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Program & Abstracts

ANTI-CORROSION TECHNOLOGY FOR INSIDE OF A WATER SUPPLY STEEL PIPE BY NMR PHENOMENON

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Abstract

Various methods of anti-corrosion are used for the rust problem which occurs inside of a water supply steel pipe, however, the conventional methods cannot solve corrosion problem completely.¹⁾ New method used of Nuclear Magnetic Resonance (NMR) phenomenon to reduce corrosion (FeO(OH)) to magnetite (Fe₃O₄) was studied as the efficient method for anti-corrosion. The effect of this method is evaluated by measuring the decrease of all the Fe ion content in water and reduction of corrosion to magnetite. All the Fe ion content decreased from 0.789mg/l to 0.262mg/l 4 months after the installation of the device of NMR phenomenon at the water supply steel pipe of the building of Hokkaido Industrial Research Institute. At the surface of corrosion where water came in contact inside of an air conditioner's hot and cold water circulation steel pipe, the weight of magnetite increased to 72.9% from 2.2% and, the 70.7% increase was confirmed after using NMR Phenomenon device.

Water is usually big masses of water molecules because of hydrogen bonds, and the electron is hardly generated by the flow of this condition of water. Then the nucleus of hydrogen which composes the water molecule is spun by the NMR phenomenon, and as a result, the water condition becomes the excited state, and generates enough electrons to reduce corrosion (FeO(OH)) to magnetite (Fe₃O₄) by pumping up this excited state of water by electric energy or dropping down from an elevated tank to lower level.

The anti-rust technology which rapidly reduces corrosion to magnetite by this method of NMR phenomenon is thought to be one of the effective methods to completely stop the corrosion inside of water supply steel pipes.

Key words: NMR, reduction, corrosion (ferric oxyhydroxides, FeO(OH)), magnetite (Fe₃O₄)
hydrogen nuclei, water molecule,

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1. INTRODUCTION

Many conventional methods, such as chemical product of antioxidant, many different types of equipment,¹⁾ and epoxy-polymer lining method, are currently taken for trying to stop the growth of corrosion inside of steel pipes for cold water and hot water supply pipes, and air-conditioning water pipes.

However, the conventional methods cannot completely stop the growth of corrosion, or cannot solve the problem of corrosion blockade that has already existed inside of the water pipes. Moreover, epoxy-polymer lining has problems of high cost and stop the operation of facilities during the construction work.

Under these circumstances, we had an experiment to reduce corrosion (ferric oxyhydroxides, FeO(OH)) formed inside of water pipes to magnetite (Fe₃O₄) by the use of technology of Nuclear Magnetic Resonance. Water molecules usually make up cohesive bonds by hydrogen bonds. The hydrogen nuclei of water molecules are spun by the phenomenon of Nuclear Magnetic Resonance (NMR), then water molecules are put in an excited state, and spinning of hydrogen nuclei makes water molecules difficult to bond again to each other, and small mass of cohesive bond of water molecules are kept. When this excited state of water flows in the pipes by the power of a pressure pump or water drop from an elevated water tank, many electrons are discharged by the friction of water molecules, and corrosion (FeO(OH)) is reduced to magnetite (Fe₃O₄) by these electrons.

All the Fe ion content in water and the magnetite weight percentage in total rust formed inner surface of water pipes, are measured to prove this study.

2. EXPERIMENTAL

As the way to confirm the reduction of corrosion (FeO(OH)) to magnetite (Fe₃O₄), the equipment of Nuclear Magnetic Resonance phenomenon was installed on a water supply steel pipe and air-conditioning steel pipe of more than 15 year-old- facilities of the real buildings, and confirmed the theory and technology.

2.1 The methods of examination that corrosion (FeO(OH)) which had already formed inside of a water supply pipe of one way flow of water, was reduced to magnetite (Fe₃O₄).

2.1.1 Installation of the equipment

Three units of the equipment which makes NMR phenomenon on the hydrogen nuclei of water molecules were installed on the outlet pipes of an elevated water tank or a pressure pump.

2.1.2 Method to take sample water for examination of all the Fe ion content

Took 500ml of the sample water from a faucet, which is 100m to 500m away from the installed place of the equipment, by using public laboratory supplied bottles. The sample water should be the first use of water after being kept in a pipe for more than 12 hours during the night.

2.1.3 Period of taking sample water

The sample water was taken 1 to 3 days before the installation of the equipment, and 2 or 3 times on a regular basis during the period of time between two weeks and 4 months after the installation of the equipment.

2.1.4 Method of measurement of all the Fe ion content in water

Two methods of ICP Emission Spectral Analysis and Flameless Atomic Absorption Spectrometry were used as the measurement methods of all the Fe ion content in water.

2.1.5 Method to confirm the reduction of corrosion (FeO(OH)) to magnetite (Fe₃O₄)

When the water soluble corrosion (FeO(OH)) which formed inside of water supply steel pipes was reduced to magnetite (Fe₃O₄), all the Fe ion content in water decreased. So it was confirmed that corrosion (FeO(OH)) was reduced to magnetite (Fe₃O₄) by examining the decrease of all the Fe ion content in water after the installation of the equipment.

2.2 The method of the examination that corrosion (FeO(OH)), which had already formed inside of the steel pipe of hot-and-cold water of air-conditioning pipe, was reduced to magnetite (Fe₃O₄).

2.2.1 Installation of the equipment

The equipment which makes NMR phenomenon was installed on the outlet pipe(inner diameter size is 200mm) of hot-and-cold water generating machine, in which all of circulating hot-and-cold water passes through.

2.2.2 Method to take sample rust for examination of magnetite's weight percentage.

Before the installation of the equipment, cut and take out 30cm long of hot-and-cold water pipe (inner diameter size is 80mm) which is located 200m far from the installed place of the equipment, and replace with the new pipe instead of the old one and fix it with pipe fitting. Within one hour, take out more than 1g of sample rust by using a metal brush from about 100cm² of rusted surface formed inside of the pipe.

After the installation of the equipment, cut and take out 10cm long of the pipe next to the pipe which is taken out before, replace with new pipe, and fix it with pipe fitting. Method of taking sample rust is the same as the first sampling.

2.2.3 Period of taking sample rust

The sample rust was taken before installation of the equipment, 3 months after, 6 months after, and 12 months after the installation of the equipment, for 4 times in total.

2.2.4 Method of measurement of the weight percentage of magnetite (Fe₃O₄) in the total rust ²⁾

1. Crushed and milled the rust sample in a mortar, and put it through a sieve of a 100μm mesh metal filter and made it fine powder.
2. Took out about 0.5g of powder rust and put it in the 100mL beaker, and weighed it correctly with four digit below zero.
3. Added 30mL of purified water in the beaker, and mixed it by a supersonic vibrator for 30 seconds.
4. Collected deposit of magnetite (Fe₃O₄) at the bottom of the beaker by using 3,000 gauss magnet which covered all the bottom area of the beaker. All water and material in the 100mL beaker except magnetite (Fe₃O₄) held by the magnet, was transferred to the 200mL beaker by hand or using pipette.
5. Added 30mL of purified water into the 100mL beaker and repeated above step No. 3 and No. 4 for three times.
6. By using 3,000 gauss magnet, collected deposit of magnetite (Fe₃O₄) at the bottom of the 200ml beaker in which there was about 90mL liquid (water with other material) transferred from the 100mL beaker, and threw away all liquid except magnetite (Fe₃O₄) held by the magnet .
7. Added about 5mL purified water into the 200mL beaker and mixed with deposit of magnetite (Fe₃O₄) and transferred all water and magnetite to the 100mL beaker in which magnetite (Fe₃O₄) was deposited.
8. Added 30mL of purified water into the 100mL beaker again and repeated the same process of above step from No. 3 to No. 7 for five times.
9. After finishing of above process, magnetite (Fe₃O₄) was deposited bottom of the 100mL beaker by the magnet.
Added about 5mL of pure methyl alcohol into the 100mL beaker and mixed it with magnetite (Fe₃O₄) by hand vibration, and 10 minutes later threw away all methyl alcohol except magnetite (Fe₃O₄) held by the magnet, and added 5mL of methyl alcohol again into the 100mL beaker and repeated this step of No. 9 one more time.
10. Dried up all methyl alcohol and deposit of magnetite (Fe₃O₄) at the bottom of 100mL beaker for 30 minutes by using vacuum dryer at room temperature, and measured dry weight of purified magnetite (Fe₃O₄) correctly by using electric fine weight checker which can detect four digit bellow zero gram.
11. Weight percentage of magnetite (Fe₃O₄) was calculated by the formula as bellow.

$$\text{Weight percentage of magnetite (Fe}_3\text{O}_4) (\%) = \frac{\text{Purified magnetite (g)}}{\text{Total weight of rust sample (g)}} \times 100 (\%)$$

2.2.5 Method to confirm the reduction of corrosion (FeO(OH)) to magnetite (Fe₃O₄)

When the corrosion (FeO(OH)) which formed inside of the hot-and-cold water steel pipe of the air-conditioner was reduced to magnetite(Fe₃O₄), the weight percentage of magnetite (Fe₃O₄) in the surface of rust contacting with water increased. So it was confirmed that corrosion (FeO(OH)) was reduced to magnetite(Fe₃O₄) by examining the increase of the magnetite weight percentage in the rust after the installation of the equipment.

3. RESULT

3.1 Corrosion (FeO(OH)) which had formed inside of a water supply steel pipe of one way flow of water, was reduced to magnetite (Fe₃O₄).

3.1.1 The result of measurement of all the Fe ion content in the sample water from the water supply steel pipe in the building of Hokkaido Industrial Research Institute.

The equipment which makes NMR phenomenon was installed on the outlet steel pipe (inner diameter size is 100mm) of an elevated tank on the building of Hokkaido Industrial Experimental Laboratory. The sample water which was not used during the night for 14 hours, was taken in the morning from the toilet's faucet of the building, and Table 1 and Fig. 1 show the result of water examination of the sample water. The average of three-time water examination of the sample water taken from a faucet of the toilet before the installation of the equipment, all the Fe ion content was 0.789mg/l. It indicates that corrosion (FeO(OH)) had formed in the water supply steel pipe, and it had dissolved into the water for 14 hours during the night. However, all the Fe ion content of the sample water decreased to 0.423mg/l in 2 months after the installation of the equipment. Furthermore, as the result of water examination of the sample water, in 4 months after the installation, all the Fe ion content decreased to 0.262mg/l.

| Term | Examination item | All Fe ion content (mg/l) |
|------|--|-----------------------------|
| | Before installation (average of three times) | 0.789 |
| | 2 months after installation | 0.423 |
| | 4 months after installation | 0.262 |

Table 1. Measurement result of all the Fe ion content in the sample water of Hokkaido Industrial Research Institute's building before and after the installation of the equipment.

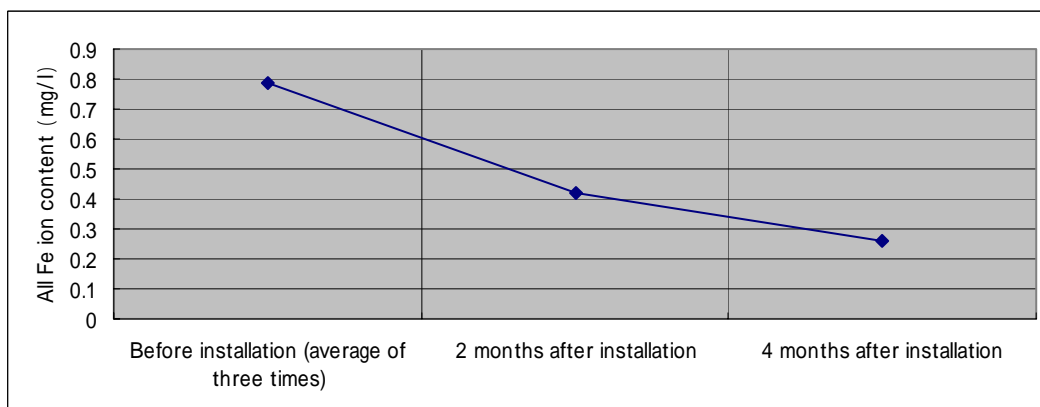


Fig. 1. Changes of all the Fe ion content in the sample water of Hokkaido Industrial Research Institute's building before and after the installation of the equipment

3.1.2 The result of measurement of all the Fe ion content in the sample water taken from water supply steel pipe in the building of Nihon University Engineering Department.

The equipment which makes NMR phenomenon was installed on the main steel pipe of water supply (inner diameter size is 80mm) which was used by two buildings, No.8 and No.9, in the testing area. The sample water which was not used during night for 12 hours, was taken in the morning from a toilet's faucet of each building of No. 8 and No. 9, and Table 2 and Fig. 2 show the result of the water examination of the sample water. Before the installation of the equipment, and the result of the water examination showed that all the Fe ion content was 7.8mg/l in No.8 building, and 1.2mg/l in No.9 building. It indicates that corrosion (FeO(OH)) had formed in the steel pipes of water supply of both buildings, and it had dissolved into the water during the night for 12 hours. However, all the Fe ion content of the sample water decreased to 0.11mg/l in No.8 building and 0.04mg/l in No.9 building in 4 weeks after the installation of the equipment. Furthermore, the all Fe ion content of the sample water decreased to 0.03mg/l in No.8 building and less than 0.01mg/l in No.9 building in 6 weeks after the installation of the equipment.

| Term | Sampling place & Examination item | No.8 building All Fe ion content (mg/l) | No.9 building All Fe ion content (mg/l) |
|------|-----------------------------------|---|---|
| | Before installation | 7.8 | 1.2 |
| | 4 weeks after installation | 0.11 | 0.04 |
| | 6 weeks after installation | 0.03 | Less than 0.01 |

Table 2. Measurement result of all the Fe ion content in the sample water of Nihon University Engineering Department's building of No. 8 and No. 9.

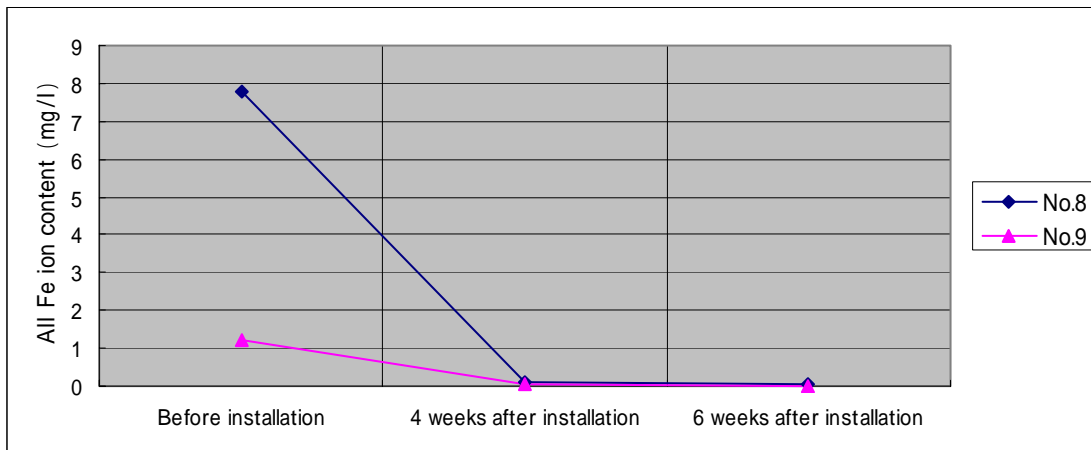


Fig. 2. Changes of all the Fe ion content in the sample water of Nihon University Engineering Department's building of No. 8 and No. 9.

3.1.3 The result of measurement of all the Fe ion content in the sample water from the water supply steel pipe in the building of Medical Center Hospital of Japanese Red Cross Society.

The equipment which makes NMR phenomenon, was installed on the outlet steel pipe (inner diameter size is 200mm) of an elevated water tank of the building in the testing area. The sample water which was not used during the night for 12 hours, was taken in the morning from the faucet of the outpatient baby room, and Table 3 and Fig. 3 show the result of the water examination of the sample water. Before the installation of the equipment, the result of the water examination showed that all the Fe ion content was 2.00mg/l. It indicates that corrosion (FeO(OH)) had formed in the steel pipe of the water supply of the building, and it had dissolved into the water during the night for

12 hours.

However, all the Fe ion content of the sample water decreased to 0.48mg/l in 2 weeks after the installation of the equipment, and all the Fe ion content of the sample water showed 0.49mg/l in 4 weeks after the installation, and then, all the Fe ion content of the sample water decreased to 0.27mg/l in 6 weeks after the installation of the equipment.

| Term | Examination item | All Fe ion content (mg/l) |
|------|----------------------------|-----------------------------|
| | Before installation | 2.00 |
| | 2 weeks after installation | 0.48 |
| | 4 weeks after installation | 0.49 |
| | 6 weeks after installation | 0.27 |

Table 3. Measurement result of all the Fe ion content in the sample water of Medical Center Hospital of Japanese Red Cross Society.

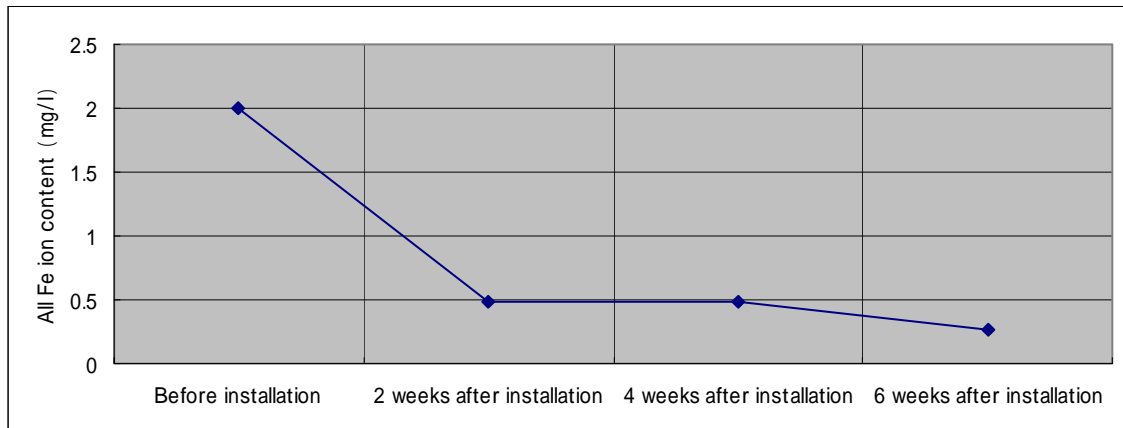


Fig. 3. Changes of all the Fe ion content in the sample water of Medical Center Hospital of Japanese Red Cross Society.

3.2 Corrosion($\text{FeO}(\text{OH})$) formed inside of a hot-and-cold water steel pipe of an air conditioner with circulating flow of the same water, was reduced to magnetite(Fe_3O_4).

3.2.1 Weight percentage of magnetite (Fe_3O_4) which was existing in the rust formed inside of the hot-and-cold water steel pipe of the air conditioner in the building of Foundation Wakabadai Administration Center, Kanagawa Prefecture, was examined.

The equipment which makes NMR phenomenon was installed on the outlet steel pipe (inner diameter size is 200mm) of the hot-and-cold water generating machine, in which all of the hot-and-cold water circulating passes through. Table 4 and Fig. 4 show the measurement results of the weight percentage of magnetite (Fe_3O_4) in the rust formed inside of the branch steel pipe (inner diameter size is 80mm). The weight percentage of magnetite (Fe_3O_4) in the surface of the rust which was contacting with water, was 2.2% before the installation of the equipment. However, the weight percentage of magnetite (Fe_3O_4) in the rust increased to 14.4% in 3 months after the installation of the equipment. Furthermore, the weight percentage of magnetite (Fe_3O_4) increased to 53.4% in 6 months after the installation, and it increased to 72.9% in 12 months after the installation of the equipment.

| Term | Examination item | Weight percentage of magnetite (Fe ₃ O ₄) (%) |
|------|------------------------------|--|
| | Before installation | 2.2 |
| | 3 months after installation | 14.4 |
| | 6 months after installation | 53.4 |
| | 12 months after installation | 72.9 |

Table 4. Measurement result of the weight percentage of the magnetite in the rust of the air-conditioner's steel pipe of Foundation Wakabadai Administration Center's building.

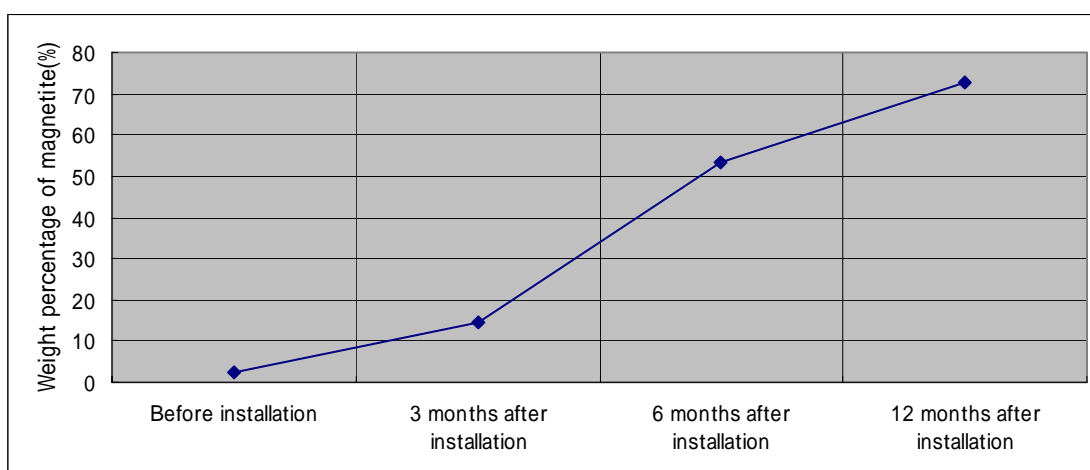
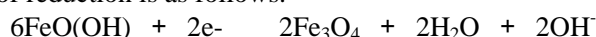


Fig. 4. Changes of the weight percentage of magnetite (Fe₃O₄) in the rust of the air-conditioner's steel pipe of Foundation Wakabadai Administration Center's building.

4. DISCUSSION

It is well known that a galvanized steel pipe, which is very popular to use for a water supply pipe and hot-and-cold water pipe of the air-conditioner, easy to lose coated zinc layer inside of the pipe in 4 or 5 years after being built, and the steel inner surface of the pipe is oxidized by water and oxygen that dissolved into the water, and formed corrosion (FeO(OH)). This corrosion (FeO(OH)) has made a red water problem since old days, because this corrosion (FeO(OH)) is easy to dissolve and spread in the water, so all the Fe ion content in the water increased when the water is kept inside of the pipe for a long time without being used, and it makes the red water problem. However, there was no solution of the corrosion and red water problem until today. This study proved that when the corrosion (FeO(OH)) was changed to magnetite (Fe₃O₄) which is not solved into the water, the corrosion and red water problem were solved.³⁾ It was proved that when Nuclear Magnetic Resonance phenomenon made hydrogen nuclei of water molecules spin, and this water was moved in the pipe by the power of pressure pump or water drop by gravity, the electrons were generated by this condition of water and reduced corrosion (Fe(OH)) to magnetite (Fe₃O₄). The reaction formula of reduction is as follows.⁴⁾⁵⁾



5. CONCLUSION

This study was carried out at the three facilities with using galvanized steel pipe of water supply as one way flow and at one facility with using steel galvanized pipes of the air-conditioner as circulating the same water. In case of the water supply pipes, the corrosion (FeO(OH)) which had

formed and dissolved into the water, were decreased step by step after the installation of the equipment of NMR phenomenon, and finally all the Fe ion content decreased to the level that there was no corrosion (FeO(OH)) formed inside of the pipe. It indicated that corrosion (FeO(OH)) was changed to different type of crystal which is insoluble and difficult to spread into the water. It is very difficult to think about other component or crystal except for magnetite (Fe₃O₄)³⁾. This indicates that the reaction of reduction occurred and, at the same time, new form of corrosion (FeO(OH)) was prevented, because it was proved by continuous decrease of all the Fe ion content in the sample water after the installation of the equipment.

In case of the inside of the hot-and-cold water pipe of the air-conditioner in which the same water was circulated, the corrosion (FeO(OH)) which formed inside of the steel pipe was reduced to magnetite (Fe₃O₄). This was proved by the increase of the weight percentage of magnetite (Fe₃O₄) in the rust formed inside of the air-conditioner's steel pipe after the installation of the equipment.

Accordingly, it was proved that, when big masses of cohesive bond of water molecules were changed to small and excited state by spin of hydrogen nuclei by Nuclear Magnetic Resonance phenomenon, corrosion (FeO(OH)) was reduced to magnetite (Fe₃O₄) by the power of the pressure pump or water drop by gravity, and forming of new corrosion (FeO(OH)) in the pipe was prevented.

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REFERENCE

1. Mototsugu Magara
Researching report concerning preparation for guideline of new technology development and evaluation system relevant to controlling supply and drain water in buildings. 45 (1988).
2. Katsuyuki Kumano, Japan System Planning Co.,Ltd
The method to analyze weight percentage of magnetite in rust
Application of patent 2003-031823 (2003).
3. H.H. Yurick, Under the editorship of Tsuyoshi Okamoto, Translated by Seigo Matsuda and Iwao Matsushima,
Corrosion and Corrosion Control. Third edition, 63 (1999).
4. M. Startman, et al.
An electrochemical study of phase transformations in rust layers
Corrosion Sci., 23, 969 (1983).
5. T. Ishikawa, et al.
Formation of magnetite in the presence of ferric oxyhydroxides
Corrosion Sci., 40, 1239 (1988).