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TITLE Storage of freshly-excavated iron objects - preliminary results

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ABSTRACTS Preliminary results are presented 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. After one year there are signs of deterioration on some objects stored at low RH but not on those buried in earth. Statistically, the difference is only marginally significant.

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

THIS REPORT IS LEVEL III

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Storage of freshly-excepted iron objects - preliminary results

At the Symposium on the Conservation of Iron held at the National Maritime Museum in July 1980 (publication of which is still eagerly awaited!), I said that I would undertake experiments to test my suggestions about the best storage conditions for freshly-excavated iron objects. These experiments have been in progress for over a year, and preliminary results are now presented.

It is my belief that the most suitable conditions would be those that best reproduce those obtaining underground, is high relative humidity and low oxygen content. I believe that desiccation with silica gel is harmful, not because it emocurages fresh corrosion, but because it dehydrates the corroded outer layers of iron objects, causing them to crack.

Experiments 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 the following controlled environments in sealed polythene boxes (Stewart Plastics' Pionic Packs).

- a. Dry low relative humidity, normal oxygen (objects stored in Silica gel)
- b. Damp high RH, low oxygen (objects stored with pads soaked in alkaline sulphite solution)
- c. Buried in earth
- d. Wet Immersed in cold alkaline sulphite solution (0.5M NaOH, 0.5M Na₂SO₃)

No attempt has been made so far to monitor the conditions inside the boxes, to establish what the RH and oxygen content actually are. This is obviously important, and suitable instrumentation is still to be found.

The contents of the boxes were examined in September 1981, and the results are shown in the table below. It is hoped to continue the experiment for another two years at least, so these results are only tentative and may prove to be misleading. It must also be borne in mind that we are dealing with a limited number of objects from a small number of sites, so there can be no claim of generality. Statistically speaking, the differences between the four environments are not significant, but it would appear, however, that storage in soil has been most successful so far. Experiments using a larger number of objects have been started in order to test this conclusion, and will be reported on in due course.

In this table, the first figure is the number of objects showing signs of deterioration (corrosion or cracking), while the second is the total number of objects concerned.

| | Environment | | | | |
|----------|-------------|------|-------|------|---------------------------------------|
| Bite | Dry | Damp | Earth | Wet | .* |
| A | 0/4 | 1/5 | 0/4 | 0/5 | > |
| B | 2/9 | 4/13 | 0/3 | 1/8 | |
| C | 2/6 | 0/7 | 0/7 | 0/5 | \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ |
| Total | 4/19 | 5/25 | 0/14 | 1/18 | |

The results from the damp environment call for comment. It was found that objects lower down in the box were in better condition than those higher up. It would appear that there was insufficient alkaline sulphate solution to absorb a significant amount of oxygen in the box, and that the liquid had drained out of the pads at the top of the box so that the ebjects at the bottom were wetted. The environment in the box was therefore probably the disastrous combination of high RH and normal oxygen, which accounts for the corrosion of the upper objects, while corrosion of the lower objects was inhibited by contract with the alkaline sulphite solution.

Pratical experience has shown that some of these methods are too inconvenient for use on site, and are therefore unacceptable to excavators. Alkaline sulphate is messy, corrosive, and has to be used with care. Storage in boxes of earth also tends to be messy, and the boxes, once full, are heavy. Silica gel, on the other hand, is fairly light and convenient to use. It is also probably harmful! What is required to take the place of earth is a light, bulky substance which retains moisture and excludes oxygen merely by filling space. Experiments are now being carried out using Pearlite, which is sold as a basis for artificial soils for pot plants.

In conclusion, I would like to say again that these are only preliminary results of experiments with a limited number of objects. The aim is to discover storage conditions which will enable iron objects to be kept in the state in which they were found, without deterioration, until they are conserved. These are not suggestions for the storage of treated iron, nor

for the long-term storage of untreated objects.

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February 1982

Appendix

Statistical analysis of the results

In order to test the null hypothesis that there is no significant difference between the numbers of objects showing signs of deterioration in each of the four environments, the χ^2 test is used.

Since 10 objects out of a total of 76 deteriorated, we would expect a fraction 10/76 = 0.13 of the objects in each environment to have done so. Thus we have:

| | Dry | Damp | Earth | Wet |
|---|------|--------------|-------|------|
| Observed | 4/19 | 5/25 | 0/14 | 1/18 |
| Expected | 2.50 | 3 .29 | 1.84 | 2.37 |
| Then $\chi^2 = \sum \frac{(0bs - Exp)^2}{(Exp)} = 4.42$ | | | | |

The number of degrees of freedom is one less than the number of environments, = 3. From tables, we find that the probability of this value of \mathbb{Z}^2 being exceeded by chance is approximately 25% - in other words there is no significant difference between the environments.

If we restrict ourselves to examining the Dry and Earth boxes only, we have 4 objects out of 33 deteriorated, giving:

| | Dry | Karth | |
|----------|------|-------|-----------|
| Observed | 4/19 | 0/14 | * comment |
| Expected | 2.3 | 1.7 | |

In this case $X^2 = 2.96$ and the number of degrees of freedom is 1, giving a probability of about 10%. The difference between these two envisonments is therefore marginally significant.