혐기성 토양에 서식하는 황산염환원세균에 의한 가스배관의 미생물부식

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CORROSION OF STEEL GAS PIPELINE INDUCED BY SULFATE-REDUCING BACTERIA IN ANAEROBIC SOIL

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ABSTRACTS - Microbiologically influenced corrosion (MIC) of carbon steel gas pipeline in soil environments was investigated at field and laboratory. MIC is very severe corrosion and it is not easy to distinguish this corrosion from inorganic corrosion because of its localized, pitting-type character. Therefore, it is important to provide proper assessment techniques for the prediction, detection, monitoring and mitigation of MIC. It is possible to predict the MIC risk, i.e., the activity of sulfate-reducing bacteria (SRB) through the analysis of soil environments. Chemical, microbiological and surface analysis of corrosion products and metal attacked could reveal the possibility of the occurrence of MIC. Various electrochemical and surface analysis techniques could be used for the study of MIC. Among these techniques, thin-film electrical resistance (ER) type sensors are promising to obtain localized corrosion rate of MIC induced by SRB. It is also important to study the effect of cathodic protection (CP) on the MIC. In case of coated pipeline, the relationship between coating disbondment and the activity of SRB beneath the disbanded coating is also important.

KEYWORDS: microbiologically influenced corrosion (MIC), gas pipeline, sulfate-reducing bacteria (SRB), anaerobic soil, cathodic protection (CP)

1. INTRODUCTION

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It is widely recognized that microorganisms attach to, and influence the corrosion of metals and alloys exposed to the environments. Microorganisms are omnipresent in nature and their ability to grow and reproduce at rapid rates accounts for their presence in soil environments. Buried pipeline is designed to have a lifetime of about 30 to 50 years. In general, the protective organic coating and cathodic protection (CP) are applied together. Despite these protection measures, however, failure cases of underground pipelines due to corrosion have been continuously reported [1-3]. Microbiologically influenced corrosion (MIC) has been identified as one of the major cause of corrosion failures of underground pipelines [4]. The first MIC case was identified the first MIC case in 1934 [5], where sulfate-reducing bacteria (SRB) resulted in failure of underground cast iron pipes. According to recent survey program performed by authors, almost all corrosion of underground gas pipeline has occurred under the disbonded coating [6]. The corrosion mechanism has been revealed mainly as the action of microorganisms. A maximum pit depth of 6 mm to 7 mm was observed. The risk of MIC must be exactly evaluated and the proper control methods prepared to mitigate MIC problems. The relationship between the activities of MIC-causing microbes, e.g., SRB and/or APB, and various soil environmental factors should be investigated and assessed. Secondly, MIC is a localized, pitting-type corrosion in most cases. Therefore, proper test methods for localized corrosion are needed.

In this study, various field and laboratory techniques for the monitoring, detection and assessment of MIC of carbon steel induced by SRB are briefly summarized.

2. FIELD SURVEY

Relationship between the activity of SRB and the risk of corrosion

The field survey of soil parameters and the analysis of sampled soil provide the useful information on the activity of SRB and therefore the risk of MIC. Chemical and microbiological analysis and the combination of the statistical methods such as multiple regression analysis are useful tools for this purpose. Fig. 1 shows the dependence of the population of SRB on the key environmental factors.

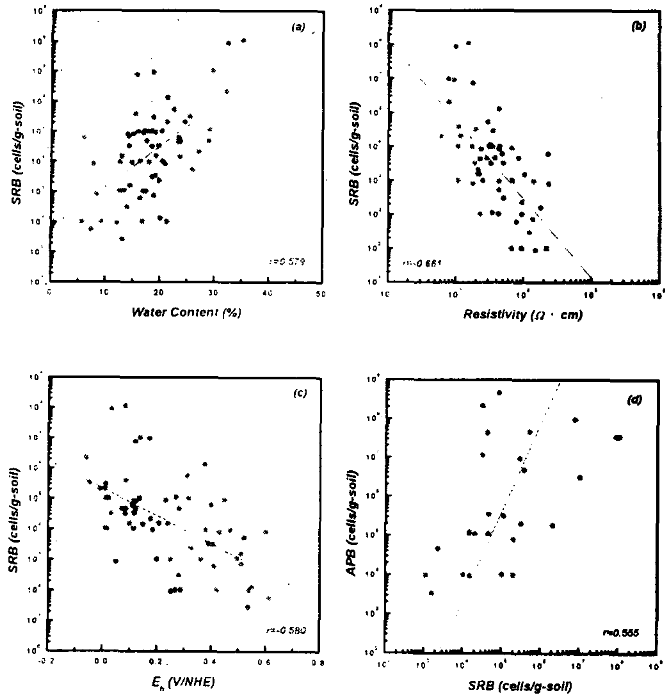

Fig. 1. Relationships between the population of SRB and environmental factors
(a) water content, (b) resistivity, (c) reduction-oxidation potential, (d) the population of APB

Using multiple regression analysis method, the population of SRB was obtained as a function of environmental factors.

$$LogSRB = 13.76 - 2.60 Log\rho - 0.19 W_c + 0.20 E_h \cdot Clay \quad (1)$$

wherein SRB: the population of SRB (cells/g-soil)
ρ: soil resistivity (Ω cm)
W_c: water content (%)
E_h: reduction-oxidation potential (V/NHE)
Clay: clay content (%)

The observed population of SRB and that of predicted value calculated by equation (1) are presented in Fig. 2.

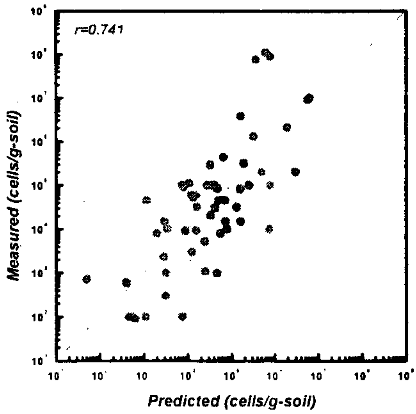

Fig. 2. The comparison of the predicted and measured population of SRB obtained by multiple regression analysis.

Efficiency of CP

CP prohibits the progress of MIC in soil environment effectively [7]. This may be due to the increase of pH induced by hydroxyl ion produced by cathodic reaction suppresses the growth of microbes. It is more important, however, that the efficiency of CP should be considered. Fig. 3 is the typical example of the disbondment of heat-shrink sleeve applied at the girth weld joint of carbon steel pipeline [6]. It is very difficult for CP current to penetrate inside this disbonded region because of defect geometry [4].

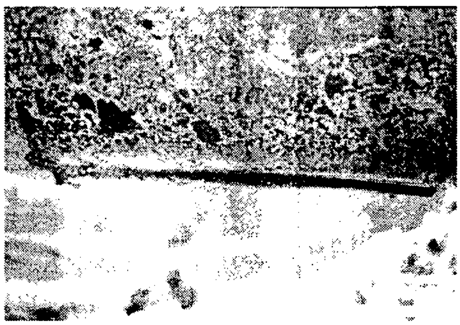

Fig. 3. Typical example of disbonded sleeves at the girth weld joints

Table 1 is the measured potential inside this disbonded coating at field by introducing the reference electrode (saturated copper/copper sulfate electrode; CSE) and platinum (Pt) electrode. CP current could not penetrate into the disbonded area, which resulted in the pipe surface exposed to anaerobic soil under the disbonded region was in freely corroding condition (-610 mV to -550 mV/CSE) even though the pipe-to-soil potential was in a range of -1200 mV - -1400 mV/CSE.

Table 1. Results of potential measurement

Types	Potential
Pipe-to-Soil Potential	-1430 - -1200 mV/CSE
Potential inside disbonded region	-610 - -550 mV/CSE
Reduction-Oxidation Potential (E_h)	-160 mV/NHE

E_h under the disbonded area was about -160mV/NHE. When SRB is cultivated in culture medium, the recommended initial E_h should around -100mV/NHE [8]. Therefore, the suitable anaerobic condition for the active growth of SRB was provided under the disbonded coatings and MIC occurred in this region mostly.

3. CORROSION POTENTIAL MEASUREMENTS

Because of its simplicity, the measurement of the corrosion potential (E_{corr}) and linear polarization resistance (LPR) method has been used to MIC studies for many years [9]. A rapid and easy interpretation of the results is achievable using these methods together. Fig. 4 shows the trends for E_{corr} and uniform corrosion rate of carbon steel obtained by LPR method exposed to anaerobic soil for 148 days in laboratory [4].

It is apparent that the existence of SRB greatly influences the corrosion behavior of carbon steel. In case of active growth of SRB, the potential increased slightly for the first 6 days and then maintained around -740 mV/SCE, but the potential fluctuated -600 mV to -800 mV/SCE after 50 days until the experiment ended. The potential in control (biocide-added) case was around -600mV and always more positive than that in SRB-active cases.

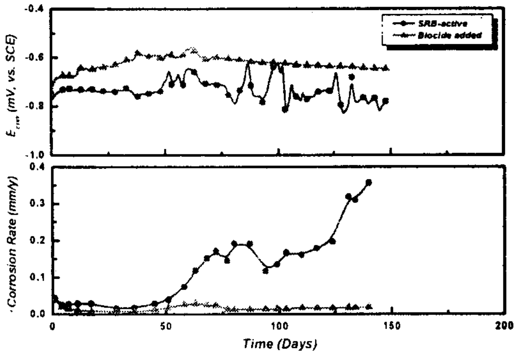

Fig. 4. Effect of SRB on the corrosion potential and uniform corrosion rate of carbon steel exposed to anaerobic soil in laboratory.

One of the mechanisms for SRB-induced MIC of carbon steel has been thought to be the galvanic action between precipitated iron sulfides and metal [2]. After 50 days exposure, E_{corr} of carbon steel in SRB-active soil fluctuated until the experiment ended with the continuous increase of uniform corrosion rate in Fig. 4. It seems that this potential fluctuation was attributed to the repetitious production and breakdown of iron sulfide film and an indicative of the onset of localized corrosion.

4. SURFACE ANALYSIS

Surface analysis technique complemented with the microscopical examination such as scanning electron microscopy (SEM) is useful in monitoring the chemical nature of biological and inorganic deposits. Fig. 5 shows the results of SEM observation in the change of surface morphology and energy dispersive X-ray analysis (EDXA) of carbon steel specimens exposed to SRB-active anaerobic soil in laboratory.

In SRB-active soil, the whole surface of the steel coupon was dense iron sulfide films at 14 days (Fig. 5 (a)). However, this sulfide film became porous at 148 days (Fig. 5 (b)). The bacterial cells were observed on the surface (Fig. 5 (c)). After removal of these films, a large pit was easily found (Fig. 5 (d)). This porous film and base metal set up the galvanic couple, and the corrosion rate increased dramatically by galvanic action as shown in Fig. 5. It is also remarkable that the S/Fe ratio in iron sulfide film increased at 148 days. Many researchers reported that the sulfide film became porous as the sulfur content in iron sulfide increased [11,12]. These facts were again proved by SEM/EDXA analysis.

5. LOCALIZED CORROSION STUDY

As mentioned above, MIC is in general localized, pitting-type corrosion. The authors have applied thin-film electrical resistance (ER) probes for the study of this localized corrosion induced by SRB.

The ER method is widely used as corrosion monitoring techniques especially in industrial field environments. At constant temperature, corrosion of the probe, which causes a decrease in cross-sectional area of probe, can be monitored by periodically measuring the electrical resistance. The corrosion rate can be determined over very short time [13]. In general, this technique is used for the measurement of uniform corrosion rate. However, thin film type ER probe shown in Fig. 6 can be used to assess the localized corrosion phenomena due to its multi-sensing line. The details of fabrication, applications are previously described [13]. Fig. 7 shows the response of thin-film ER probes immersed in various electrolytes. Nitrogen was purged in all cases to maintain anoxic environments.

It is apparent that the responses of each probe were quite different. From these results, the corrosion behavior of carbon steel can be divided as three categories in the absence of oxygen, i.e., 1) anaerobic inorganic corrosion which depends on the ability to utilize the cathodic reactants, which may be water or hydrogen ion. As shown in Fig. 10, the anaerobic, inorganic corrosion rates are in a range of 0.016 mm/y to 0.026 mm/y, and showed the uniform corrosion characteristics regardless of the types of electrolytes (NaCl and deionized water). 2) the precipitation of protective films (carbonate/bicarbonate); in this case, hard and protective film precipitated on the metal surface and remained for a long time, which resulted in no decrease of electrical resistance, i.e., no start of corrosion, 3) MIC induced by SRB; initially transient protective iron sulfide film prohibited the progress of corrosion for about 4 days, however, the film became ruptured and the localized corrosion developed (stepwise increase of resistance).

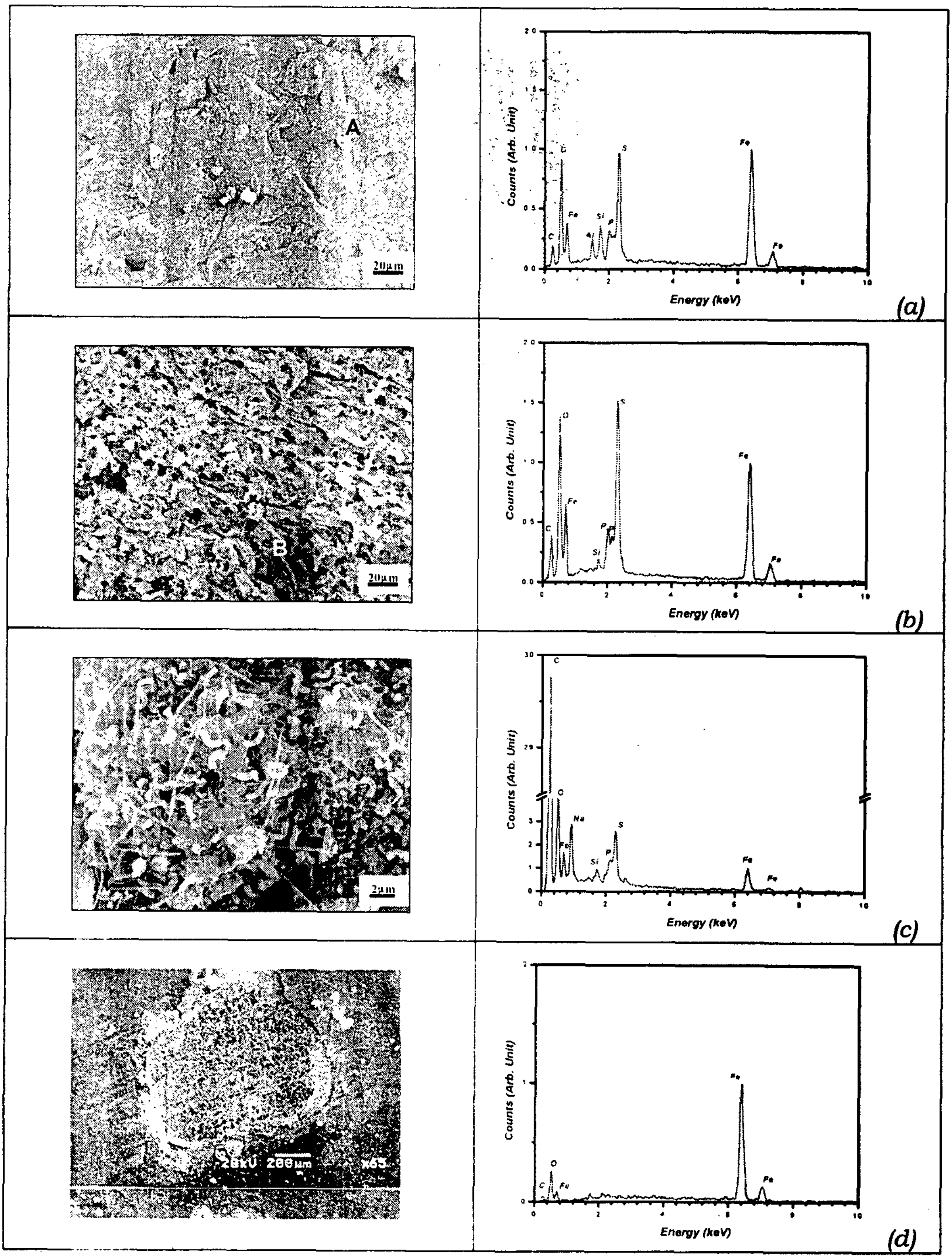

Fig. 5. Surface morphology and the results of EDXA of carbon steel exposed to SRB-active soil; (a) for 14 days, (b) for 148 days, (c) SRB mixed with iron sulfide film after 148 days, (d) pit morphology after removal of surface deposit

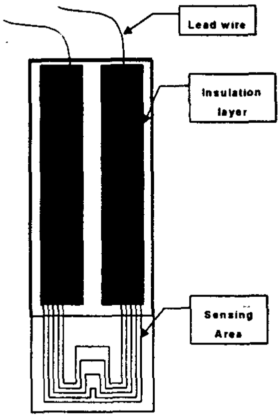

Fig. 6. Schematic diagram of thin film electrical resistance (ER) probe

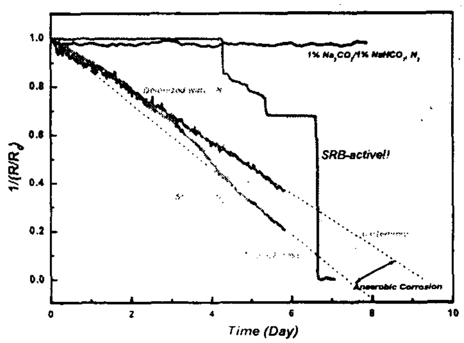

Fig. 7. The response of electrical resistance (ER) probes in anoxic environments.

This ER technique is very effective to investigate the uniform corrosion characteristics, the change of corrosion behavior, and the localized corrosion characteristics within relatively short period compared with conventional electrochemical methods. In addition, MIC induced by SRB is distinguishable because of the unique response of ER probes in anaerobic environments.

6. CONCLUSIONS

(1) It is possible to assess the activity of SRB, i.e., the risk of MIC from the relationship with key environmental factors qualitatively and this risk is directly related to the corrosion rate by field survey and the statistical approach. However, the occurrence of coating disbondment and the effectiveness of CP should be considered together for the precise risk

assessment in coated steel pipes buried in soil.

(2) Microbial colonization of carbon steels can drastically alter their corrosion behavior. Electrochemical measurements can be made under MIC condition and showed good results. However, all electrochemical methods are averaging techniques that work best when the chemical and electrochemical conditions on the metal surface are uniform and steady state and provide no information on the localized corrosion.

(3) The thin film ER probe test makes it possible to shorten the experimental periods and to study the localized corrosion behavior, which is a characteristics of MIC.

(4) It is important that the study of MIC requires a multi-disciplinary approach comprising different combination of microbiological, electrochemical and microscopic measurement as well as the consideration of CP that may be the only protective measure in soil environments.

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