

TITLE Storage of freshly-excavated iron objects - second year report

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DATE November 1982

ABSTRACTS Results are presented on the second year of experiments on the storage of freshly-excavated iron objects in the following environments: low RH, normal oxygen; high RH, low oxygen; buried in earth; immersed in alkaline sulphite solution. The results are compared with objects stored in uncontrolled conditions.

KEYWORDS storage, iron, relative humidity (RH), silica gel, corrosion, cracking, alkaline sulphite.

THIS REPORT IS LEVEL III

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STORAGE OF FRESHLY-EXCAVATED IRON OBJECTS - SECOND YEAR REPORT

INTRODUCTION

The experiments described in last year's preliminary report (AM Lab Report No 3717) have been continued for another twelve months. More definite conclusions can now be drawn about suitable storage environments.

To recapitulate, experiments were started in September 1980 with freshly excavated iron objects from three sites. In addition to the majority of iron objects which were stored in uncontrolled conditions, selected items were stored in four different controlled environments in sealed polythene boxes (Stewart Plastics' Picnic Packs).

1. Dry - low relative humidity, normal oxygen (objects stored with silica gel).
2. Damp - high RH, low oxygen (objects stored with pads soaked in alkaline sulphite solution).
3. Buried in earth.
4. Wet - objects immersed in cold alkaline sulphite solution.
5. Uncontrolled - objects stored in paper or plastic bags in cardboard boxes in a finds store.

Results

The contents of the boxes were examined again in August 1982, with the results shown in the table below. In each column the first figure is the number of objects showing signs of deterioration (cracking, flaking or active corrosion), while the second is the total number of objects concerned.

| Site | Dry | Damp | Earth | Wet | Uncontrolled |
|-------|------|-------|-------|------|--------------|
| A | 0/4 | 2/5 | 0/4 | 1/6 | 41/91 |
| B | 3/9 | 5/13 | 0/3 | 1/8 | 9/15 |
| C | 1/14 | 24/44 | 0/29 | 0/7 | 31/70 |
| Total | 4/27 | 31/62 | 0/36 | 2/21 | 81/176 |

Notes

1. The objects in the dry boxes show minor signs of deterioration. Those marked have cracked slightly, but show no signs of flaking and akaganeite formation. After two years the silica gel was no longer bright blue but rather greyish. Nevertheless Humidial RH indicating cards inserted into the boxes showed that the RH was still less than 10%. The silica gel was then dried to constant weight at 120°C, and showed an average weight loss of about 5%. This suggests that the water content of iron objects is quite small, and that water vapour permeation into the boxes is very slow.
2. Attention was drawn in the preliminary report to the fact that the damp environment was unsuccessful. However, none of the objects marked has cracked or disintegrated - all that has happened is that an orange precipitate of "ferric hydroxide" has formed on the surface. This does not necessarily indicate that active corrosion is occurring. Nevertheless, this part of the experiment has been discontinued, and all the objects have been immersed in alkaline sulphite.
3. Water had condensed inside the lids of the earth boxes, showing that the relative humidity within was very high. Nevertheless there were no signs of deterioration.
4. The surfaces of some of the objects immersed in alkaline sulphite appeared blackish, which may indicate that superficial reduction has occurred.
5. Nearly half the objects stored in uncontrolled conditions showed signs of deterioration - cracking, flaking with akaganeite formation, and in some cases disintegration.

Conclusions

1. The difference between storage with silica gel and storage in earth is small, as regards number of objects deteriorated, but the difference is statistically significant (see appendix). Further experiments in progress with larger numbers of objects should remove all doubt.
2. Storage in conditions of high humidity and low oxygen was not successful, but the failure was more due to the method used to obtain these conditions than the conditions themselves. For reasons of practicality it is not worth pursuing this idea.
3. Although storage in alkaline sulphite appears to be generally successful, there are worries that the high pH may damage organic remains and tinning which may be present on iron objects. In view of this, and because of the practical difficulties, this method cannot be recommended for use on site. It may still be useful for the storage of selected objects in the laboratory, however.
4. Although the "wet or dry" controversy has still not been conclusively resolved, one should not lose sight of the fact that nearly 50% of iron objects stored in uncontrolled conditions have deteriorated, some seriously, in two years. The store in question is heated in winter, (but the relative humidity is not controlled,) and would be considered by most people to be an acceptable environment for archaeological storage. However, these results show that both dry storage and earth storage would be preferable. Doing nothing is no longer an acceptable option!

Appendix

Statistical analysis of the results

The χ^2 test is used to test the null hypothesis that there is no significant difference between storage with silica gel and storage in earth. Since 4 objects out of a total of 63 deteriorated, a fraction $4/63 = 0.0635$ of the objects in each environment would be expected to have done so.

Thus:

| | Dry | Earth |
|----------|------|-------|
| Observed | 4/27 | 0/36 |
| Expected | 1.7 | 2.3 |

$$\chi^2 = \sum \frac{(\text{Obs} - \text{Exp})^2}{(\text{Exp})} = \frac{(4 - 1.7)^2}{1.7} + \frac{(0 - 2.3)^2}{2.3} = 3.1 + 2.3 = 5.4$$

There is one degree of freedom (one less than the number of environments). From tables, the probability of this value of χ^2 being exceeded by chance is approximately 2% - in other words there is a significant difference between the two environments.

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October 1982