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Long term stability of iron for more than 1500 years indicated by archaeological samples from the Yamato 6th tumulus

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A B S T R A C T

One of the candidate materials for overpack in the Japanese engineered barrier system for high-level radioactive waste (HLW) is iron and therefore its long-term stability for at least 1000 years is very important for safety analysis of the repository system. Therefore, *several of the iron artifacts excavated from the* Yamato 6th tumulus (ancient tomb) in Nara prefecture were analyzed using X-ray computed tomography (CT) to determine corrosion depth. The samples analyzed, both of two large and 11 smaller iron artifacts are called 'Tetsutei'. The thickness of each rust layer was measured from a cross-section image of the sample and the difference in material density between rust and iron was shown by the image density by the X-ray CT. In the case of pitting corrosion in the sample, the depth of the pits was measured directly and estimated as total corrosion depth with general corrosion layer. The corrosion depths are 0.5–2.1 mm. These data indicate conservative predictions for the extrapolations based on experimental studies. Such corrosion data from archaeological samples are useful in analogue studies of high-level radioactive waste disposal as evidence of long-term stability of a waste container.

1. Introduction

For a safety assessment, it is important to estimate the longevity and the effectiveness of sealing of a carbon-steel container (overpack) in Japanese high level radioactive waste disposal [1]. The thickness of corrosion is examined to have confidence that the life time of a container will be at least 1000 years after disposal. The corrosion rate, which is used for the examination, is required experimentally and conservatively with consideration of factors such as corrosion by microbes. In order to show a prediction is certainly conservative, the information based on archaeological analogue studies were utilized. In this paper, we show data obtained on corrosion rate of archaeological iron artifacts buried underground for about one thousand years for a analogue study to increase confidence in the robustness of using overpack material as a engineered barrier in the Japanese high level radioactive waste disposal system.

Considering archaeological artifacts in order to determine the corrosion of iron in the context of 'nuclear waste storage', some paper are reported and describe that main corrosion product is goethite by microscopic technique in atmosphere [2–4]. Understanding corrosion kinetics is also important to predict the long-term corrosion for 'nuclear waste disposal'. The mechanism of rusting process in normally oxidizing soil is assumed to be similar to that in atmosphere. In limited mount of oxygen of underground condition, ferrous ions produced through corrosion precipitates as the inner magnetite (Fe_3O_4) and the outer lepidocrocite (γ-FeOOH). Further lepidocrocite dissolves and goethite (α-FeOOH) is produced as a stable oxide. It is conformed that the analysis results of artifacts buried in soil indicate that the rust is composed of a double layer of magnetite and goethite [5].

On the other hand, a single layer of magnetite is assumed to grow in a slightly oxidizing or reducing condition which is considered similar to a nuclear waste disposal condition. In this paper, some samples buried in the environment and covered by magnetite single layer are reported. Analyzed samples are two big and 11 small iron artifacts which are called 'Tetsutei', and which have been lying below ground for 1500 years at a tumulus. From the view point of Japanese history, the iron artifacts come from the 'Kofun Jidai' or tumulus period, the earlier part of the Yamato period, which is from the latter half of the 3rd century to the middle of the 5th century. The largest tumulus in Japan was built in the 5th century. It is the Daisen Kofun, located at Sakai in Osaka. There are thirty tumuli in Japan over 200 m length. Some large tumuluses are always accompanied by several secondary tumuli, called 'Baicho', in which the remains of followers or sacrifices were buried. The iron artifacts studied were also buried as a sacrifice, because iron plates were important and valuable materials in the period.

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X-ray computer tomography was used to nondestructively analyze the thickness of rust on the iron artifacts in this study.

2. Experimental

2.1. Excavation site

The Yamato 6th tumulus where 'the Tetsutei' have been excavated is located at Nara in Nara Prefecture, a recognized 'Baicho' of the main tumulus the Uwanabe Kofun (Fig. 1). It may have been constructed in the late 5th century as was the Uwanabe Kofun. This 'Baicho' was leveled in order to build the US Army's facility for the occupation forces in Nara Prefecture in December, 1945 immediately after World War II [6,7]. At that time, many iron artifacts were excavated and preserved. According to speculation based on a limited report, this tumulus was circular type and thought to have been 30–36 m across. The height of this tumulus was 3 m when leveled, but was probably higher at the time of construction prior to erosion of the mound. The site had been protected by a sacred area and covered with woodland, before being leveled by bulldozing. The 'Tetsutei', the iron artifacts, were arranged for burial as in Fig. 2. The artifacts were excavated directly from the top center of the tumulus less than 60 cm from the surface at 1945 by archaeologist. Unfortunately, as the excavation was performed suddenly, the data of chemical or geological information was not obtained. The sacrifices are usually storage into wood box and surrounded by clay material in the case of other tumuli. We considered that the burial condition of the artifacts is slightly oxidizing or reducing environment because of the surface of the area was covered with vegetation and the artifact rust was consisted of single magnetite layer.

2.2. Sample

The artifacts excavated directly from the Yamato 6th tumulus consisted of 872 'Tetsutei' artifacts, 281 axes, 138 sickles, and 284 of small swords. The 'Tetsutei' can be classified into two types based on size, large ones about $400 \times (70\text{–}130) \times 3$ mm and smaller ones $150 \times (20\text{–}30) \times 3$ mm (Fig. 3). The artifacts have been buried for about 1500 years and some have kept their original condition without any treatment for saving after being excavated by conservation in a storage box.. These samples are also covered with the black brown rust. The thickness of the rust and depth of pitting corrosion were measured by X-ray CT method and structural composition of the rust was analyzed by XRD.

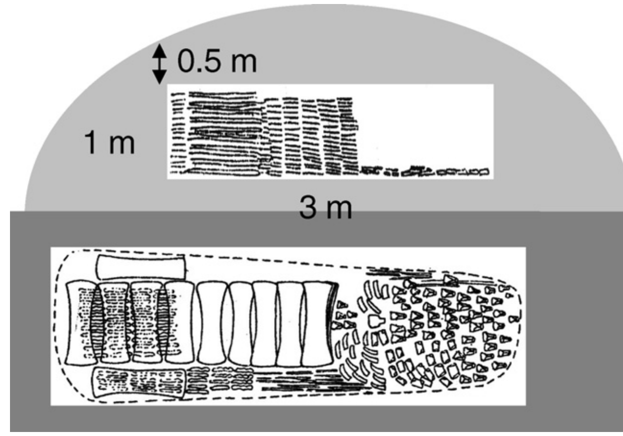

Fig. 2. Schematic drawing of excavated samples from the 6th Yamato Ancient tumulus.

Samples analyzed consist of two of the larger type and 11 smaller iron artifacts and had been below ground for 1500 years in the tumulus. These sample were selected in the point of both of best and also worst preserved sample from their appearance.

2.3. X-ray computer tomography (X-ray CT)

The MeV energy region X-ray CT instrument (HiXCT-6M), developed for industrial use was used for the computer tomography. The layout of this instrument is shown in Fig. 4 and the equipment are shown in Fig. 5. It is arranged with the X-ray generator (accelerator) opposing the detector and with the sample between them. The tomographic picture is analyzed by the computer from the X-ray signal obtained using a rotating scan [8]. Basic specification of this instrument is shown in Table 1. The part of the X-ray generator irradiating the electrons accelerated by the electronic linear accelerator to the tungsten, generates the powerful X-ray in the Mev energy region which is available to detect until 28 cm depth as iron material. The X-ray spreads in a fan-like shape in the horizontal direction and irradiates the sample as it rotates on the turntable. The transmitted X-rays were measured with high sensitivity silicon semiconductor detectors arranged in a line [9]. It is possible using this computer tomography to make nondestructive observations of the inner structures, e.g. density of material inside the sample Thus by using this equipment, measurements by X-ray

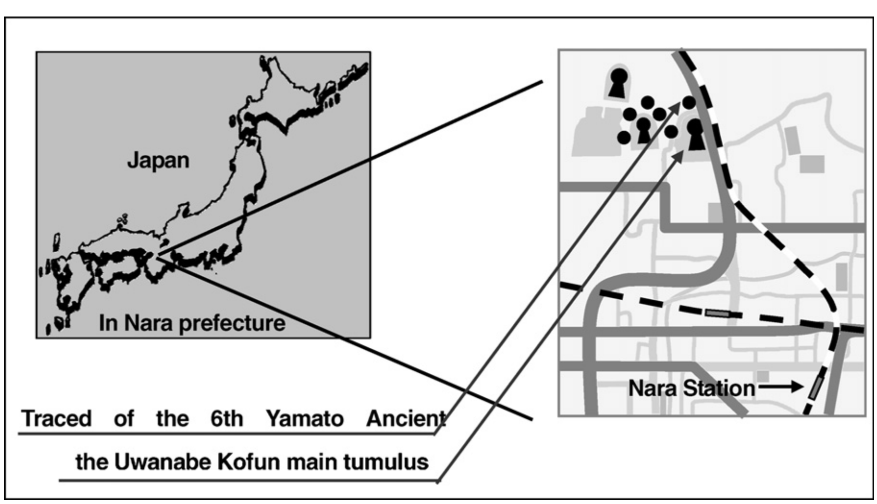

Fig. 1. Location of the Yamato 6th tumulus. This tumulus is located around main tumulus, the 'Uwanabe Kofun' 2.5 km north from Nara station.

Fig. 3. Iron artifacts samples – 'Tetsutei'.

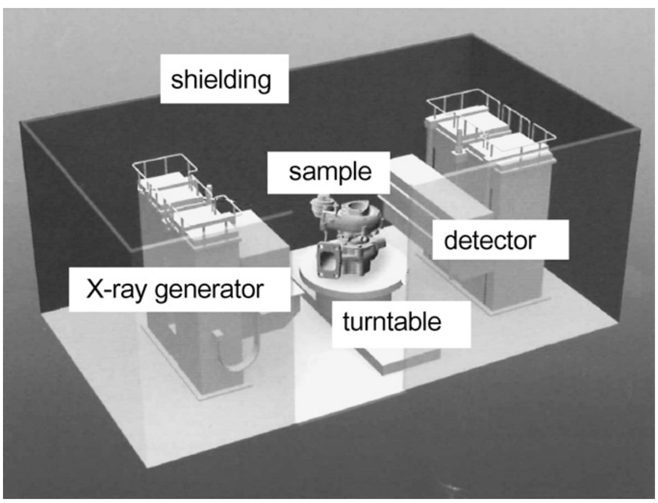

Fig. 4. Configuration of an X-ray CT scanner.

computed tomography are possible for a 28 cm thick iron sample with a resolution of 0.2 mm. It is possible to scan multiple samples simultaneously, if the distance of the iron component is in the measuring range. Acquired data have shown that the sample density is also the difference in permeability of the X-ray. In the present experiment, an iron component in which density was high (7.86) was observed as a white area on the image, whereas air appeared as an area of black. Therefore, rust component as magnetite (4) or goethite (2) was easy to see separately (Fig. 6).

Table 1
Basic specification (HiXCT-6M)

Component	Specification	Component	Specification
Maximum weight for measurable sample	100 kg	Slice width	0.4 mm/ 1.0 mm/ 2.0 mm
X-ray energy	Max. 6 MeV	Detector	Semiconductor detector
Transmission length	Iron:280 mm aluminium:790 mm	Measuring time	15 s/slice

3. Results and discussion

3.1. Depth of corrosion layer

The outline of part of a sample is shown in Fig. 7. The surface is covered by the corrosion product, and there are some pitting

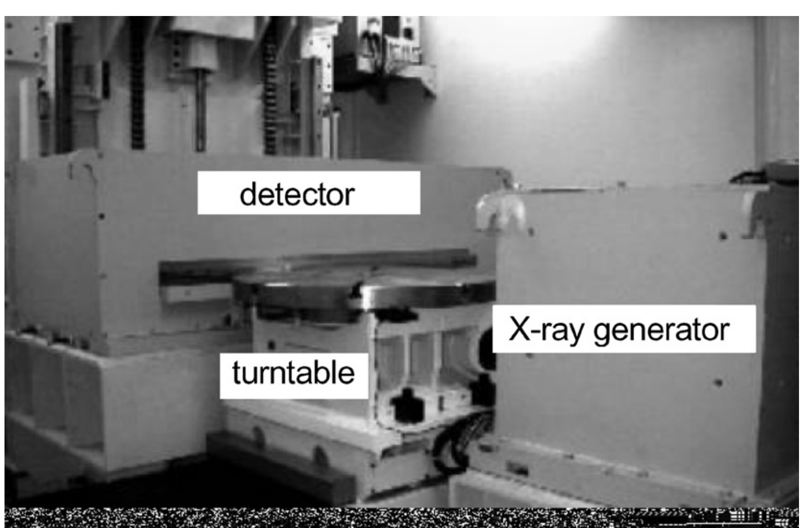

Fig. 5. Appearance of HiXCT-6M.

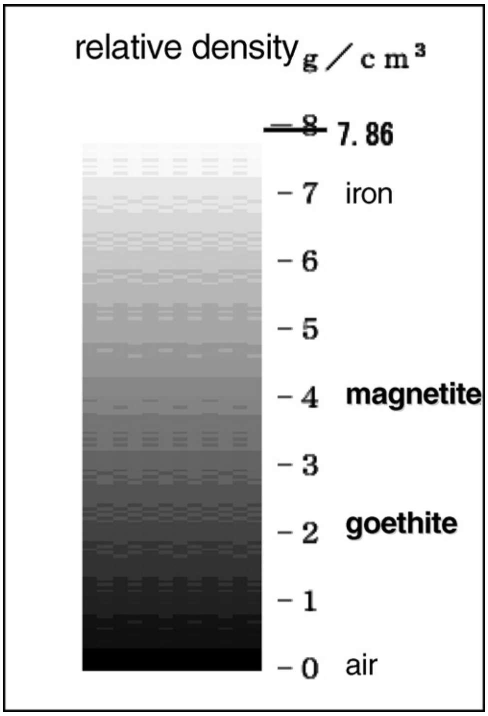

Fig. 6. Density distribution obtained by X-ray CT.

corrosions on the surface. In the cross section photograph of the cut sample, metallic luster was observed indicating the iron metal had remained in good condition without corrosion at its center. An example of X-ray computed tomography of an untreated sample is shown in Fig. 8. In the left optical photograph of the sample, the surface is uniformly covered with brown corrosion product with some localized pitting corrosion.

Analysis of the crystallographic structure of the corrosion products was carried out using XRD measurements qualitatively (Table 2). Magnetite and goethite were identified as the main components. Because of the surrounding soil of the artifacts contain some iron as background and the solubility of iron in groundwater is very low, almost migrated iron element from artifact by corrosion reaction are deposit around it as corrosion layer. When the thickness of the corrosion layer can be obtained, reduction in thickness of the original material can be calculated by converting from the ratio of the iron component in the rust [10]. A 1 mm thickness of rust is considered equal to 0.35 mm thickness of iron metal, when the rust component is assumed to be due to magnetite. Rust of 1 mm thick goethite is the equivalent of 0.14 mm iron. The distinction of each rust is possible by X-ray computed tomography from the difference in the ratio of the iron components, because it is proportional to the difference in specific gravity of the rust. In the case of slightly oxidized or reducing condition, the single corrosion layer is similarly component to magnetite, and two corrosion layers are similarly both magnetite and goethite. These layers are not 100% crystal component and are mixture other corrosion material including amorphous components. In this study, iron content for these layers was analyzed and estimated the ratio of iron for the corrosion material. It is possible to calculate reduction in thickness of iron metal from the thickness of the rust acquired from the X-ray computed tomography data. The X-ray computed tomographic images of cross sections 1 (A–A') and 2 (B–B') are shown on the right side of Fig. 9. The cross section of 1 (A–A') is the location of pitting corrosion. Depth of the pitting is about 1 mm covered by 2 mm high corrosion products (A–A'). At cross Section 2 (B–B'), general corroded area was covered by rust with a thickness of

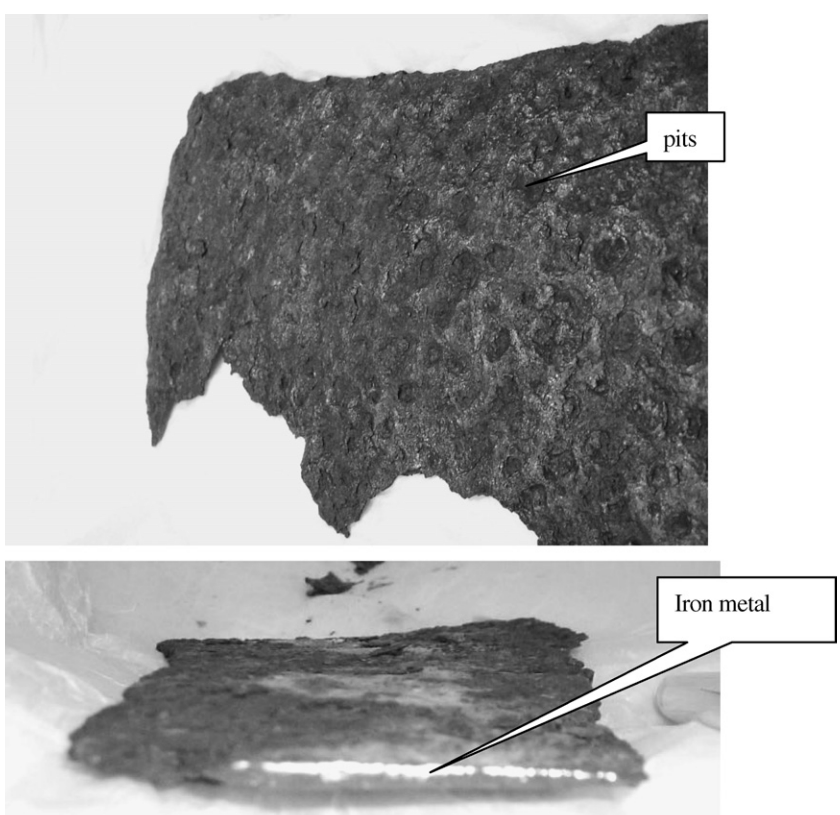

Fig. 7. Image of X-ray CT for 'Tetsutei' sample.

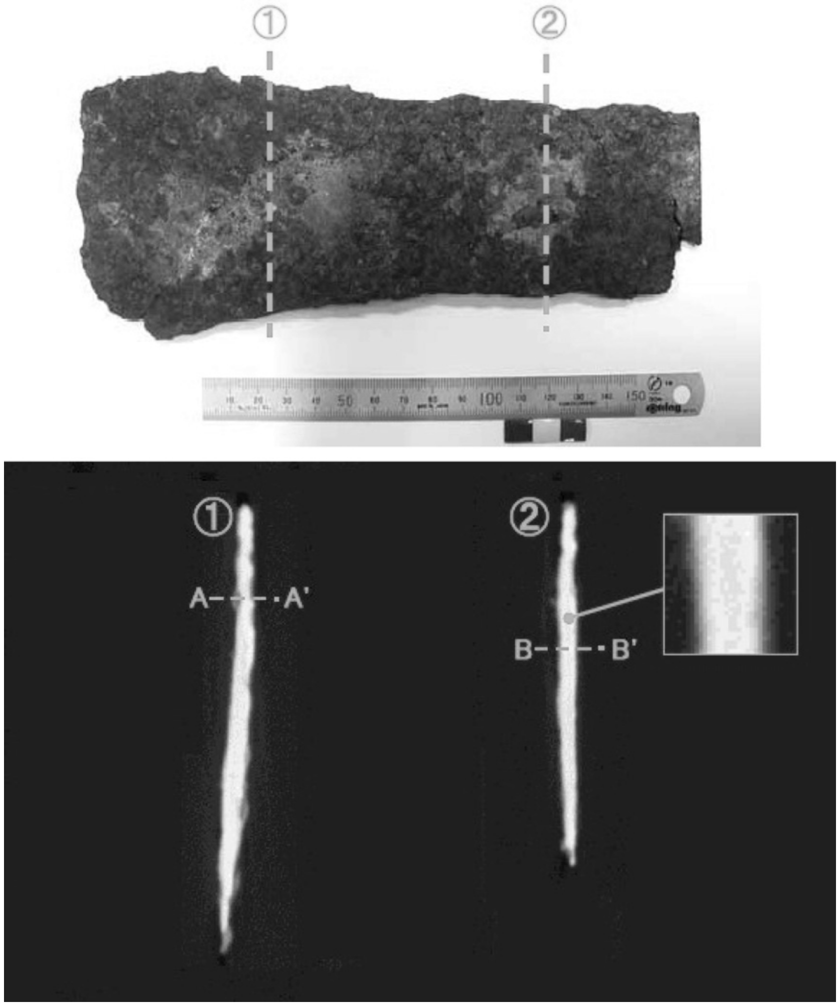

Fig. 8. Pitting corrosion on surface of the 'Tetsutei' sample and its cross section.

Table 2
Chemical structure analysis for rust

Sample no.	Type	Fe_3O_4 magnetite	α-FeOOH goethite	γ-FeOOH lepidocrocite	β-FeOOH akaganeite
232	large	++	++	+	+

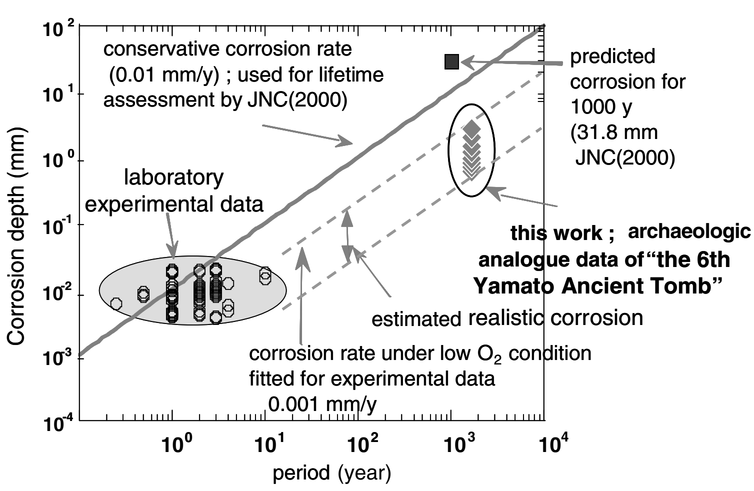

Fig. 9. Comparison of this archaeological analogue data with laboratory and predicted corrosion data.

Table 3
Analytical results of total corrosion depth

No.	Type	Width (mm)		Length (mm)	Thickness (mm)	Weight (g)	Max. depth of pitting corrosion (mm)	Total corrosion
		Center	Edge					
231	Large	78	130	375	2.3–3.3	310	1.5	2.0
232	Large	56	105	417	2.3–3.3	381	1.4	1.9
250	Small	17	23	121	1.5–1.6	18	0.3	0.8
251	Small	21	32	131	1.5–1.7	23	1.0	1.5
256	Small	18	31	120	1.3–1.9	20	ND(<0.1)	0.5
258	Small	12	20	128	1.6–1.8	16	0.4	0.9
267	Small	11	29	152	1.5–2.0	23	1.6	2.1
271	Small	13	33	135	1.6–2.5	20	0.6	2.1
272	Small	15	24	134	1.4–1.8	19	0.5	1.0
273	Small	10	29	142	1.7–2.0	22	0.7	1.2
275	Small	9	33	140	1.4–1.5	16	0.7	1.2
277	Small	14	28	130	1.0–1.1	15	ND(<0.1)	0.5
278	Small	15	19	134	1.0–1.1	14	0.2	0.7

The total corrosion depth was summation of general corrosion depth 0.5 and each pitting corrosion depth.

about 1.0 mm around iron with a thickness of about 2–4 mm and it showed that the corroded depth of the base metal was 0.5 mm.

The authors consider that the existence of pitting corrosion in single corrosion layer type reflects the initial stage environment for iron artifacts in the ground. In the initial stage, the oxygen, which is present in the pore water of the soil and the heterogeneous contact between metal and soil, induce rusting principally as pitting corrosion. The oxygen in the subsurface environment is reduced in the next stage, and general corrosion seems to progress. As the pitting corrosion area were also covered by magnetite single layer, the corrosion environment was considered to change to anoxic. If there were enough oxygen as an oxidizing environment, the corrosion would be increased and made two corrosion layers like slag. From the viewpoint of long term corrosion stability in a reducing environment expected in the high level radioactive waste disposition program, the time when conditions change to a reducing environment, should be known, though it is not possible to confirm the time variation of the underground environment in detail. The total corrosion depth of the iron after 1500 years was evaluated conservatively as a summation of depth of localized pitting corrosion and general corrosion mass losses of the entire sample surface. The maximum pitting corrosion depth for each sample and the calculated values of total corrosion depth and general corrosion depth (maximum 0.5 mm) were also determined and are shown in Table 3. The total corrosion depth acquired from these 13 samples has values between 0.5 from 2.1 mm. There were also some samples without significant pitting corrosion. It can be said that the result of corrosion action on the sample used in this study was dominantly pitting corrosion. For example, 1.5 mm iron was corroded by pitting and 0.5 mm was by general corrosion with estimated maximum corrosion of 2 mm.

3.2. Estimation of amount of corroded iron base material for 1000 years

We assume the quantity of rust after 1000 years for carbon steel by some experimental corrosion data, and a value of 31.8 mm is conservatively recommended in the evaluation of long term stability of overpack material in our second progress report [1]. Corrosion tests in reducing conditions on carbon steel have been carried out in the laboratory, and the results from 5 years of study has been reported [11]. The predictive value after 1000 years and the results of corrosion testing for the last 10 years experiments are plotted in Fig. 9. The evaluated data of rust for the 13 artifacts which were corroded under slightly oxidizing or reducing environment based on corrosion type, are also plotted in the same figure. The fluctuation of data seems to show realistic rates below minimum 0.001 mm/y corrosion rate in a experimental data of reducing environment. The difference between pitting corrosion data seems to be largely dependent on dispersion, even if they have been excavated from the identical environment in the tumulus. From corrosion evaluation of the ancient iron samples used in this research, it was shown that the conservative evaluation of the predictive corrosion value for overpack material for 1000 years is conservative by about one order of magnitude.

4. Conclusions

Some iron archaeological artifacts found at an ancient Japanese monument 'the Yamato 6th tumulus' after burial underground for 1500 years were analyzed using X-ray computer tomography. While the results of XRD measurements indicated mainly amorphous materials, structures of the crystal part of the rust were goethite (α-FeOOH), magnetite (Fe_3O_4), lepidocrocite (γ-FeOOH), and akaganeite (β-FeOOH). The rust layer was determined to be about 0.3–0.5 mm as general corrosion for not treatment samples using X-CT nondestructively. Some samples could be considered to have been under slightly oxidizing conditions with corrosion depth between 0.2 and 1.6 mm for pitting corrosion. Maximum total corrosion depth of iron matrix was estimated by summation and therefore, 0.5–2.1 mm for 1500 years. The measured corrosion rates are one order of magnitude less than the design allowance of 40 mm/ka of Japanese high level radioactive waste disposal system, which supports the argument that the designed corrosion allowance is conservative.

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