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Advanced Rust Research

From artificial intelligence to bacteria

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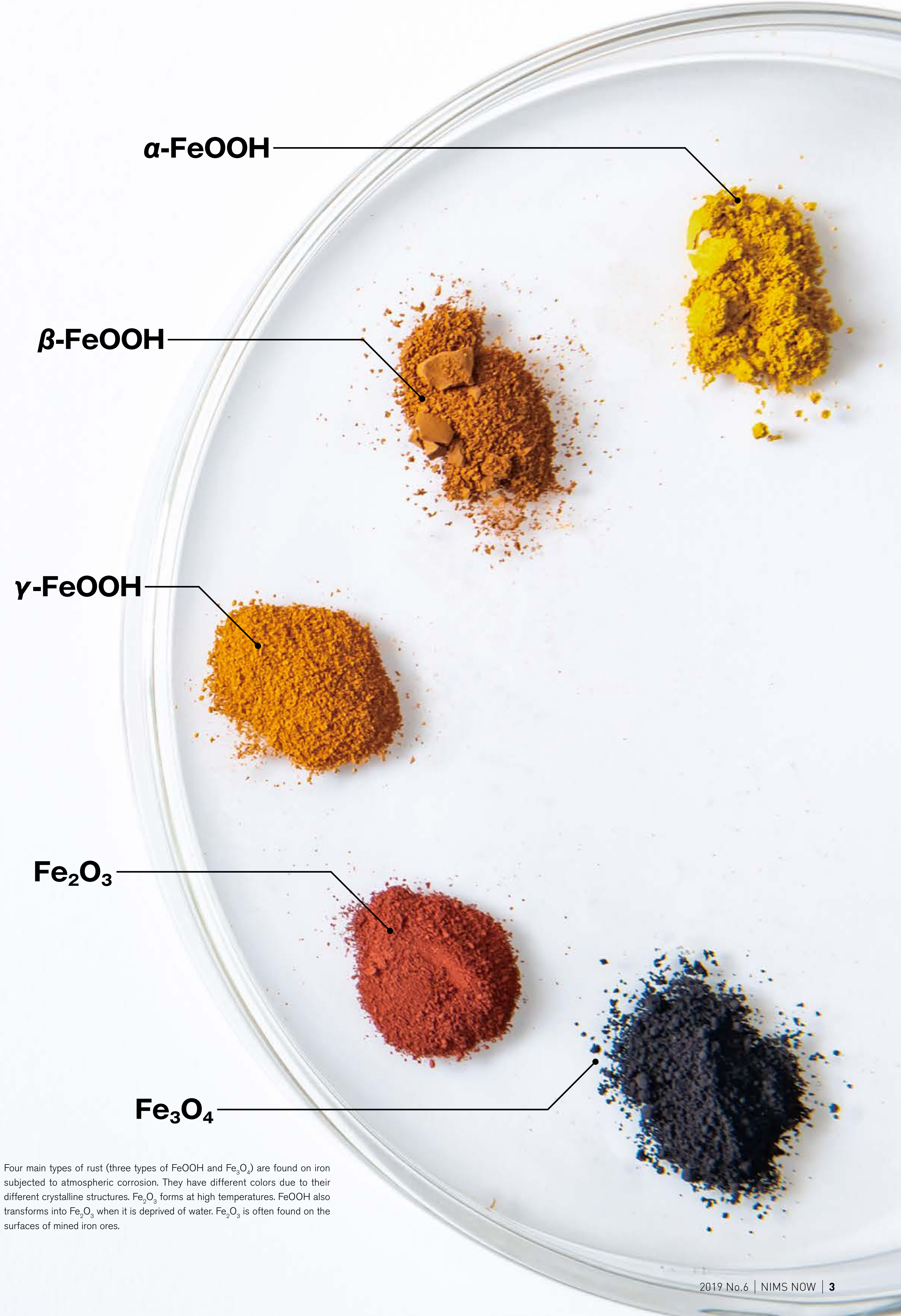
Much of Japan's public infrastructure and buildings were constructed during the post-war period of rapid economic growth. Their advanced age has raised serious concerns about their structural integrity. Iron—an indispensable structural material—weakens as it forms rust and corrodes. Humans have struggled with rust since our distant ancestors began using iron. However, iron corrosion is an extremely complex process involving interactions between a variety of environmental factors. Humans still struggle to prevent iron corrosion.

NIMS has been using advanced techniques to tackle rust issues. It has developed an AI system capable of modeling the relationship between the environment and corrosion, and a corrosion testing technique designed to intentionally accelerate rusting processes. In addition, NIMS has identified bacterial corrosion mechanisms using electrochemical methods. This NIMS NOW issue spotlights the latest results from NIMS' innovative research approach to the centuries-old battle against rust.



Four main types of rust (three types of FeOOH and Fe_3O_4) are found on iron subjected to atmospheric corrosion. They have different colors due to their different crystalline structures. Fe_2O_3 forms at high temperatures. FeOOH also transforms into Fe_2O_3 when it is deprived of water. Fe_2O_3 is often found on the surfaces of mined iron ores.

Do we really know what rust is?

Tadashi Shinohara
NIMS Special Researcher
Corrosion Property Group
Research Center for Structural Materials

Rust: an act of God seemingly designed to challenge humans

Iron is the fourth most abundant chemical element on the earth after oxygen, silicon and aluminum. It is the cheapest metal capable of generating a variety of physical properties when processed into alloys and can be called the most important metal to humans.

Iron, however, has a major weakness: it rusts. "Iron is the only metal that is prone to rust in all conditions, whether acidic, basic or neutral," said Tadashi Shinohara, a leading rust researcher in Japan. "When I was a college student, my mentor often joked that God had designed iron to be extremely susceptible to rust in order to give humans—who depend so heavily on iron—a great challenge."

Naturally occurring iron exists as ores in which iron is bonded with oxygen. Iron manufacturers dissociate oxygen from oxidized iron to strengthen it. However, processed iron, from which oxygen has been forcibly removed, has a strong tendency to return to its original, more stable state by bonding with oxygen again, forming rust.

Four major types of common rust exist which vary widely in color depending on their composition and crystalline structure (see the photos on p. 3). The rust we usually encounter is a combination of these different types.

Conditions conducive to rusting

When iron objects rust severely, they become thinner, porous and brittle. Such these condition is called corrosion, many different measures to prevent it have been studied. Much of Japan's public infrastructure (e.g., bridges, tunnels, roads and water pipelines) was built about 50 years ago during the period of rapid economic growth. Its advancing age has been a pressing concern in recent years. Steel beams and rods—commonly used structural materials—have been severely corroding, weakening structures.

"The development of anti-rust measures effective in aged public infrastructure requires an understanding of the correlative relationships between corrosion and the environment," Shinohara said. "The types of rust that form on iron and the rate at which iron corrodes vary significantly depending on the way iron is used and the associated environment."

The presence of moisture triggers the onset of corrosion. When iron surfaces get wet, iron atoms turn into iron ions by releasing electrons and being dissolved in water. These iron ions then undergo chemical reactions, producing rust. Salt is also a major factor promoting corrosion. Salt absorbs moisture from the atmosphere and transfers it to iron. Complex interactions between salt and other conditions (e.g., pH and temperature) determine the rate of corrosion.

"Surrounded by the sea in all directions, Japan has hot and humid summers and its atmosphere tends to be high in moisture and salt, creating environments highly favorable for iron corrosion," Shinohara said.

Latest NIMS research to prevent iron rust

Given that the rate of iron corrosion is influenced by environmental conditions, different anti-corrosion measures need to be developed for the conditions in which iron is used. For example, steel beams in bridges are in direct contact with the atmosphere, making them susceptible to rusting. To prevent corrosion damage, the surfaces of these beams are zinc-coated or painted. However, these measures are not perfect; zinc coatings themselves are subject to corrosion and paint peels over time. The corrosion of iron due to atmospheric exposure therefore continues to be a threat to public safety.

The best approach to studying anti-corrosion measures is to make observations at field sites where corrosion has been an issue.

"NIMS has been conducting atmospheric exposure tests for about 20 years," Shinohara said. "Iron test plates are placed outdoors and monitored for the purpose of determining the relationship between corrosion and the ambient environment (see p. 9). A total of 20 sites across Japan have been used for these tests, ranging from the northernmost site in Hokkaido to the southernmost site on Miyakojima Island. We have tested various forms of iron materials, including pure iron and carbon steels, low alloy steels, coated steels, and so on."

The results of these tests—which are accessible globally—have been used as references in efforts to develop anti-corrosion measures not only in Japan but also in other Asian countries with environmental conditions comparable to those of Japan.

"NIMS has also launched a new research project which may be viewed as an advanced version of the atmospheric exposure test," Shinohara said. "An AI-based corrosion prediction model is being developed using machine learning techniques to process corrosion data collected in the field and meteorological data across Japan (see p. 6)."

Iron is commonly used to reinforce concrete. Although the external concrete component of reinforced concrete is highly resistant to deterioration, steel rods embedded in it are subject to corrosion and ultimately breakage.

"As steel rods embedded in concrete corrode, they expand to two to five times their initial volumes, causing the surrounding concrete to crack," Shinohara said. "Cracks allow water and salt to enter reinforced concrete structures, rapidly increasing the rate of corrosion. Because steel rods expand more slowly when embedded in concrete than when exposed to the atmosphere, it takes decades for reinforced concrete to crack. Therefore, waiting for field tests to generate results may delay our efforts to protect structures currently in use until it's too late. To address this issue, NIMS has been developing an 'accelerated corrosion test'; a technique that can be used to evaluate corrosion damage more quickly."

This technique is capable of expediting rust-forming chemical reactions, allowing reinforced concrete to deteriorate more quickly. Using this technique, NIMS has succeeded in reproducing corrosion more quickly and accurately than is possible using existing testing methods (see p. 10). This technique is potentially useful in prioritizing the repair needs of public infrastructure.

A less well-known cause of iron rust is bacteria. Bacteria that uses iron as an energy source is known to exist mainly under the sea. As a result, rusting is a constant threat to iron structures exposed to seawater, such as bridges between islands and underwater petroleum pipelines. NIMS has been exhaustively analyzing the mechanisms by which this bacteria causes iron to rust. The results produced in this project may lead to the development of a breakthrough approach to inhibiting iron-rusting bacteria (see p.13).

"The information to be gained from these research projects will facilitate the development of procedures for making iron structures," said Shinohara. "We will continue its research efforts with the aim of protecting public infrastructure assets currently in use and to be developed in the future."

(by Kumi Yamada)

Coverage cooperation

Hideki Katayama

Director of the Analysis and Evaluation Field
Leader of the Corrosion Property Group
Research Center for Structural Materials

Research 1

Estimating corrosion damage using AI

Steel corrosion progresses under complex environmental conditions and is extremely difficult to predict.

However, it is also unrealistic to conduct field exposure tests at all of the huge number of sites that take into account any environment.

The use of cutting-edge technology to predict the progress of corrosion from weather data using AI (artificial intelligence) has begun to produce promising results.

Urgent need to prioritize 720,000 bridges for repair

Japan currently has more than 720,000 bridges. Half are at least 50 years old and urgently in need of repair or reconstruction work. However, because the structural soundness of bridges is greatly influenced by environmental conditions, a bridge's need for repair does not always directly correlate with its age. The choice between repair and reconstruction has to be made for each individual bridge based on its specific physical condition as determined by safety inspections. Nevertheless, some municipalities are short of adequately skilled inspectors, slowing bridge inspection efforts. Although NIMS has been conducting atmospheric exposure tests (see p. 9)—a type of field corrosion test—it would be impractical to implement these tests at all of the critical sites in Japan. For this reason, the development of tools capable of estimating the severity and progression of corrosion damage in public infrastructure, thereby facilitating safety inspections, has been drawing a great deal of interest.

Utilizing agro-meteorological data as teaching data for machine learning

Katayama, the leader of the Corrosion Property Group, has been investigating the factors that enhance corrosion and methods of preventing it. "The relationship between corrosion and the environment is not simple," Katayama said.

"Steel materials are widely used in the construction of bridges, where they react with water and oxygen to form rust," Katayama said. "For this reason, rain, condensation and relative humidity greatly affect the corrosion rate of steel. In addition, when airborne sea salt is deposited on steel surfaces, corrosion progresses even more rapidly. The effects of ultraviolet radiation and other factors are also important."

To address this complexity, Katayama considered the use of machine learning techniques. These techniques are used to analyze large amounts of data to identify patterns in complex interactions. Katayama decided to develop an AI-based corrosion prediction model capable of estimating the severity of corrosion damage at sites using environmental data. This was an unprecedented, challenging effort. The first step was to collect the corrosion and associated environmental data to be used to construct a corrosion prediction model.

"NIMS has collected a large amount of corrosion and associated environmental data by atmospheric exposure tests," Katayama said. "However, this test data is only collected at most every six months. As a result, the influence of environmental factors on corrosion has been generalized, making corrosion-environment relationships difficult to determine. It is desirable for teaching data to be used in machine learning to be collected at shorter intervals. Fortunately, we had data from an e-ASIA project on the corrosion of carbon steels exposed at six Japanese sites collected on a monthly basis for one year. Although several organizations have been conducting atmospheric exposure tests, corrosion data is rarely collected as frequently as it was in this project. I thought that the data would be useful in the development of a new corrosion prediction model."

71 corrosion data points were collected during the e-ASIA project. However, only a few types of associated environmental data were collected from each site, making these datasets unsuitable for use in machine learning. To address this issue, Katayama considered the use of the Agro-Meteorological Grid Square Data (AMGSD) developed by the National Agriculture and Food Research Organization (NARO). NARO used a unique algorithm to generate a 1 km grid meteorological data map across areas between meteorological observatories throughout Japan. Designed to help farmers schedule agricultural activities, such as seeding and harvesting, a user can input the latitude and longitude of a specific location on the AMGSD website and obtain 14 types of meteorological data for that location, including historical data and near-future projections. Katayama chose nine meteorological parameters (e.g., average temperature and precipitation) relevant to corrosion for use as teaching data.

The AMGSD does not have data on airborne sea salt concentrations—an important parameter for predicting corrosion. Katayama substituted the square of wind velocity for this parameter on the basis of earlier research indicating that these two variables are proportional to each other. Through these procedures, he ultimately prepared 71 sets of corrosion and associated environmental data to use in machine learning.

Algorithm: prediction accuracy determinant

"Many algorithms have been produced using machine learning," Katayama said. "However, the prediction-making processes of many of these algorithms are 'black boxes.' For example, the credibility of even a highly accurate prediction model would be significantly undermined if the algorithm on which it is based contains a component counter-intuitive to corrosion researchers (e.g., the corrosion rate increases as the average daily maximum temperature decreases)."

To construct a credible model, Katayama tested several machine learning algorithms. He first used 63 of the 71 field datasets (90%) as teaching data for machine learn-

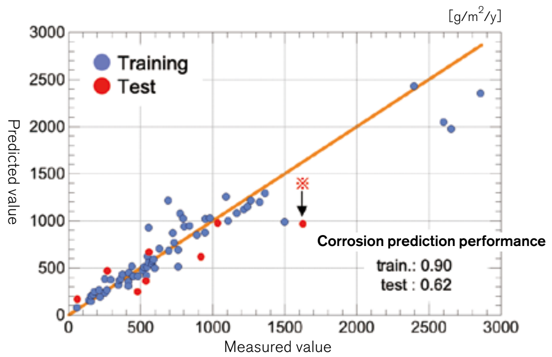


Figure 1. Of 71 sets of corrosion and associated environmental data prepared, 63 sets (blue dots, accounting for 90% of the data) were used as training data for machine learning processes to construct a model that describes the correlation between corrosion and environmental factors (yellow line). The remaining eight datasets (red dots, accounting for 10% of the data) were used to verify the fit of the model. One data point (marked with "※") deviated greatly from the model due to the influence of a typhoon. The value indicating the model's corrosion prediction performance was 0.62 when the outlier was included but was greater than 0.8 when it was not.

ing to construct a correlation model. He then used the remaining eight datasets (10%) to verify the model. Among several machine learning techniques tested, the random forest method—an extended decision tree analysis method—produced the best results.

"A decision tree is a decision support tool that uses a tree-like model consisting of a series of conditions to be selected by users. Sequential decisions lead to an outcome. Decision trees are common in daily life; personality self-tests in magazines are an example. For our specific purposes, we used decision trees to command the model to meet a sequence of conditions (e.g., "Corrosion occurs / does not occur when the air temperature is higher than X degrees"). This method has a disadvantage, however: the first condition that we command the model to meet has a dominant influence on the outcome it produces. To correct this, we combined the decision tree method with the ensemble learning process, which uses the majority rule principle. This process first generates many models with different decision tree sequences. It then compares the accuracy of the estimates made by these models, determines the importance of individual parameters and weighs them accordingly. This integrated approach is called the random forest technique."

The performance of the AI-based corrosion prediction model constructed using this algorithm has been verified using testing data to have a performance indicator value greater than 0.8 (Figure 1).

Encouraging results in Choshi City

Will this AI-based model really be capable of predicting corrosion damage in actual bridges? Katayama answered this question by carrying out verification tests with the cooperation of the Choshi City municipal government. He first created a corrosion map (Figure 2) by entering meteorological data on Choshi City obtained from the AMGSD into the AI-based model and running it. He then compared actual corrosion measurements and corrosion damage predicted by the map for four bridges in the city, including Choshi-ohashi Bridge. As a result, Katayama found the model's predictions to be accurate for bridges in coastal areas. On the other hand, the model overestimated corrosion damage to bridges in inland areas, giving predicted values that were twice the field measurements. Nevertheless, Katayama was encouraged by these results. Bridge inspectors in Choshi City reacted positively, stating that the results shown in the corrosion map agreed with their observations in inspecting these bridges. Katayama thinks that these results demonstrate the potential usefulness of the corrosion prediction model. Room for improvement remains due to the fact that only 71 sets of field data were available. Reliable AI-based models are generally said to require more than 1,000 datasets. Katayama plans to collect more field data, use it to train the model and obtain data on actual airborne sea salt concentrations to replace the calculated variable he has been using as a substitute. These measures are expected to improve the model's prediction accuracy in regions where it is currently low. He has begun steadily collecting data from bridges in Choshi City, including amounts of sea salt deposited on bridge surfaces.

"The integration of machine learning into corrosion research is a pioneering approach," Katayama said. "No country's public infrastructure is immune to corrosion and I hope NIMS can take the lead in this research field. It is Japan's responsibility to provide developing Asian countries with information on safety and maintenance in addition to advanced construction technology." The AI-based corrosion prediction tool developed in Japan may make public infrastructure safer globally.

(by Akiko Ikeda, Sci-Tech Communications)

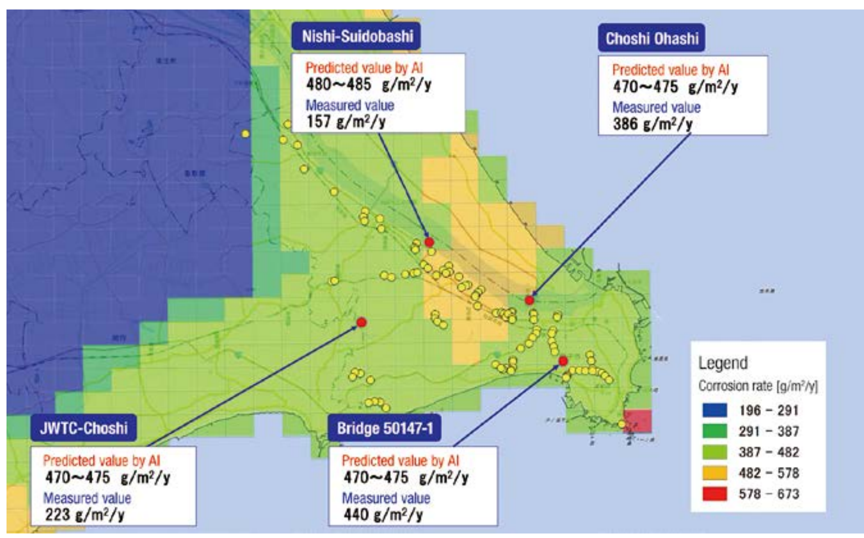


Figure 2. Choshi City corrosion map

The amount of corrosion was predicted at a 1 km × 1 km spatial resolution by entering the city's environmental data into the AI-based corrosion model. The actual measurements and predicted values were compared at four Choshi City sites and the predictions were found to be more accurate at coastal sites than at inland sites.

COLUMN

NIMS' atmospheric exposure tests

The Corrosion Data Sheet—a compilation of atmospheric exposure test results—can be viewed online.

The susceptibility of metallic materials to corrosion is greatly influenced by environmental conditions. Current international standards can be used to predict corrosion damage in metals.*1 These standards have been established based on corrosion data and associated environmental data (e.g., temperature, humidity and pollutants) collected globally. However, metals have been found to corrode more severely in Japan than these standards predict. This is because most corrosion test data has been generated in Europe. Countries that are surrounded by the sea, such as Japan and Southeast Asian nations, have a more corrosion-conducive environment, causing corrosion to advance rapidly beyond the range predicted by the international standards. Japan therefore needs to carry out own corrosion studies in order to protect infrastructure.

NIMS has been carrying out atmospheric exposure tests for about 20 years. During these tests, a series of metal test plates are placed outdoors (see the cover photo), changes in which corrosion progresses while the plates are affected by environmental factors in the atmosphere are periodically recorded. These tests are currently ongoing at 10 locations across Japan, including NIMS in Tsukuba City, where test racks have been set up.

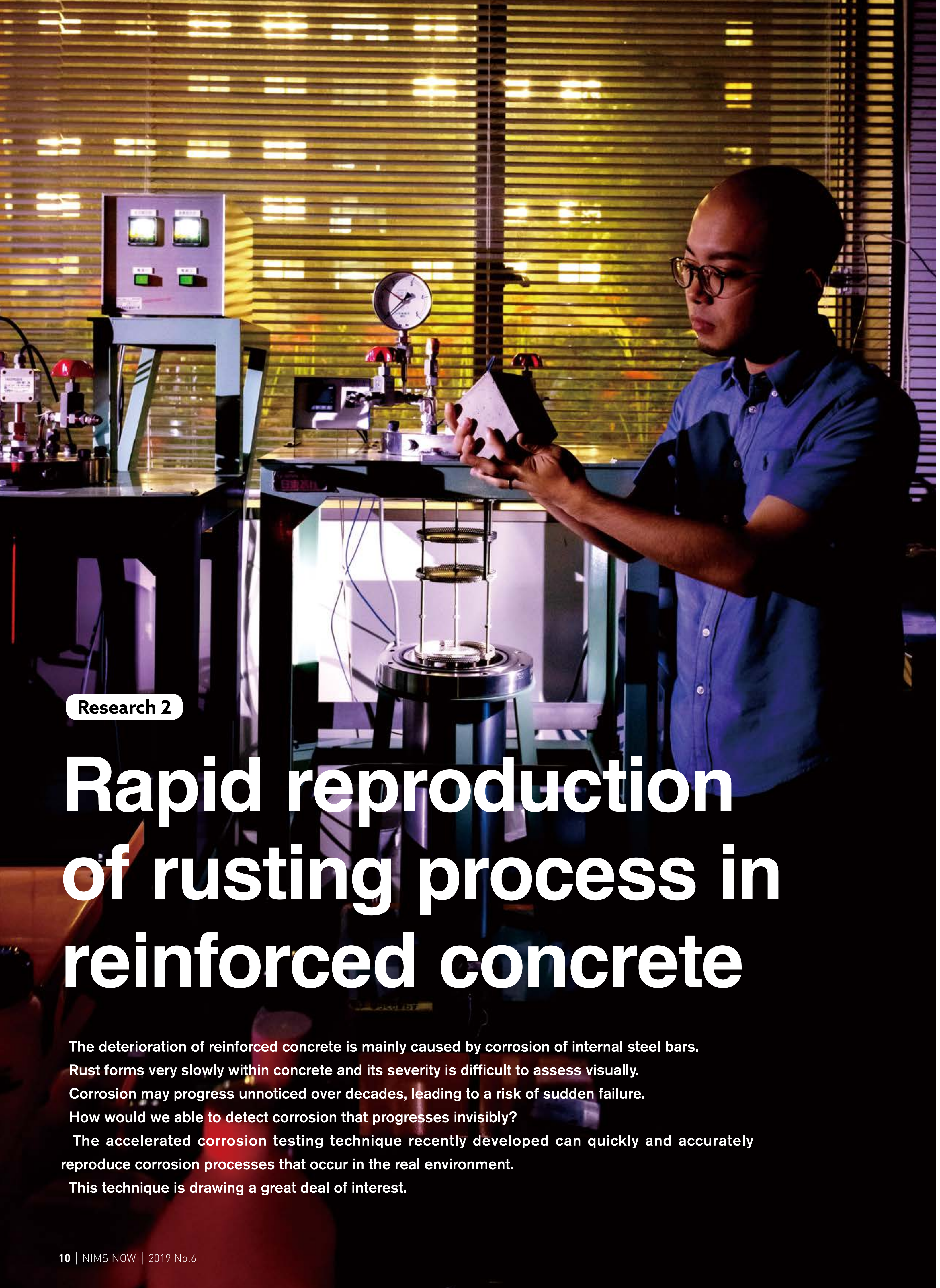
The test duration varies widely for different materials, from a minimum of six months to 10 to 20 years in some cases. Metal plates being tested need to be diligently managed manually in order to ensure accuracy. The positioning of metal test plates (e.g., their angles and orientations) has to meet the JIS standards*2 and inspections need to be carried out regularly to ensure that the samples' positions have not been altered by strong winds, heavy rain or other factors. In addition, several test plates are installed for each material, and some of them are removed from an exposure test every year to record the change in corrosion.

After test plates are exposed to the atmosphere for a scheduled time period, they are washed to remove rust. The severity of the corrosion damage is quantified by comparing the masses of the plates before and after exposure testing. NIMS has combined site-specific corrosion data with associated environmental data and built corrosion databases specific to Japanese conditions. They have been published online as a "Corrosion Data Sheet."*3 Any registered user can access this information.

NIMS is currently working on a challenging research project: estimating the severity of corrosion damage by incorporating environmental data into AI (see p. 7). However, this technique is expected to be effective only if sufficient amounts of corrosion data and associated environmental data are obtained from the field. Atmospheric exposure tests will continue to be important as a means of increasing the ability of AI to make accurate corrosion predictions and of collecting basic data on new materials. Material users in Japan and many other Asian countries have been counting on NIMS' field tests as a reliable source of information on safe and secure utilization of materials.

Testing site at NIMS

*1. ISO 9223
*2. Japanese Industrial Standards (JIS) Z 2381: General requirements for atmospheric exposure test
*3. NIMS Corrosion Data Sheet: https://smds.nims.go.jp/corrosion/



Research 2

Rapid reproduction of rusting process in reinforced concrete

The deterioration of reinforced concrete is mainly caused by corrosion of internal steel bars. Rust forms very slowly within concrete and its severity is difficult to assess visually. Corrosion may progress unnoticed over decades, leading to a risk of sudden failure. How would we able to detect corrosion that progresses invisibly? The accelerated corrosion testing technique recently developed can quickly and accurately reproduce corrosion processes that occur in the real environment. This technique is drawing a great deal of interest.

Weakness of reinforced concrete

Concrete is resistant to compression but susceptible to tensile stress. By contrast, steel is resistant to tensile stress but susceptible to compression. Reinforced concrete combines these two materials to compensate for their respective weaknesses. It has proven to be a valuable, strong structural material.

However, reinforced concrete also has major problems. Many concrete bridges and tunnels have aged considerably and are in urgent need of repair. The corrosion of the steel bars embedded in concrete is the main cause of the deterioration and this is difficult to detect externally.

Steel bars expand when they corrode and rust forms. Expanding steel bars apply pressure from the inside to the concrete that surrounds them, causing it to gradually crack. Once cracks form, large amounts of air and rainwater intrude into the concrete, rapidly advancing the deterioration. The continued safety of reinforced concrete structures needs to be ensured. It is therefore desirable to develop tools that will help us determine when internal corrosion—the "silent killer" —will cause concrete to crack, the appropriate time to take action and the types of measures that should be taken.

To address these issues, urgent efforts are being made to develop an accelerated corrosion testing technique. This technique is intended to accelerate the corrosion of steel bars embedded in concrete, thereby allowing corrosion researchers to evaluate corrosion risk much more quickly than would be possible via field exposure tests. When this testing technique becomes available for practical use, it is expected to facilitate the development of new materials capable of effectively preventing reinforced concrete from deteriorating. For example, this technique can be used to quickly test the effectiveness of corrosion-resistant steel—which has been actively developed in recent years—and materials used to repair concrete cracks.

Several different types of accelerated corrosion tests have been proposed, although they all have issues (e.g., slow acceleration and inadequate accuracy). Kotaro Doi, who participated in a national project aimed at developing durable public infrastructure, developed a testing technique capable of reproducing corrosion about 30 times more quickly than actual field conditions can achieve. How did he accomplish this?

Limitations of existing accelerated corrosion tests: efforts to reproduce real-environment processes

Accelerated corrosion tests are intended to reproduce corrosion in steel bars embedded in concrete using scientific equipment.

"The alkaline condition of concrete drives the formation of "passive films"—thin, fine-textured oxide films—on the surfaces of internal steel bars," Doi said. "These films prevent iron dissolution on steel bar surfaces, significantly slowing the rusting process when compared to steel bars exposed to the atmosphere. However, if rainwater and seawater enter the concrete, the salt which destroys passive films, causing iron to dissolve and diffuse into the surrounding concrete, forming rust. Rust slowly spreads and ultimately causes concrete to crack."

Efforts have been made to develop a variety of testing techniques capable of reproducing and accelerating steel bar corrosion by facilitating iron-dissolving chemical reactions. Anodic current supply is a widely known technique. In this method, test specimens of reinforced concrete are first prepared. Anodic currents are then applied to steel bars in the specimens to forcibly destroy the passive films formed on their surfaces. The anodic current supply has advantages: it can significantly accelerate corrosion and allows researchers to control the amount of steel bar dissolution by adjusting the amount of applied charge. However, this method was recently found to have a problem.

"Satoshi Takaya, Assistant Professor in Kyoto University made an important discovery in 2013," Doi said. "He found that rust formed by anodic current supply is composed mostly of special types of rust that do not occur in the real environment."

The biggest issue with this finding is the fact that steel bars exposed to anodic current supply and to real environment expand at considerably different rates. This difference critically undermines the test accuracy given that concrete deterioration is caused by the expansion of corroded steel bars.

"Actual corrosion processes are very complex," Doi said. "Professor Takaya's discovery taught us that intentionally accelerating the dissolution of iron by destroying passive films does not adequately reproduce real-environment processes. I speculated that other chemical and electrochemical reactions are also vital and need to be taken into account when reproducing corrosion processes. It turned out that oxygen was the key."

Development of a testing method capable of perfectly reproducing corrosion processes

Doi explained the reason why he thought oxygen was a key player.

Rust formed on steel bars embedded in concrete. Corroded steel bars expand, causing the surrounding concrete to crack.

Coverage cooperation
Kotaro Doi
Independent Scientist
Research Center for Structural Materials

"I closely examined corrosion processes. After passive films are destroyed, two electrochemical reactions take place concurrently: the oxidation reaction, in which iron atoms lose electrons and the resulting iron ions diffuse into the surrounding concrete, and the oxygen reduction reaction, in which oxygen accepts the released electrons. Existing accelerated corrosion testing techniques promote the oxidation reaction but not the oxygen reduction reaction. I thought I could facilitate the oxygen reduction reaction by supplying pressurized oxygen gas, thereby allowing iron in test specimens to be exposed to high concentrations of oxygen."

Doi collaborated with a scientific equipment manufacturer and developed an original system capable of supplying large amounts of pressurized oxygen into a test chamber (figure). He then prepared test specimens of reinforced concrete. During this preparation, concrete raw materials were mixed with salt water and steel bars were subsequently embedded in the concrete material to facilitate the destruction of passive films on steel bar surfaces. He then placed the test specimen in the gas pressure test chamber and allowed the system to supply pressurized oxygen gas. After the specimen was subjected to this treatment, Doi analyzed the rust formed within the specimen and found that its composition matched that of rust formed in the real environment.

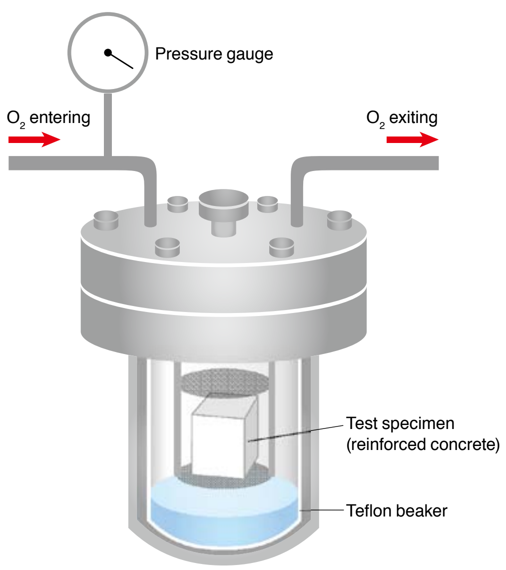
"We collected rust on Hashima Island (commonly known as "Battleship Island") in Nagasaki Prefecture and used it as a reference," Doi said. "The approximately 100-year-old abandoned concrete buildings preserved on the island are the oldest reinforced concrete structures in Japan. We decided to analyze rust samples from this island to identify the types of rust formed in the real environment. Our group, including myself, went to the island and collected rust from cracked reinforced concrete. We then analyzed both the rust from the island and the rust formed using the technique we developed. The types of rust we found in these samples matched perfectly."

Subjecting the test specimens to pressurized oxygen gas exposed them to approximately 30 times more oxygen than they would be exposed to in the field. In this way, Doi succeeded in causing steel bars embedded in concrete to corrode approximately 30 times faster than they would in the real environment.

Doi said that the accelerated corrosion testing technique he developed could be combined with other methods to enable scientists to predict the lifetime of various materials depending on the environmental conditions in which they are used. For example, reinforced concrete used in highways deteriorates not only due to corrosion but also due to cyclic stress generated by traveling vehicles. Integrating the accelerated corrosion testing technique with mechanical testing techniques may enable accurate prediction of age-related damage in different materials.

"Recently, we are simplifying the equipment so that many researchers can perform this testing technique without significant capital investment." Doi said. "I hope that the technique we developed will serve as a standard in accelerated corrosion tests for the steel bars in concrete."

(by Kumi Yamada)



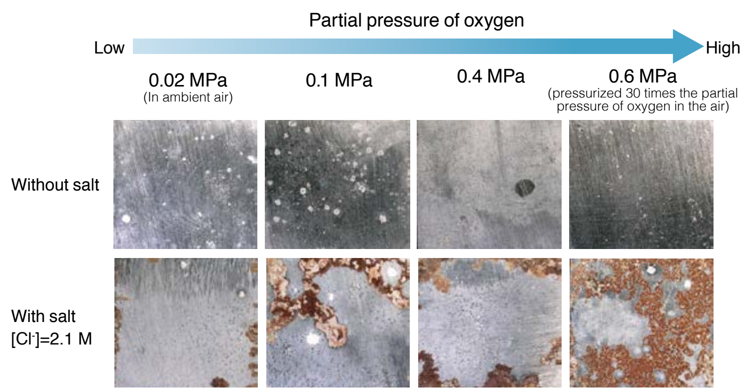


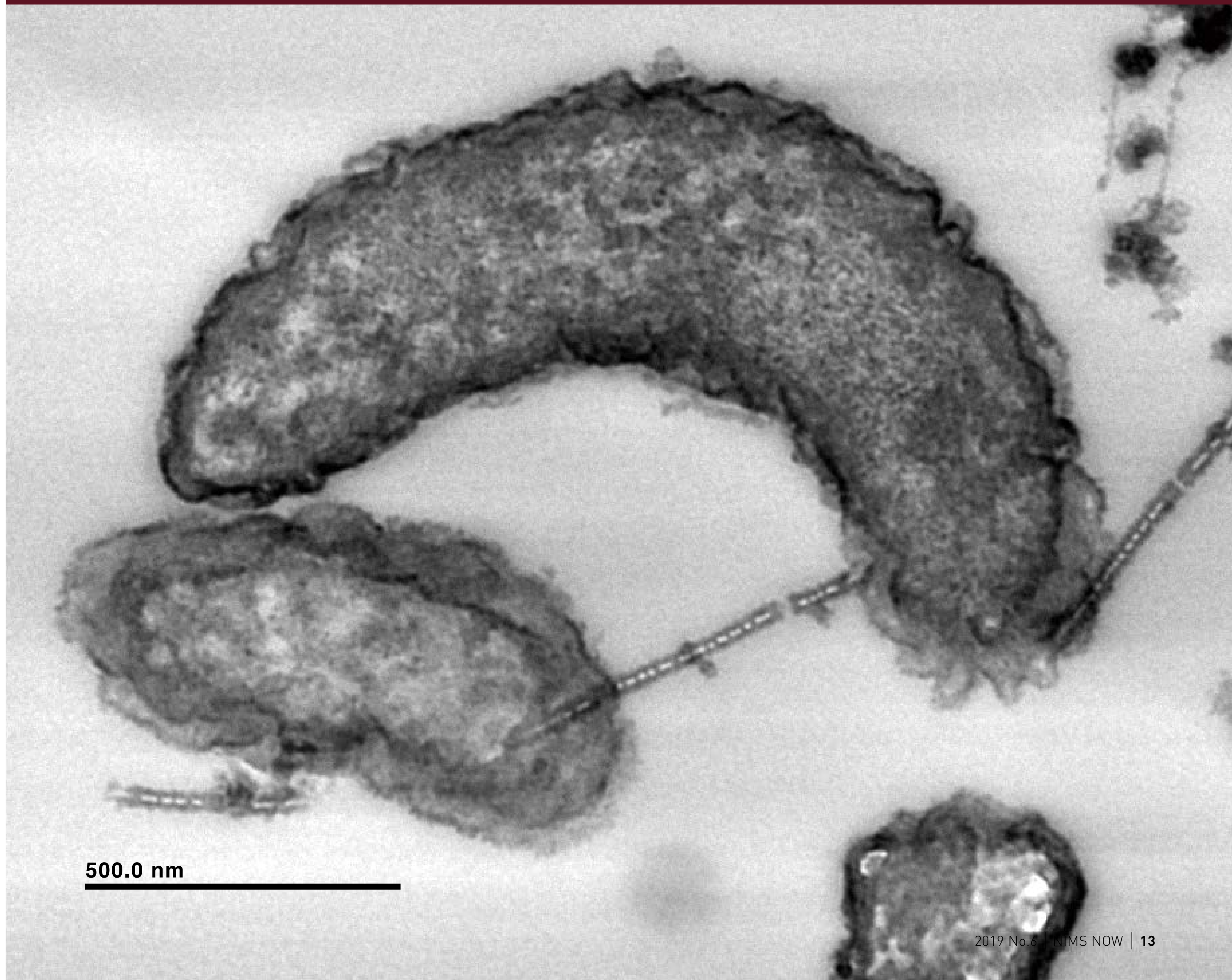
Figure. Equipment of Hyperbaric-oxygen accelerated corrosion test developed by Doi (left) and the appearance of the surfaces of iron specimens after subjected to gas exposure (right)

Schematic diagram of the gas pressure test chamber, the heart of the testing system. The system is capable of increasing the pressure of oxygen gas to as high as 2 MPa (100 times higher than the partial pressure of oxygen in the air) and supplying it to the chamber. The solution in the beaker ensures that humidity remains constant. To perform a corrosion test, a test specimen of reinforced concrete is placed on a shelf in the chamber and pressurized oxygen gas is supplied to it to accelerate corrosion. After a testing period, the specimen is ejected from the chamber and the composition of the rust formed on the iron specimen is carefully analyzed using a Laser Raman spectrometer (photo above on this page).

Research 3

Unmasking iron-rusting bacteria

Iron normally rusts when it reacts with water and oxygen. However, rust can form in another way. Some bacteria are capable of causing serious iron corrosion. Sulfate-reducing bacteria—a major iron-corroding bacterial group—produce iron sulfide, a type of rust, as part of its life cycle. The bacterial corrosion mechanism had long been a mystery despite efforts to uncover it. Akihiro Okamoto recently succeeded in identifying this mechanism for the first time in the world.



What are sulfate-reducing bacteria?

Bacteria are ubiquitous throughout our environment and are present in the air, water and soil. Although some bacteria benefit humans by playing vital roles in fermentation, drug production and other activities, others cause surprising types of harm, including metal corrosion.

This type of damage is particularly serious when it occurs in iron used in petroleum pipelines. Pipeline corrosion has resulted in oil spills, causing major problems in oil-producing countries. The cost amounts to 30 to 50 billion dollars annually in the United States alone. Environmental contamination caused by oil spills is also a grave concern. This is also an issue of great importance to Japan as it is a huge petroleum importer. A known cause of pipeline corrosion is "sulfate-reducing bacteria." This bacterial group takes in sulfate ions from its surroundings and produces hydrogen sulfide, which reacts with iron to form iron sulfide—commonly known as "black rust"—on its surface.

Mysterious, unstoppable corrosion

This rust-forming reaction alone does not explain the severity of corrosion that causes thick-walled, heavy-duty pipelines to fail.

"Once iron surfaces are completely covered with rust, the reaction between iron and hydrogen sulfide should cease according to the conventional wisdom," said Akihiro Okamoto, who has been researching bacteria from the perspective of materials science since doctoral course. "However, corrosion continues to advance even after this condition is reached. This has been a long-standing mystery for corrosion researchers, who have debated this subject extensively."

Although the mystery remained unresolved, a research report published in 1988 provided a clue: a group of electricity-producing bacteria was discovered in a lake in New York State. These bacteria are capable of exchange electrons with solid substances and harvesting energy from them.

"Researchers theorized that the existence of sulfate-reducing with electricity-producing abilities could explain continued corrosion of pipelines after they are completely covered with rust," Okamoto said. "They suspected that such bacteria would be able to remove electrons from iron surfaces and thereby corrode them even after they are covered with iron sulfide because electrons can travel through it. To prove this, I had to demonstrate that sulfate-reducing bacteria possess the "membrane enzymes" used by electricity-producing bacteria to remove electrons from substances. However, membrane enzymes had never been found in sulfate-reducing bacteria."

Corrosion researchers initially expected that the discovery of electricity-producing bacteria would expedite efforts to understand the relationship between corrosion and bacteria, but it only triggered new debate. Nevertheless, Okamoto and his colleagues finally brought the more than 30 year debate to an end in February 2018.

Finally capturing the moment of electron extraction

"Sulfate-reducing bacteria normally use abundant organic substances, such as lactic acid, as energy sources," Okamoto said. "I assumed that if sulfate-reducing bacteria also possess the electron extraction capabilities as electricity-producing bacteria, they would always use organic material first and begin consuming electrons as an "emergency food" when the organics are depleted. My plan for testing this assumption was to first starve sulfate-reducing bacteria—thereby forcing it to use electrons as an energy source—and then identify the enzymes it uses to extract electrons. To prepare for this experiment, I started culturing sulfate-reducing bacteria in a solution that lacks lactic acid and other nutrients."

Okamoto's group selected Desulfovibrio ferrophilus strain IS5 (hereinafter referred to simply as the "IS5 stain") for the study. The IS5 strain—which is only capable of using iron as an energy source—had been thought to be the most likely sulfate-reducing bacteria to possess the characteristics of electricity-producing bacteria. After the IS5 strain was cultured for five days, Okamoto's group observed it in detail under a transmission electron microscope.

"We confirmed that the bacteria possess electrically conductive nanowires extending from their cellular surfaces and membranes," Okamoto said. "We also clearly observed a high concentration of membrane enzymes along cell membranes and nanowires using a redox protein staining technique (see the photo on p. 13). We then measured electrical currents generated by the bacteria and found that the IS5 strain extracts electrons from an electrode only when a high concentration of membrane enzymes was detected." This study confirmed that the IS5 strain actually possesses membrane enzymes and is indeed a group of electricity-producing bacteria. It also suggested that this strain is able to survive even when organic material and other energy sources are unavailable.

Oil-producing countries have been using large, very costly amounts of chemical microbicides to kill sulfate-reducing bacteria which cause pipeline corrosion. These microbicides also pollute the environment. "Sulfate-reducing bacteria develop resistance to microbicides after repeated use, trapping oil producers on a 'pesticide treadmill,'" Okamoto said. "The membrane enzymes we have identified can be used as a microbicide target site. This approach may enable scientists to develop a type of microbicide to which sulfate-reducing bacteria are less likely to develop resistance, thereby reducing the cost of bacterial management and environmental impact."

(by Kumi Yamada)

Sulfate-reducing bacteria in culture. Okamoto's group has been studying the impact of the bacteria on corrosion by changing the medium composition and manipulating bacterial genes. Iron sulfide (black rust) has been deposited at the bottom.

Coverage cooperation

Akihiro Okamoto

Independent Scientist
International Center for Materials Nanoarchitectonics (WPI-MANA)

Focus

Contribution of the electrochemical discovery in bacteria to life science and medicine

As a student researcher, Okamoto studied "artificial photosynthesis," which takes advantage of biological catalytic activities. Since then, one of his research interests has been the use of electrochemistry in solving the mysteries of living organisms. The discovery of the membrane enzymes described above is significant not only in corrosion research but also in life science.

After performing an in-depth genetic analysis on the membrane enzymes of the IS5 strain, Okamoto's group found that the genes for these membrane enzymes are substantially different from those of electricity-producing bacteria, although tthey perform the same function. In addition, they have found that a wide range of deep-sea bacteria also have genes that code for membrane enzymes.

"Deep-sea bacteria had previously been thought to use hydrogen as an energy source. However, our results indicated that this bacterial group likely extracts electrons from mineral deposits in the deep sea for use as an energy source. Our discovery has therefore helped unveil the ecology of primordial deep-sea bacteria and raises new questions about evolutionary history," said Okamoto proudly.

Okamoto is affiliated with the NIMS Center for Functional Sensors and Actuators where he has been researching sensing techniques to detect pathogenic microorganisms hidden in human bodies. "Pathogens multiply in the human body by using ions and electrons as energy sources," Okamoto said. "I am attempting to use this mechanism to our advantage: the growth rates of pathogens may be estimated by measuring the movement of electrons. I hope this sensing technique can be used to detect various diseases early in their development."

MANA INTERNATIONAL SYMPOSIUM 2020 Jointly with ICYS

3/1 ~ 3
sun tue

Time and date: **March 1-3, 2020**
Banquet: March 2, 18:30-20:30

Venue: **Tsukuba International Congress Center EPOCHAL TSUKUBA**

Symposium Registration Fee: **free** / Banquet Participation Fee: 3,000yen, 1,500yen (student)

Sponsored by
National Institute for Material Science (NIMS)
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Requires Online-Registration prior to February 21, 2020. Please access the following web site.

https://www.nims.go.jp/mana/2020/registration.html

The International Center for Materials Nanoarchitectonics (WPI-MANA) is attempting to create a new paradigm for materials science, called "nanoarchitectonics", based on an innovative nanotechnology. WPI-MANA has held the MANA International Symposium every year to discuss the current status and the future perspective of materials science based on the state-of-the-art nanotechnology together with many distinguished scientists and young scientists from around the world.

In the 13th MANA International Symposium (jointly organized with ICYS: International Center for Young Scientists), we design the symposium to overview present status and future prospects of "New Trends in Materials Nanoarchitectonics". In addition to keynote and invited speakers, the researchers from MANA and ICYS will present their latest findings for extensive discussion for future.

We hope many scientists, researchers and students who are interested in materials science and technology will join this symposium and obtain fresh inspiration from the talks and discussions towards the future.

Keynote Speakers

Prof. Robert A. Wolkow (University of Alberta, Canada)
"Atom Defined Fabrication Comes of Age: Binary Logic and an Ising Simulator"

Prof. Kazuyuki Kuroda (Waswda University, Japan)
"Synthetic Chemistry of Nanostructured Silica and Silicates"

Prof. Shinji Tsuneyuki (University of Tokyo, Japan)
"Firsi-Principles Material Simulation and Beyond"

※All lectures will be conducted in English.
※Programs are subject to change without notice.

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