around the steel cylinder. Therefore, it can be safely operated even when the applied internal and external pressure is high. PCCP are extensively used as seawater pipes which are used for cooling in nuclear power plants. One moot point to be considered is that the internal surface of PCCP is exposed to seawater, while the external surface is in direct contact with underground soil. Therefore, we need to employ materials and strategies that

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would reduce the corrosion of its cylindrical body and external wiring, both of which are made from steel[4]. To alleviate the failure of PCCP, operators provided a cathodic protection to prestressing wires[5]. They posited that cathodic protection reduces the rate of corrosion and minimizes corrosion-based failures in PCCP. Nevertheless, an uncontrolled or unidentified stray current can cause rapid deterioration of PCC pipelines by bridging about hydrogen embrittlement (HE). Although cathodic protection has been used to control corrosion in PCCP, it can be the cause of failures in some situations[6]. In two studies supported by the American Water Works Association Research Foundation (AWWARF) researchers developed methodologies to identify the sources of stray currents in order to protect pipelines from the adverse effects of stray currents. They also identified issues that need to be tackled while grounding electric utility items[7, 8]. Many researchers have proposed the use of pulsed cathodic protection[9].

There is a significant interest in the preserving and extending the shelf-life of water mains, especially PCCP[10-13]. The efficiency of cathodic protection is governed by the anodic performance of the system. While implementing cathodic protection, we select a material that exhibits excellent electric conductivity and use it as the anode. Some typical anodic materials include graphite, high Si cast iron, and electric conductive oxide coated valve metals. Since consumption rate of graphite or high Si cast iron etc. is relatively high, they are not suitable to be used in long-term protection or high protection current systems. Dimensionally Stable Anode (DSA) electrode was developed to meet criteria of low over potential and high corrosion resistance[14-16]. This electrode was composed of metal oxide such as RuO_2, IrO_2, and Co_2O_3. In order to improve corrosion resistance capacity, several oxides such as Ta_2O_5, TiO_2, MnO_2 were mixed with them[17-19]. In addition to low over potential, the lifespan of this novel anode had to be maximized. In particular, the lifespan of the anode is essential to improve the performance of steel cylinder and wiring that is used in PCCP. With this objective, many researchers have suggested strategies to improve the lifespan of anode. This includes lowering the evolution potential of oxygen and minimizing the consumption rate of surface oxide[20,21]. The lifespan of DSA is dependent on the single component used for coating. Furthermore, the performance of DSA can be dependent upon both the components when a binary coating system is employed. In addition, the performance of anode can be improved by increasing coating cycles; however, a minimum number of coating cycles have to be carried out contain the cost of materials. In this research study, we focused on efforts on deducing the relationship between $RuCl_3$ concentrations and coating cycle by performing electrochemical and lifespan evaluation tests.

2. EXPERIMENTAL METHODS

Preparation of MMO anode ; Ti Grade 2[22] plate (10×80×1mm) was used as the base metal; coating was performed on this base metal. We used a SiC paper #220 for mechanical polishing. After completion of this process, Ti plate was immersed for 30 minutes in 35 % HCl solution at room temperature. Thereafter, this plate was rinsed with distilled water. In order to prepare a stable RuO_2 sol at room temperature, we used ruthenium chloride hydrate ($RuCl_3 \cdot 3H_2O$, Kojima Chemical Co. Saitama, Japan) at a fixed concentration. Isopropanol ($(CH_3)_2CHOH$, Aldrich, St. Louis, USA) was used as the solvent. Subsequently, we performed sol-gel coating on Ti plate, through the following procedure: a single cycle coating process of dip-coating was performed at the rate of 1.0 cm/min. Thereafter, the coating was subjected to the first drying step at 130 °C for 10 minutes. Finally, the coating was subjected to a second drying step at 450 °C for 10 minutes. After coating the plate for a requisite number of cycles, final heat treatment was performed at 450 °C for 1h. After coating, the surface was observed using a scanning electron microscope (SEM, JSM-6300, 20 kV, 80 μA, Jeol Corporation, Tokyo, Japan).

Lifespan evaluation test ; Lifespan was evaluated according to National Association of Corrosion Engineer, NACE TM0294[23] in sodium chloride (30 g/L NaCl), sodium hydroxide (40 g/L NaOH), and simulated pore water (0.20 % $Ca(OH)_2$ + 3.20 % KCl + 1.00 % KOH + 2.45 % NaOH + 93.15 % H_2O)). When using accelerated life test, the anode shall be demonstrated to survive a minimum total charge density 38,500A-h/m^2. This is the amount of total charge density an anode is subjected to if operated at a current density of 110 mA/m^2 of anode surface for 40 years.[23] Lifespan was calculated according to the above relationship. A current was constantly applied at 320 mA that was modified to facilitate the test, and the experiment was performed until the electrode potential of 4 V was attained with respect to the saturated calomel electrode (SCE), which is a reference electrode in electrochemical studies.

Electrochemical tests ; Polarization test (scan rate: 1 mV/sec) and cyclic polarization test (scan rate: 1 mV/sec) were performed using a potentiostat (Gamry Instruments, DC 105, Warminster, USA) in deaerated 1 M H_2SO_4 at

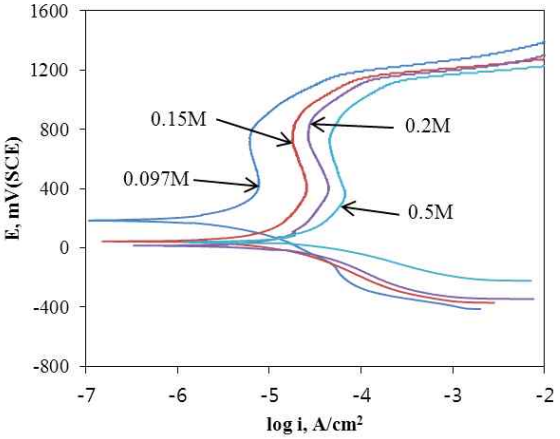


Fig. 1. Effect of $RuCl_3$ concentration on the polarization in deaerated 1M H_2SO_4 at 25°C (three cycles).

25 °C. Moreover, alternating current (AC) impedance was measured in deaerated 1 M H_2SO_4 at 25 °C using an AC impedance analyzer (Gamry EIS 300) which was operated between 0.01 Hz and 100,000 Hz at the potential of +600 mV(SCE).

3. RESULTS and DISCUSSION

3.1 Effect of $RuCl_3$ concentration on electrochemical properties of MMO electrode

The electrode showing excellent electrochemical properties and corrosion resistance is only used as the anode while assembling cathodic protection system in a concrete structure. Fig. 1 shows the effect of $RuCl_3$ concentration on polarization behavior, which is carried out in deaerated 1 M H_2SO_4 solution at 25 °C. Three cycles of coating were performed. After every coating, we maintained the first drying temperature at 130 °C for 10min. and the second drying at 450 °C for 10 min. The test electrode was fabricated by carrying out final heat treatment at 450 °C for one hour. The different concentrations of $RuCl_3$ were as follows: 0.097 M, 0.15 M, 0.2 M, and 0.5 M. After measuring open circuit potential OCP), polarization was carried out at a potential that was - 0.5 V below OCP. Within the range of cathodic polarization, we normally observed activation polarization.

Fig. 2(a) shows open circuit potential and oxygen evolution potential. Fig. 2(b) shows passive current density at +600 mV(SCE). It also shows oxygen evolution current density at oxygen evolution potential, which was determined from Fig. 1. The measured OCPs were as follows: +184 mV(SCE) (0.097 M $RuCl_3$), +43 mV(SCE) (0.15 M $RuCl_3$), +15 mV(SCE) (0.2 M $RuCl_3$), +40

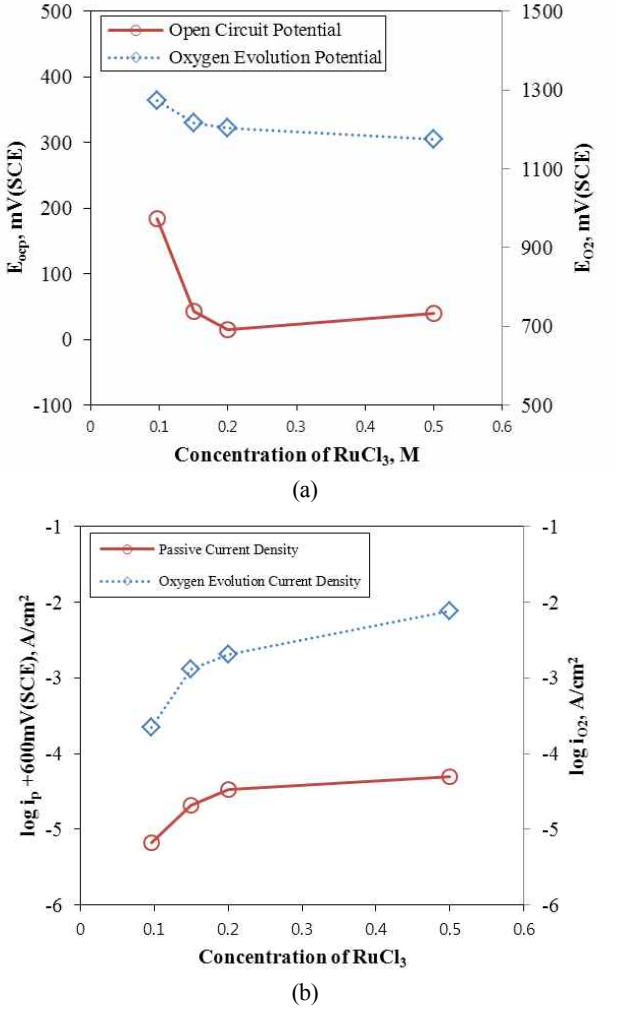
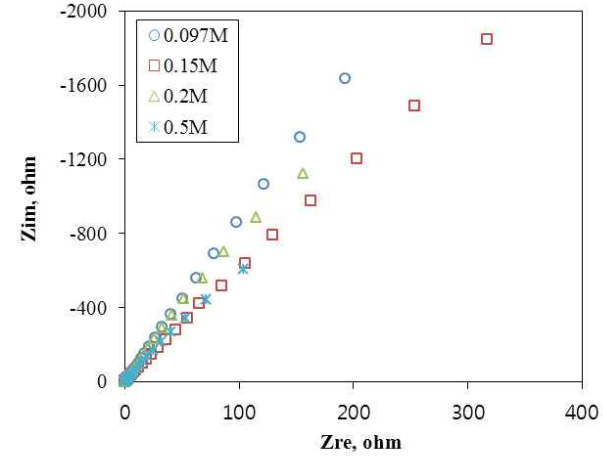
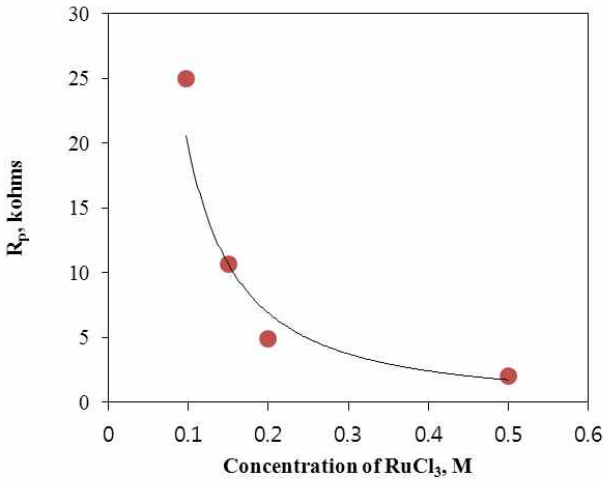


Fig. 2. (a) Open circuit potential and oxygen evolution potential, and (b) passive current density at +600 mV(SCE) and oxygen evolution current density at oxygen evolution potential determined from Fig. 1 (a).

mV(SCE) (0.5 M $RuCl_3$). This indicates that OCP generally decreases by increasing the concentration of $RuCl_3$. In contrast, oxygen evolution potential decreases with a decrease in the concentration of $RuCl_3$. Thus, we imply that increasing the concentration of $RuCl_3$ would form a more conductive oxide: OCP and oxygen evolution potential would be lowered consequently. By performing anodic polarization, every electrode revealed passive state. Passive current densities at +600 mV(SCE) were $10^{-5.18}$ A/cm^2, $10^{-4.68}$ A/cm^2, $10^{-4.48}$ A/cm^2, $10^{-4.3}$ A/cm^2 using the following respective concentration of $RuCl_3$: 0.097 M, 0.15 M, 0.2 M, and 0.5 M. Moreover, the current density at which oxygen gas evolved gradually increased with the increasing concentration of $RuCl_3$. This indicates that increasing the concentration of $RuCl_3$ would form a more conductive oxide increasing passive current density and



(a)



(b)

Fig. 3. Effect of $RuCl_3$ concentration on (a) Nyquist plot in deaerated 1M H_2SO_4 at 25°C (three cycles) and (b) polarization resistance obtained from Fig. 3 (a).

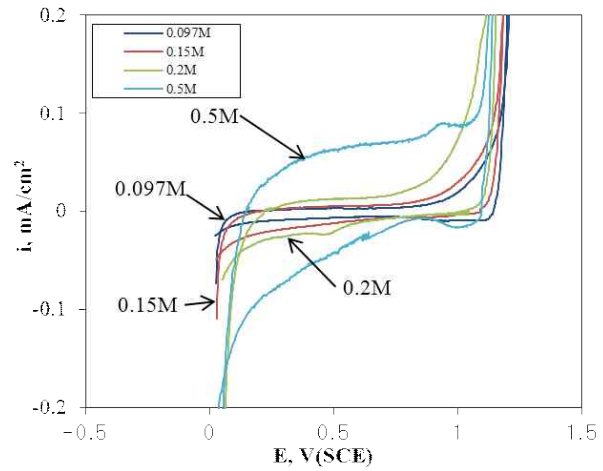
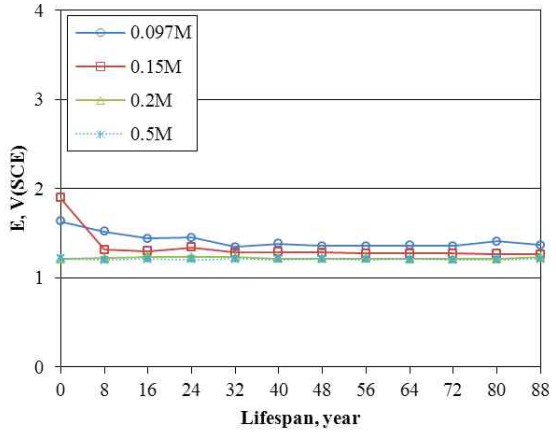
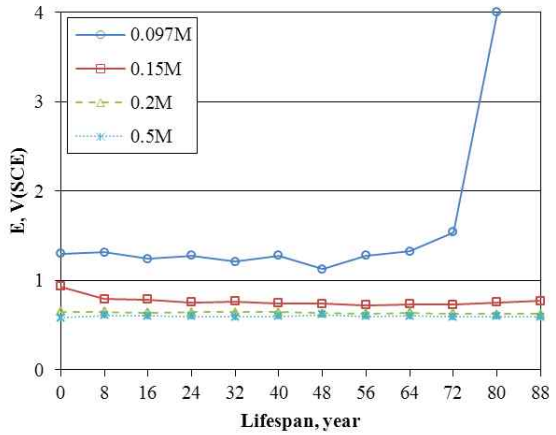


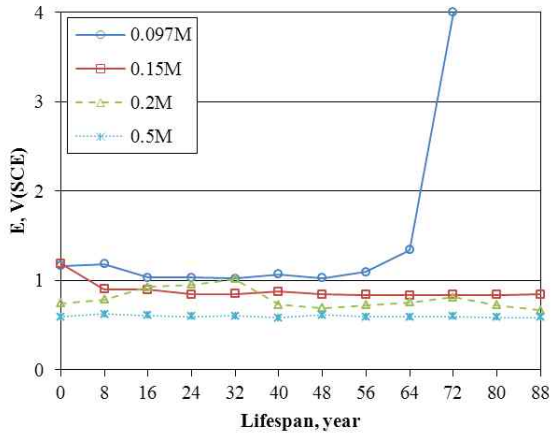
Fig. 4. Effect of $RuCl_3$ concentration on cyclic polarization of three cycle's coating in deaerated 1M H_2SO_4 at 25°C.



(a)



(b)



(c)

Fig. 5. Effect of $RuCl_3$ concentration on lifespan of three cycle's coated specimen: (a) 3% NaCl, (b) 4% NaOH, and (c) simulated pore water.

oxygen evolution.

Fig. 3(a) shows the effect of $RuCl_3$ concentration on

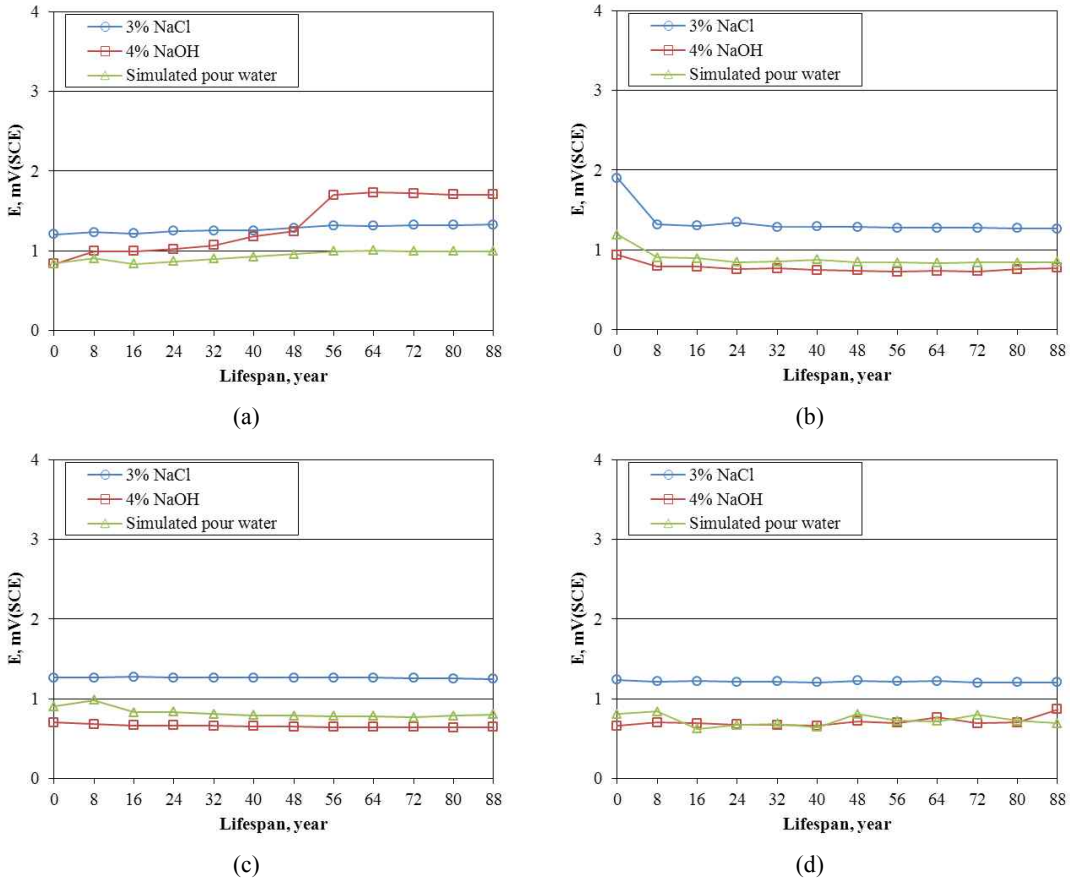


Fig. 6. Lifespan of optimum cycle's coated specimen with $RuCl_3$ concentration: (a) 0.097M - five cycles, (b) 0.15M - three cycles, (c) 0.2M - two cycles, (d) 0.5M - single cycle.

Nyquist plot in deaerated 1 M H_2SO_4 at 25 °C (3 cycles). Fig. 3(b) shows the effect of $RuCl_3$ concentration on polarization resistance, which is calculated from the data shown in Fig. 3(a). We measured the AC impedance at +600 mV(SCE) in the range of 0.01 Hz to 100 kHz. Polarization resistance was calculated using Randle Cell model. At varying concentration of $RuCl_3$, the polarization resistances were as follows: 25.0 kohms (0.097 M $RuCl_3$), 10.7 kohms (0.15 M $RuCl_3$), 4.9 kohms (0.2 M $RuCl_3$), and 2.0 kohms (0.5M $RuCl_3$). When the concentration of $RuCl_3$ was increased, polarization resistance greatly reduced. The relationship between the concentration of $RuCl_3$ and polarization resistance could be derived from the following expression: 'R_P, kohms = 0.60*[Concentration of $RuCl_3$, M]$^{-1.5}$'.

Fig. 4 shows the effect of $RuCl_3$ concentration on cyclic polarization of three cycle coated specimen in deaerated 1 M H_2SO_4 at 25 °C. The following quantities of electric charge were obtained at varying concentrations of $RuCl_3$: 5.2 C (0.097 M $RuCl_3$), 4.9 C (0.15 M $RuCl_3$), 2.6 C (0.2 M $RuCl_3$), and 1.9 C (0.5 M $RuCl_3$). The polarization behavior, AC impedance, and electric charge increased when the amount of conductive oxide was increased by increasing the concentration of $RuCl_3$.

3.2 Effect of $RuCl_3$ concentration on the lifespan of MMO anode

According to NACE TM0294[23], the accelerated lifespan evaluation can be determined in three kinds of solutions: 30 g/L NaCl, 40 g/L NaOH, and simulated pore water. Fig. 5 shows the effect of $RuCl_3$ concentration on the lifespan of the specimen subjected to three-cycle coating procedure. In 3 % NaCl, potentials were developed by applying an electric and their values were under +2 V(SCE) regardless of $RuCl_3$ concentration. Thus, the anode exhibited good performance. In 4 % NaOH, potentials under 1 V(SCE) were attained except 0.097 M $RuCl_3$. Furthermore, in simulated pore water, potentials developed under 1 V(SCE); the concentration of 0.097 M $RuCl_3$ was an exception. Except at 0.097 M $RuCl_3$ concentration,

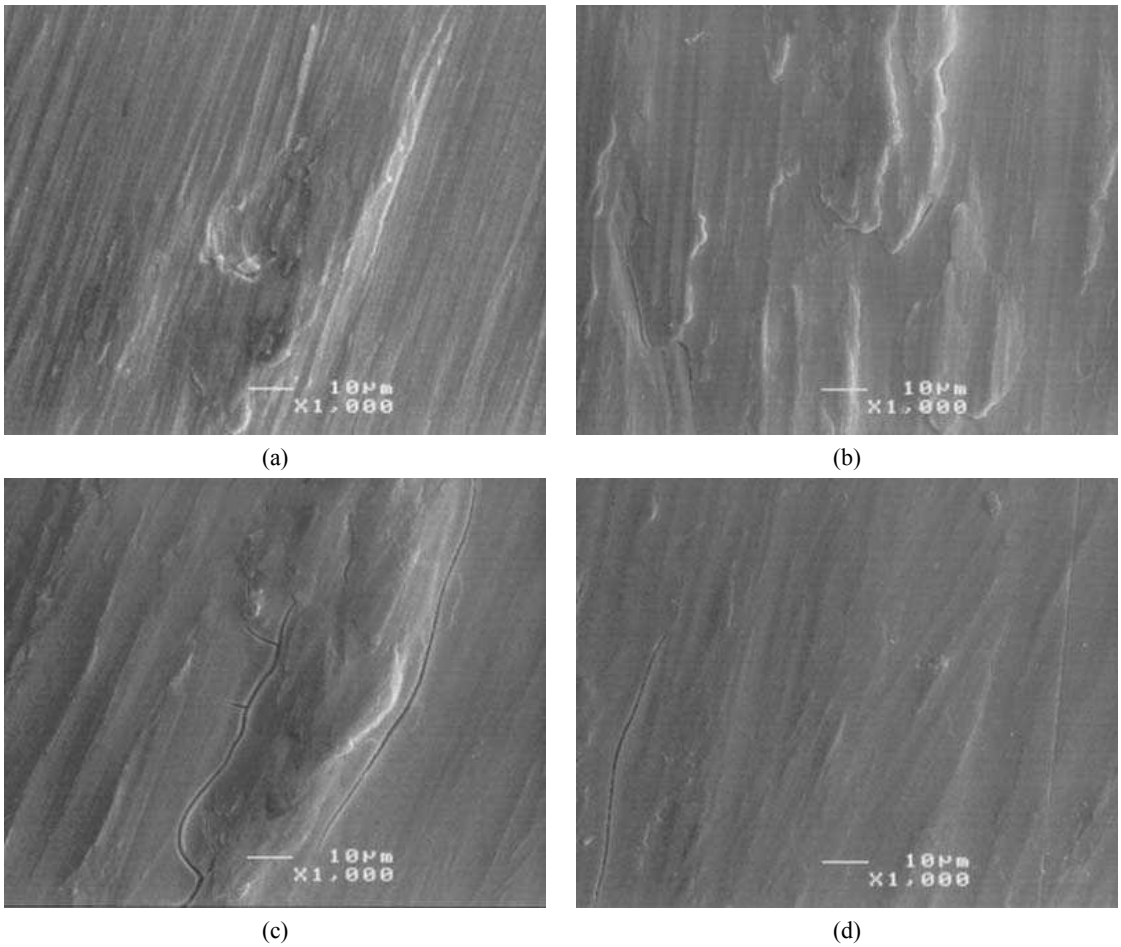


Fig. 7. Surface appearance of the coatings by sol-gel method with $RuCl_3$ solution: (a) 0.097M – five cycles, (b) 0.15M – three cycles, (c) 0.2M – two cycles, (d) 0.5M – single cycle.

the specimen showed excellent performance; it met all the requisite conditions that indicated its lifespan would have extended over 80 years. Its behavior was closely related to the electrochemical properties of the aforementioned conductive oxide.

Fig. 6 shows the relationship between the lifespan of optimum cycle's coated specimen and $RuCl_3$ concentration. At a concentration of 0.097 M $RuCl_3$, the estimated lifespan extended beyond 80 years in the three different test solution provided five cycles of coating were performed on the specimen. At a concentration of 0.15 M $RuCl_3$, the estimated lifespan of the anode extended over 80 years in the three different test solutions provided the specimen was coated through three cycles. At a concentration of 0.2 M $RuCl_3$, the estimated lifespan of the anode was beyond 80 years in the three different test solutions provided at least two cycles of coating were performed on the specimen. At a concentration of 0.5 M $RuCl_3$, the estimated lifespan extended beyond 80 years in the three different test solutions provided the specimen was coated

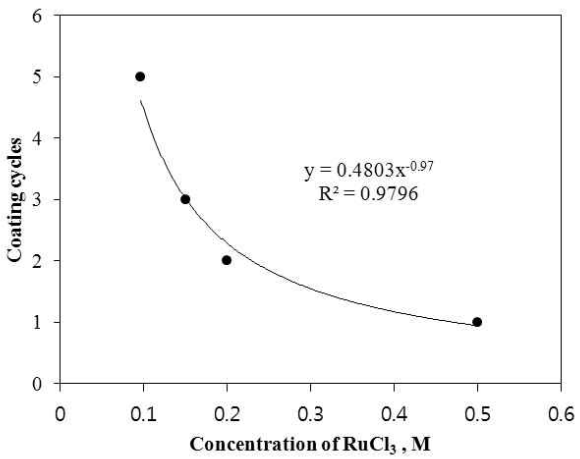


Fig. 8. Relationship between $RuCl_3$ concentration and coating cycles exhibiting the best lifespan of over 80 years.

for one cycle. This behavior is also closely related to the electrochemical properties of aforementioned conductive oxide. Fig. 7 shows the surface appearance of coatings, which were formed by sol-gel method using $RuCl_3$ solution. Although the concentration of $RuCl_3$ is dilute, the surface becomes rougher as we increase the cycles of coating procedure.

As described earlier, by an increasing concentration of $RuCl_3$, we can minimize the number of coating cycles on the specimen; these cycles are carried out to achieve an excellent lifespan of over 80 years. Fig. 8 shows the relationship between $RuCl_3$ concentration and coating cycles exhibiting maximum lifespan (over 80 years). Thus, we have deduced that the relationship between the concentration of $RuCl_3$ and the number of coating cycles can be expressed as follows: 'No. of coating cycle = 0.48* [$RuCl_3$ concentration, M]$^{-0.97}$'. In addition, if the concentration exceeds 0.5 M $RuCl_3$, even a single cycle coating would be sufficient to attain the optimum lifespan of the MMO anode. In summary, an increasing concentration of $RuCl_3$ can reduce coating cycles required to attain an excellent lifespan of over 80 years.

4. CONCLUSIONS

We evaluated the effects of $RuCl_3$ concentration on the electrochemical properties and lifespan of MMO anode. With an increasing concentration of $RuCl_3$, the oxygen evolution potential lowered and polarization resistance also minimized, but there was an increase in passive current density and oxygen evolution current density. To improve the electrochemical properties of MMO anode, $RuCl_3$ concentration was increased. As a result, the number of coating cycles reduced substantially and the MMO anode achieved an excellent lifespan of over 80 years. Thus, we concluded that the relationship between $RuCl_3$ concentration and coating cycles can be summarized as follows: No. of coating cycle = 0.48*[$RuCl_3$ concentration, M]$^{-0.97}$.

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References

1. AWWA C301-99, AWWA Standard for Prestressed Concrete Pressure Pipe, Steel-Cylinder Type, AWWA, Denver CO, USA (1999).
2. ASTM A82-34, Standard Specification for Cold-Drawn Steel Wire for Concrete Reinforcement, ASTM (1979).
3. ASTM A648-72, Standard Specification for Steel Wire, Hard Drawn for Prestressing Concrete pipe, ASTM (1988).
4. A. E. Romer, D. Ellison, G. E. Bell, and B. Clark, Failure of Prestressed Concrete Cylinder Pipe, IWA publishing, AWWARF, USA (2008).
5. M. S. Zarghamee, R. P. Ojdrovic, and R. Fongemie, *Proceedings of the 1998 Pipeline Division Conference*, p. 702, August 23-27, 1998, San Diego, California, USA, (1998).
6. D. H. Marshall, *Proceedings of the 1998 Pipeline Division Conference*, p. 556, August 23-27, 1998, San Diego, California, USA (1998).
7. S. J. Duranceau, M. J. Schiff, and E. C. Bell, Effect of Electrical Grounding on Pipe Integrity and Shock Hazard, AWWARF, Denver, CO, USA (1996).
8. A. E. Romer and G. E. C. Bell, External Corrosion and Corrosion Control of Buried Water Mains, AWWARF, Denver, CO, USA (2004).
9. T. Doniguian, H. Kips, and J. Barnes, *Proceedings of the 1998 Pipeline Division Conference,* p.367 August 23-27, 1998, San Diego, California, USA (1998).
10. S. R. Fiori, D. R. Kendall, and S. B. Mulligan, Pipelines 2001-Advances in Pipeline Engineering & Construction, J. Castronovo, ed., ASCE, Reston, VA, USA (2001).
11. W. J. Moncreif, D. R. Kendall, S. B. Mulligan, R. C. Blake, and C. M. Watkins, Pipelines 2001-Advances in Pipeline Engineering & Construction, J. Castronovo, ed., ASCE, Reston, VA (2001).
12. T. Suydam, J. Woods, E. Stewart, and M. T. Stift, Pipelines 2001-Advances in Pipeline Engineering & Construction, J. Castronovo, ed., ASCE, Reston, VA, USA (2001).
13. K. McCaffrey, D. R. Kendall and S. Mulligan, *Proceedings of ASCE Pipelines 2006 Conference*, p.1, ASCE (2006).
14. P. C. S. Hayfield, *Platinum Metal Rev*., **42**, 27 (1998).
15. D. Miousse and A. Lasia, *J. New Mat. Electrochem. Systems*, **2**, 71 (1999).
16. A. T. Marshall, S. Sunde, M. Tsypkin, and R. Tunold, *Int. J. Hydrogen Energy*, **32**, 2320 (2007).
17. J. Kristof, T. Szilagyi, E. Horvath, R. Frost, and A. De Battisti, *Thin Solid Film,* **485**, 90 (2005).
18. C. Felix, T. Maiyalagan, S. Pasupathi, B. Bladergroen, and V. Linkov, *Int. J. Electrochem. Sci.*, **7**, 12064 (2012).
19. J. M. Hu, H. M. Meng, J. Q. Zhang, and C. N. Cao, *Corros. Sci.,* **44**, 1655 (2002).
20. Y. R. Yoo, H. Y. Chang, S. G. Jang, H. S. Nam, and Y. S. Kim, *Corros. Sci. Tech*., **6**, 44 (2007).
21. Y. R. Yoo, H. Y. Chang, S. Take, and Y. S. Kim, *Corros. Sci. Tech*., **5**, 45 (2006).
22. ITA, Specifications Book, 4th Ed., International Titanium Association, Broomfield, CO, USA (2005).
23. NACE TM0294, Testing of Embeddable Impressed Current Anodes for Use in Cathodic Protection of Atmospherically Exposed Steel-Reinforced Concrete, NACE International, Houston, TX, USA (2007).