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Copper

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Stockholm, Sweden, 1983-01-02

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By Åke Bresle, Royal Institute of Technology, Stockholm

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PITTING CORROSION ON ARCHAEOLOGICAL BRONZES

Introduction by Birgit Arrhenius

Ever since the dawn of the science of archaeology, metal artifacts have played an important role as preserved evidence of a lost culture. It was also noted early that metal objects were subject to progressive degradation in the soil, and conservators at archaeological museums came to devote a great deal of effort to stopping the process of corrosion. It was hereby observed quite soon that once the objects had been taken up out of the soil and placed in the museums' storerooms, a new degradation of the material took place.

Since the degradation of metal artifacts that took place in the museums took place right in front of the eyes of the museum staff, archaeological corrosion research came to be concentrated largely on this problem. The study reported here is therefore unique in a way, since it has nothing to do with the problem of preserving the archaeological bronzes in question, but is instead concerned solely with measuring the pitting factor.

Special problems have been encountered in this measurement of pitting corrosion, since pitting corrosion can only be studied on relatively well-preserved bronzes, whereas in most cases general corrosion has completely ruined the original surface. The selected material is also skewed due to the fact that the studied material has already undergone one selection, so to speak, in that it has exhibited a corrosion resistance that has enabled it to survive at all. We can deduce from the many tombs that have been found empty of artifacts or where the only metal artifacts are of gold that only a very small portion of the original archaeological metal material has been preserved through the millenia. The fact that the time exponent is an important factor here is indicated by Saers' observation that the measured mean pit diameter on the studied bronzes increases with the age of the finds. The theory that a time factor directly influences the corrosion process can also offer new perspectives on the incidence of ancient archaeological finds.

But the present material also indicates that the time factor has had greater importance for the course of pitting corrosion than e.g. environmental conditions and alloying materials. This can probably be explained by the skewing of the material mentioned above. In other words, due to unstable alloys or a poor preservation environment, the object has not been preserved at all or has only been preserved in the form of fragments that are useless for the purposes of this study.

An interesting find is therefore the low pitting factor in this bronze material, which represents numerous rather impure alloys, i.e. alloys with many trace elements. Metallurgy was not particularly advanced in the Bronze Age, and it is also probable that little effort was made to achieve pure alloys. The ancient metallurgist was much more interested in other properties than the purity of an alloy, such as the ease with which it could be melted, its fluidity and the ease with which it could be worked. Composite alloys actually have advantages in these respects, advantages which the ancient bronzesmith knew how to exploit. But it might also be worth considering that these ununiform alloys may have offered a resistance to pitting corrosion of quite another kind than that exhibited by modern, well-defined pure alloys. Individual trace elements may have acted as corrosion inhibitors if they occurred in the right proportions, while the same trace elements may have contributed towards accelerated degradation at other concentrations.

The interesting results yielded by this study should therefore be supplemented with metallurgical analyses in order to more closely characterize the distribution of the trace elements and the crystalline structure of the alloys. This should also shed additional light on ancient metallurgy. Such knowledge might also permit modern practical applications, where the original alloys, possibly arrived at by chance, can provide indications for the formulation of copper alloys possessing high resistance to corrosion.

PITTING CORROSION ON ARCHAEOLOGICAL BRONZES

By Åke Bresle, Royal Institute of Technology, Stockholm

Introduction

This work comprises the final report on a study carried out during the period January-June 1982 commissioned by the Swedish Nuclear Fuel Supply Co, Department for Handling and Final Storage of Nuclear Power Waste (SKBF/KBS), Stockholm, Sweden. The commission entailed determining the pitting factor in archaeological copper objects. The experimental work was performed at the Archaeological Research Laboratory at the University of Stockholm, primarily in conjunction with a represervation project involving material from the Museum of National Antiquities in Stockholm.

Background

Copper has been proposed as a canister material for use in the long-term storage of radioactive waste from nuclear power reactors. The waste is to be enclosed in cylindrical canisters of pure copper, which are then placed in vertical holes in the bedrock, 500 metres below the surface of the ground, and embedded in a clay buffer consisting of compact bentonite. The storage period has been set to at least 100 000 years, during which time the copper cylinders must remain intact so that the contained waste has no possibility of leaking out.

Copper has been judged to be suitable for the purpose in mind, since the slight general corrosion that is expected to occur on the copper surfaces of the canisters can be balanced by providing them with a calculable wall thickness.

There is, however, a factor of uncertainty: due to the composition of the groundwater that will surround the cylinders, the risk of localized corrosion in the form of pitting on the copper cannot be ruled out.

The intensity of this pitting corrosion can be expressed by the pitting factor P, defined as the maximum pit depth within a given surface area divided by the average value of general corrosion within the same area. Hence, in order for it to be possible to determine the pitting factor experimentally on a corroded copper surface, two measurements must be performed: determination of the depth of a selected pit and determination of the average corrosion (penetration) around the pit, see figure 1.

The rate of such a pitting attack cannot be predicted theoretically, but a representative field study (Denis and Romanoff 1950), where copper material buried in soil was exposed for up to 14 years in different soils, shows that the possibility of relatively rapid pitting cannot be excluded, given the existence of special conditions.

An extrapolation of such a 14-year measured value to a time period that is roughly four powers of ten longer is, however, unrealistic. The possibilities of obtaining experimental measured values of pitting on copper base material for periods of at least 1 000 years, or on that order of magnitude, have therefore been discussed.

One such possibility is to study how corrosion has developed on buried archaeological objects of sufficient age and with as high a copper content as possible as well as with relatively well-known conditions of burial. The commission from SKF/KBS has therefore included exploring what possibilities exist for the study of such material as regards its tendency towards pitting corrosion.

After a special cleaning procedure, the depth of the pits was measured within a number of representative surface domains on selected copper-base objects whose composition is known or has been determined and whose prehistory as regards archaeological residence environment is relatively well known. With knowledge of the age of the object and after estimating the general corrosion to which the object should have been subject during its burial, it has then been possible to calculate an approximate value of the objects pitting factor.

Literature search

The literature that was studied in connection with the investigation was collected in several different ways. Special literature on the handling and disposal of radioactive waste was furnished by the client, while another group of articles - dealing with pitting corrosion on copper-base material - was collected by a selective search of corrosion journals.

A search has also been carried out in the reference journal, Arts and archaeology technical abstracts, covering the past 10 years. Some 50 references to original articles were obtained in this literature search. However, these articles were only indirectly concerned with the task at hand, since they consisted for the most part of analytical and preservation-related investigations of copper-base objects. No articles were found that had a direct bearing on the problem at hand, aside from the special references mentioned above.

Archaeological material studied

The archaeological material was obtained from five different areas, see below, for the purpose of shedding light on the problem from as many angles as possible. To facilitate the reporting of data on the individual objects included in the study, they have been assigned an internal object number, KBS followed by a consecutive number. In cases where the object comes from the National Museums of Antiquity, its SHM number is also given.

Group A Here, some 50-odd bronze objects from the Swedish Bronze Age have been selected. The objects come from different sites in southern and central Sweden. A figure of 3000 years ± 300 years has been assumed as a realistic average value for period of burial. Primary archaeological data are presented in table 1, chemical analysis data in table 2.

Group B Five coins from Roman times. All objects were heavily corroded. Primary archaeological data in table 3. The places where the coins were struck were located around the Mediterranean coast, Italy and Greece. The time of striking can be roughly put at the last few centuries before the birth of Christ. The coins probably lay buried for 1000-1500 years, and the finds can be presumed to have been made during the 18th century. A chemical analysis of the coins is presented in table 4 (KBS 48-KBS 52).

Group C Three metal fragments from Roman vases, found on Gotland. The finds are described in detail (Lindeberg 1973), primary data in table 5. The environment during the period of burial of these objects has been in cremation graves with a filling of morain gravel, sometimes mixed with limy material. There was probably some aeration in the soil environment during the burial period. The age of the finds is from 50 B.C. to 350 A.D., permitting the period of burial to be approximated at 1800 years. Quantitative chemical analysis, KBS 53-KBS 55, is provided in table 4.

Group D Approximately 300 copper coins included in a wreck find from a ship that sank during the 17th century. The find was made in the 20th century, enabling the period of submersion to be set at about 300 years.

Find site in Östergötland, Gryt archipelago outside of Härad Island. The wreck lay in a depression between a shoal and a rocky knoll. The wreck was covered by a thin layer of mud, but many of the coins were visible at the start of the salvage operation. The water depth was about 20 metres. The coins consisted of so-called "round coins" of denominations öre, half öre and quarter öre, coining period 1627-1646. The average weight of one coin is about 40 grammes. According to a royal edict from 1634, coins of this type are to consist of pure copper. Although the coins have not been analysed, judging from their appearance, they probably consist of relatively pure copper.

Group E This group only includes one object. It is a small lump of copper, which is actually not an archaeological find, but has nevertheless been deemed to be of comparative value in this study. The object has been placed at our disposal by the client. Chemical analysis, see table 2, object KBS 48.

Previous pitting measurements

The technique that has been used in the pitting corrosion measurements referred to in KBS 1978 was as follows, see Romanoff 1957. After recovery of the soil-exposed specimens, they were cleaned mechanically and then pickled in a solution containing 5% nitric acid and 2.5% oxalic acid. The pickling time was generally five minutes. The depth of the pits in the surface of the specimen was then measured with a special micrometer gauge. Pits shallower than 0.15 mm were disregarded. The general corrosion of the specimen was then calculated from the weight measured before and after exposure.

No information is given on whether any inhibitor has been added to the pickling acid to prevent undesired dissolution of metal, nor on the design dimensions of the millimeter gauge that was used to permit calculation of the smallest diameter of a single measured pit.

Technique used in own pit measurements

We have used the following technique to study the depth of pits on selected archaeological objects.

A metal microscope is focused so that a sharp image is obtained of the area around the mouth of a pit. The focus is then moved to the bottom of the pit. The distance moved by the focal point will be a measure of the depth of the pit and can be stated in ordinary units of length measurement. Photographs of these different stages in the measurement procedure are given in figure 2.

In order for it to be possible to obtain a correct value with this technique, the bottom of the pit must clearly be optically denuded of corrosion products. In many cases, however, it is not known how well the pits in the object have been subjected to washing with various chemicals prior to the first pit measurement. It is therefore necessary to determine how well a pit can be regarded to have been denuded by means of different techniques. The following experiments have therfore been carried out.

A representative and flat area on the surface of an object - a domain - was masked off with wax so that a selected area of about 0.25 cm^2 was obtained. A small quantity of 6% EDTA solution (disodium salt of ethylenediaminetetraacetic acid with pH adjusted to 7.0) was added to the surface in a number of treatments. After each treatment, a number of pit depths were measured using the technique described above. In some cases, the wash liquid was exchanged for ammonia after several EDTA treatments. It can be estimated that each individual treatment lasted about 3 hours.

In some cases, the selected pit area with its liquid coating was then evacuated, after which normal atmospheric pressure was once again applied to the specimen. The purpose of this technique is to get the wash liquid to penetrate through the porous layers of corrosion products, which previously contained air but are now evacuated, so that the liquid can exert its dissolving effect all the way down to the bottom of the pit.

It is impossible to perform all measurements on one and the same pit with this procedure. Instead, a number of pits within a selected domain were measured after the repeated treatments. A mean value, standard deviation and median value were then calculated from the measurement results. Furthermore, pit frequency and mean pit diameter were estimated. The results are given in table 7 and figure 3.

The following is found: Washing with EDTA plus NH_3 appears to give satisfactory denuding of the pits, possibily in combination with the evacuation technique described above. Furthermore, there does not appear to be any appreciable difference between the mean value and the median value.

Estimating general corrosion

Besides the pit depth, it is also necessary to know the general corrosion rate in order to calculate the pitting factor. It has not been possible to perform direct measurements on the individual objects, except possibly in one case, but it is possible to obtain some idea of this quantity by means of an indirect method.

First, a description of the direct measurement that has been made. Object KBS 43, a fragment of bronze fibula, is richly ornamented, where the individual engravings in the metal surface are projected very distinctly in the surfaces of the corrosion layer. This continuous corrosion layer, which adheres directly to the metal surface, consists here (as in many studied cases) of red, hard cuprous oxide. Measuring the thickness of this layer and converting the results to equivalent quantity of copper gives an estimated general corrosion of about 0.3 mm per 3000 years. See figure 4 for a photograph of the fibula.

This is obviously a minimum value, since the possibility cannot be ruled out that certain quantities of corrosion products have been removed from the surface of the object by different means, either during the period of exposure or in connection with cleaning of the object.

Some notion of the intensity of general corrosion on archaeological artifacts containing copper is reported (Johnson and Francis, 1980, chapter 3: Estimates of corrosion rates on archaeological artifacts). Here, roughly 40 objects from all over the world and with burial periods of between 300 and 8 000 years have been studied. Approximate minimum and maximum corrosion rates have been estimated. A selection of data from this table with relevance to the problem at hand gives a value (naturally highly uncertain) for general corrosion of about 0.5-1 mm per 3 000 years.

A very roughly estimated value of the general corrosion rate for buried copper-base material would therefore lie somewhere around 0.2 mm per 1 000 years.

Results from own pitting corrosion measurements

With the cleaning and measuring techniques described above, measurement data have been obtained on pit depth, pit frequency and mean diameter of the pits from a number of archaeological Bronze-Age objects.

The results for objects included in Group A are presented in table 8. This table gives reason for the following comments. The distribution of pits over the surface appears to be rather even, the basic frequency lies within the range 1-10 pits per 0.25 cm^2. Similarly, variations in mean diameter are not particularly great, with a concentration around 0.4 mm. As far as maximum pitting is concerned, there are a few values above 1 mm, while most fall within the interval 0.1-0.6 mm.

The pitting factor (P) can now be calculated. Based on the value for the mean corrosion rate assumed above (0.2 mm per 1 000 years, or 0.6 mm per 3 000 years), we obtain:

$$P = \frac{\text{measured pit depth + general corrosion}}{\text{general corrosion}} = \frac{0.6 + 0.6}{0.6} = 2.0$$

A similar calculation for the deepest pits (KBS 32 and KBS 37) gives P values of 2.7-3.1.

The results from pitting corrosion measurements of the Group B objects are given in table 9. The following results are obtained:

If the fake (modern) coin KBS 48 is excluded, the pit frequency is moderate, on the same order as that measured for the Group A objects. It has not been possible to obtain any value for the pitting factor, but there is no reason to believe that it reaches any high values. It can be estimated to be of the same order of magnitude as has been measured for Group A.

The Group C data from pit measurement are presented in table 10. The same conclusions can be drawn here as for objects from Group B here above.

No direct measurements have been made on objects from Group D, only microscopic studies of the coins (cleaned previously, but in another context). As a final result of the studies of some 30 coins, randomly selected from the collection, it was found that no pronounced pitting corrosion could be observed, only widespread general corrosion.

Group E. This group includes only one specimen, a small lump of native copper, KBS 48. Its weight is 37 grammes and the specimen has been sawn out of a larger piece, see figure No. 5. Two of the sides of the specimen are covered by green corrosion products. Analysis of the specimen (see table 2) shows that its copper content is 98% and that it contains only insignificant amounts of metallic impurities.

The specimen comes from an area near Lake Michigan in the USA, where large quantities of pure native copper have been mined up to 1960. A large number of copper masses, weighing from a few grammes up to more than 8 tonnes, have been transported long distances within this area in connection with different glacial periods. The following is said about a copper specimen similar to the one examined here (Johnson and Francis 1980, paraphrase): "Masses of this kind appear to have been transported from the primary copper deposits in Upper Michigan by the Pleistocene glaciers. The glacial period extended from 2-1/2 million years ago to the most recent incursion which began about 20 000 years ago and receded 8 000-11 000 years ago. Copper masses of this kind are often found embedded in glacial outwash consisting of sand and gravel. The specimen in question was buried about 0.6 m, annual moisture fall in the area is about 1 000 mm with a pH controlled mainly by carbon dioxide of about 8.5 units. The annual mean temperature in the area is 7°C."

The lump in question was pickled in a solution consisting of 5% sulphuric acid containing 5% EDTA salt. The customary pitting corrosion measurements were then carried out on the denuded surfaces. The results from a number of measured pits were as follows.

Number of measured pits	Mean pit depth, mm	Maximum pit depth, mm	Pit frequency, number per 0.25 cm^2	Mean diameter of pits, mm
18	0.06	0.35	>10	approx. 1

It has not been possible to obtain a value for mean corrosion, but the following is said about the comparable specimen from the reference cited above. The thickness of the adhering layer of copper oxide can be estimated at between 0.15 and 0.6 mm and would seem to have developed during a period of 8 000 years. From these values emerge a minimum value of the general corrosion rate of 0.08-0.30 mm per 8 000 years.

It is naturally risky to calculate a value of the pitting factor on the basis of these values, but if this is nevertheless done, a value of P is obtained from the data given above of between 2 and 6 units for the copper lump in question.

Chemical analysis

In order to obtain an idea of which elements should be included in the quantitative chemical analysis of all the objects studied, a number of these objects have been analyzed by means of X-ray fluorescence. No more advanced attempt has been made to quantify the signals from the indicated elements beyond a semiquantitative estimate based on the intensity of the signals. Table II presents the results of this evaluation. Copper has been left out here, since this element is the base metal in all specimens.

The quantitative analysis of all studied objects was performed by Analytica AB, Sollentuna, Sweden, see table 2. The principal method used was atomic absorption spectrophotometry.

The results of the analyses give cause for the following comments:

The X-ray examination provides some picture of the composition of the specimen. The sensitivity of the method for the different elements varies widely, however, and certain elements can sometimes evade detection. See, for example, specimen No. KBS 27, with the highest zinc content according to the atomic absorption analysis, but where the X-ray analysis has not detected any zinc content. Similarly, arsenic has evaded detection by means of the X-ray technique, despite relatively high concentrations in certain specimens, e.g. KBS 4.

The specimens can be characterized as bronzes with a tin content of around 10% and with smaller quantities of other metallic components as impurities. Since the sum of analyzed elements is less than 100%, other elements than those directly determined are also present. The X-ray analyses give here an indication that these other elements may include certain quantities of aluminium and silicon, presumably as oxides.

In some cases, two independent specimens taken from the same object have been analyzed, see KBS 10, KBS 23, KBS 26a and KBS 27. A detailed study of these analysis values shows - as expected - that the specimens possess some non-homogeneity with respect to their metal composition.

Furthermore, the chemical analysis has been extended to a study of how the balance between some components in the metal is reflected in corrosion products formed on the surface of the metal in the following manner.

Specimens of corrosion products from four objects from Group A were studied. The results are presented in table 6, from which the following information can be extracted.

The analyzed objects can be characterized as bronzes with small quantities of metallic and non-metallic impurities. Among the impurities, arsenic and nickel were chosen for comparative study. By and large, these elements are found in the same proportions in both the object and the corrosion product. The situation is another one with respect to the main components, copper and tin. A marked increase of the Sn/Cu ratio in the corrosion product in relation to the same metal ratio in the metal object is clearly demonstrable in three of the four studied objects. In the fourth object, however, the ratio is virtually the same. The most probable explanation for this enrichment of tin in the corrosion product is that copper-base corrosion products have been leached out of the total corrosion product mass.

Corrosion pits and other pits

A corrosion pit is a defect in the outer layer of the metal. The pit is formed as the result of a chemical process between the metal object and certain components in the environment in which the object has landed after its period of use. A corrosion pit is characterized by the fact that when the pit has reached a steady state, its growth rate is more rapid in a direction perpendicular to the metal surface than parallel with it. A true corrosion pit will therefore assume a more or less cylindrical shape, reminiscent of a drilled hole in the surface layer of the metal.

Another form of metal defect is the gas bubbles that can form in the metal when it solidifies from a molten condition. This occurs because many metals and alloys can keep certain gases dissolved in the molten state, but these gases are then liberate and separated from the homogeneous metal at the instant of solidification. A practical example of this phenomenon is what happens when ordinary water freezes to ice. The air that was previously dissolved in the water is liberated at the instant the ice is formed, but remains in the ice in the form of small gas bubbles. These gas bubbles give the ice a milky, opaque appearance.

Apparently, both corrosion pits and the superficial gas bubbles will be recorded by the technique described above for measurement of corrosion pit depth on metal surfaces. Since the present study is primarily concerned with only one of these two types of pits, namely the pits formed by corrosion processes, it is important to know how large a portion of the measured pits belong to one category or the other.

There is one speculative possibility for such a classification. In a piece of cast metal that has not been subjected to any extensive mechanical deformation after being cast, any entrained gas bubbles will remain intact. If, however, the piece of cast metal is subjected to forging, cold hammering or other more severe mechanical working, the gas bubbles in the metal will be flattened and completely or partially eradicated. A comparison between the pitting frequency on forged and unforged cast metal objects should provide some indication of the proportion between the two kinds of pits, since the pits in the forged pieces should primarily be of the corrosion pit type.

The objects in Group A offer a possibility for being divided into one group with only cast and another group with only forged objects. The socketed axes included among the studied objects in Group A have probably not been subjected to any extensive working after having been cast. They can therefore be regarded as representing only cast objects. The razors, on the other hand, bear clear signs that show that the metal workpiece has been subjected to deformation working. They can therefore be regarded as representing forged objects in this study. Measurement data for these two different groups are presented in table 13. The following comments can be made on the tabulated data.

A comparison between cast and forged objects shows that no significant difference exists between them as far as maximum pit depth and mean pit diameter are concerned. This applies especially to objects within the two frequency groups 1-10 and >10 pits per surface area studied. If we go to the frequency group <1 pit per unit area, the results are more difficult to interpret. However, the possibility cannot be ruled out that the two objects included here as representatives of cast objects may possibly belong to a third group of metal objects, namely those with casting defects, in which case they fall outside the scope of this study. The extremely high values of the mean diameter of the pit would seem to point towards this conclusion.

In summary, this study supports the contention that the pits observed on the objects in Group A primarily belong to the category of pits formed by corrosion processes.

Discussion of results

The measurement data presented here, both from the optical pit measurement and from the chemical analysis, naturally possess a relatively high level of uncertainty. The studied material is non-homogeneous, the sample quantities taken for chemical analysis have not been allowed to exceed a few milligrammes per specimen and the data available for calculating pit depth and general corrosion are scanty. Nevertheless, the observations made fall into a certain pattern that provides a basis for assessing the risk of tendencies towards abnormally high values of the pitting factor in material of the type studied here.

No all-encompassing and widely accepted theory of the origin and maintenance of corrosion pits in copper-base material appears to exist, see e.g. R. May 1953 and E. Mattson 1977 in the list of references, which also includes a number of other articles related to this phenomenon. Certain uncontested facts do exist, however: pitting corrosion is an electrochemical process where the bottom of the pit acts as the anode while its upper parts, the mouth and the surrounding metal, constitute the cathode. In other words: pitting corrosion should be favoured by a low surface frequency of pits, since a large number of pits in a metal surface entails competition for the cathode surfaces, which does not favour the formation of particularly deep pits. And conversely: a high pit frequency should be coupled with low values of pit depth, cf. fig. 6.

This can be studied with the aid of experimental material from Group A and Group E. Values for mean pit depth, maximum pit depth and mean pit diameter for objects from Group A are presented in table 12, together with data from the object from Group E for comparison.

Table 12 furnishes the following information: in the case of objects from Group A, a higher surface frequency of corrosion pits results in a lower maximum pit depth. The mean depth of all pits, measured within a selected area, shows the same tendency. The mean diameter of the pits also decreases as the pit frequency increases. Thus, these measurement data confirm the above assumption.

This can now be compared with corresponding data on the native copper lump in Group E. The pit frequency on this object is large. If the measured pit data for the native copper lump are now compared with the corresponding data for the objects from Group A taken from the fraction with the highest pit frequency, the agreement is found to be very good. In other words, there is support for the contention that pure copper material, such as the native copper in Group E, is comparable with respect to pitting with the copper-base objects examined in detail in the study presented above.

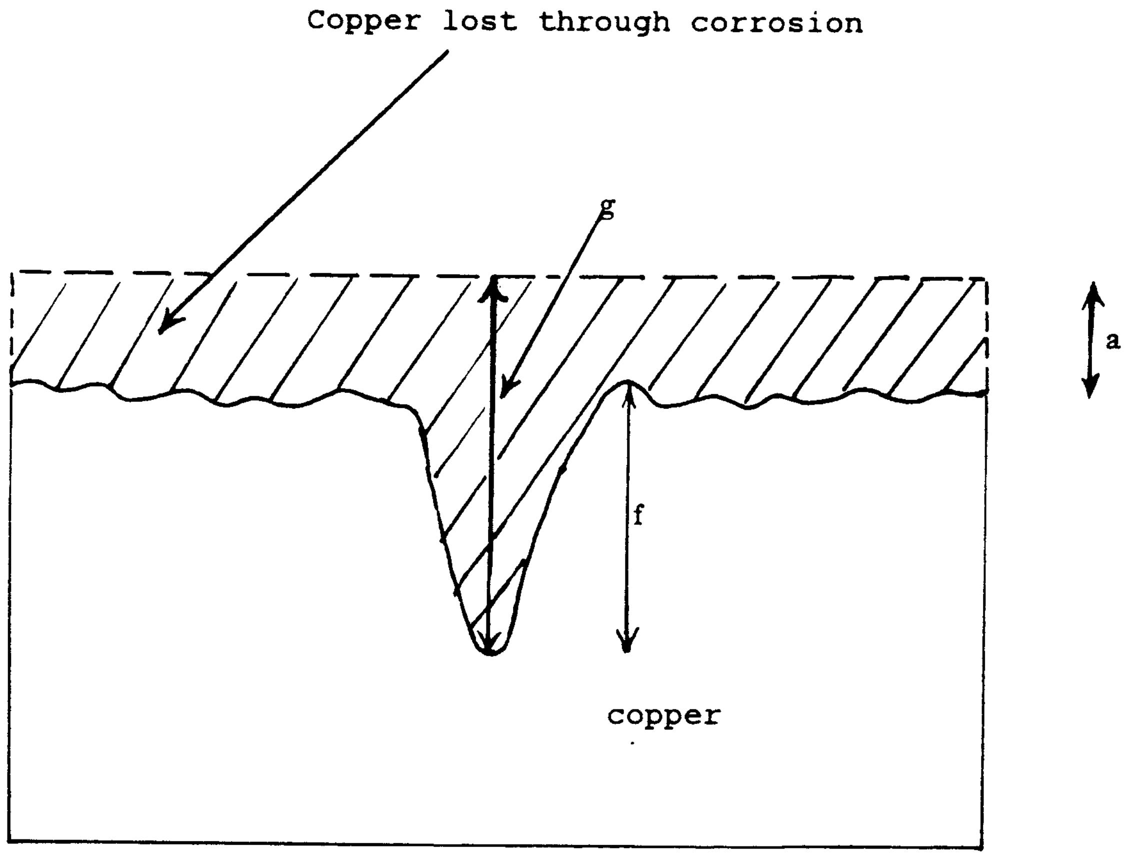
The absolute values of the pitting factor obtained in this study are generally very low. In the case of the most thoroughly studied material - Group A - the pitting factor is only slightly more than three units. Nor does the native copper, with a presumed burial period of about 8 000 years, exhibit particularly high values. The figure of P = 6 for the pitting factor appears to be an upper limit here. In summary, it can therefore be concluded that the present study does not provide support for the assumption of extremely high pitting factors in copper-base material that has been buried for periods of several millenia.

Åke Bresle
2 January 1983

List of references

Arts and archaeology	1973-1981	Arts and archaeology technical abstracts. New York.
Brown, B F (ed)	1977	Corrosion and Metal Artifacts A Dialogue between conservators and archaeologists and corrosion scientists. NBS Special Publication 479. US Department of Commerce.
Denison, I A and Romanoff, M	1950	Soil-Corrosion Studies 1946 and 1948: Copper Alloys, Lead and Zinc. US Department of Commerce. Research Paper RP 2077, March 1950.
Johnson Jr, A B and Francis, B	1980	Durability of metals from archaeological objects. Battelle Pacific Northwest Lab. Report PNL-3198 USA 1980.
KBS	1978	KBS Technical report No 90 March 1978.
Lindeberg, I	1973	Die Einfuhr römischer Bronzegefässe nach Gotland. Saalburg-Jahrbuch XXX-1973, Berlin.
Lucey, V F	1972	Developments leading to the present understanding of the mechanism of pitting corrosion of copper. Brit. Corrosion Journal. Vol. 7, 1972, pp 185-191.
Lucey, V F	1975	Lochkorrosion von Kupfer in Trinkwasser. Werkstoffe und Korrosion, Vol. 26, Heft 3/1975, pp 185-191.
Mattsson, E and Fredriksson, A M	1968	Pitting corrosion in copper tubes - Cause of corrosion and counter-measures. Brit. Corrosion Journal, Vol. 3, pp 246-257, 1968.

Mattsson, E	1977	Localised corrosion. 6th European Congress on Metallic Corrosion (Eurocorr.), 19-23 Sept, 1977, pp 219-237.
Mattsson, E	1981	Canister materials proposed. KBS Technical Report No. 81-05.
May, R	1954	Some observations on the mechanism of pitting corrosion. Journal of the Institute of Metals, Vol. 32, 1953-1954, pp 65-74.
Romanoff, M	1957	Underground Corrosion. National Bureau of Standards, Circular 579, April 1957.



Depth of corrosion pit = g mm

General corrosion = a mm

Measured depth of corrosion pit = f mm

Pitting factor = P

$$P = \frac{g}{a} = \frac{f+a}{a} = \frac{f}{a} + 1 \approx \frac{f}{a}$$

Fig. 1. Pitting factor on corroded copper.

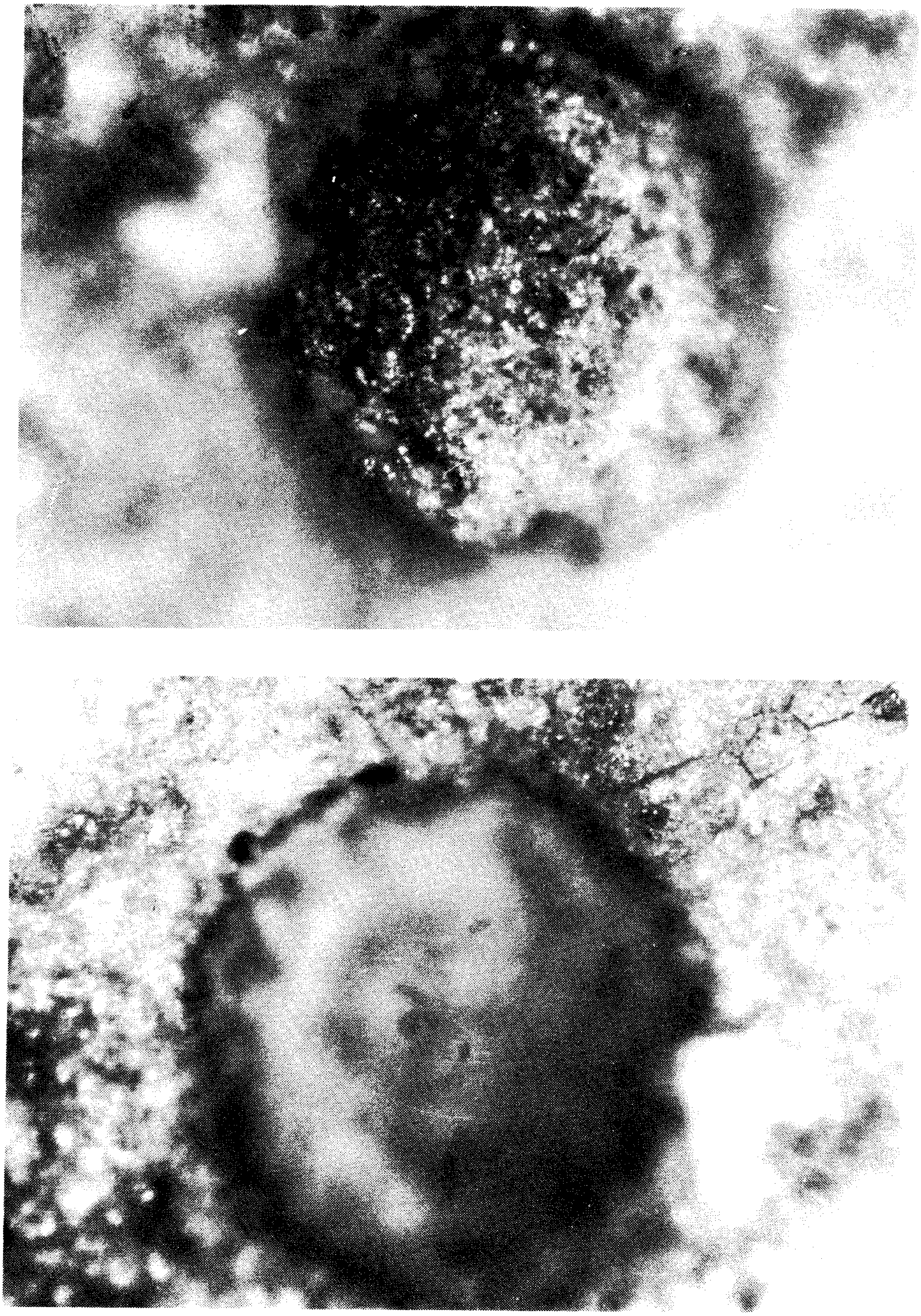


Fig. 2. Photos of corrosion pit with focus at bottom of pit (top) and at mouth of pit. Magnification 350 x.

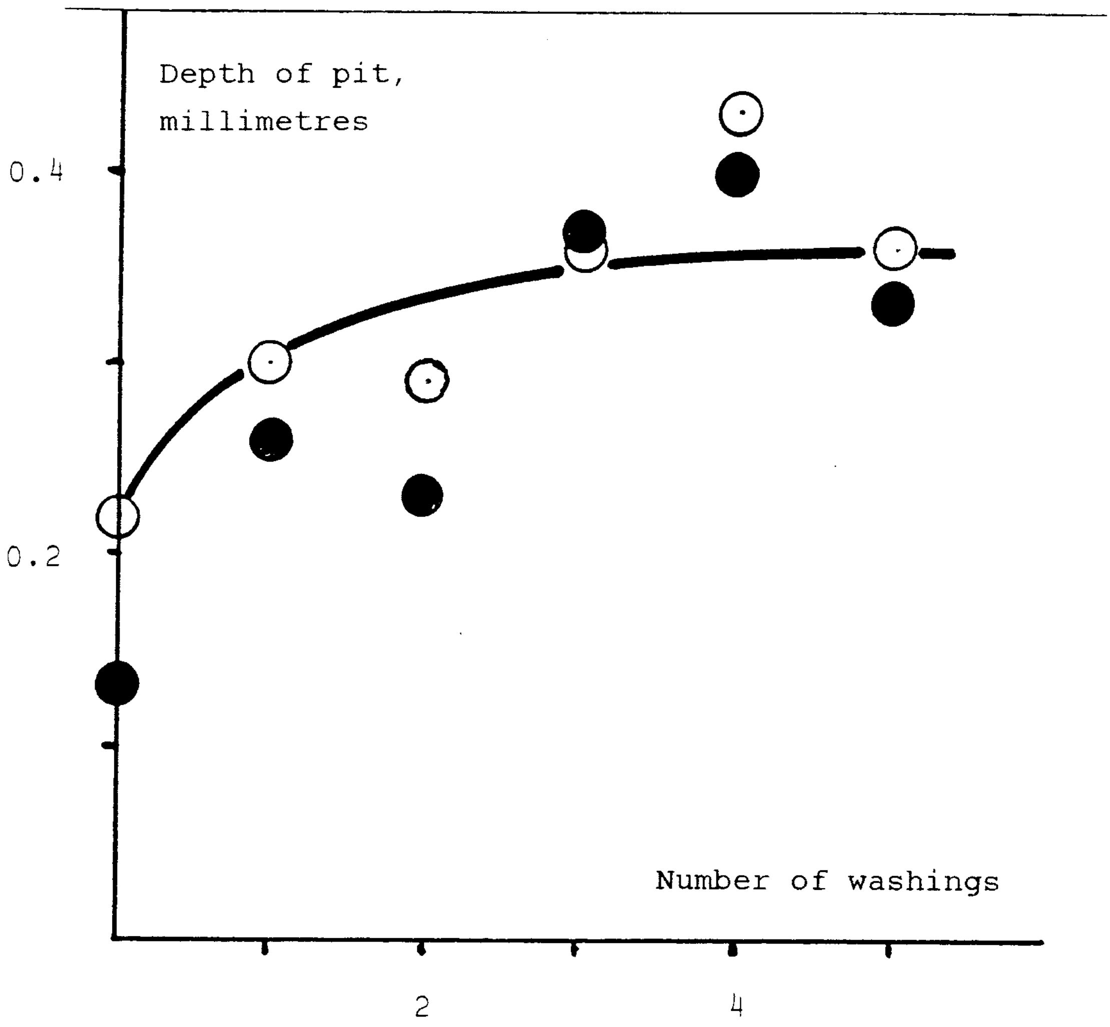
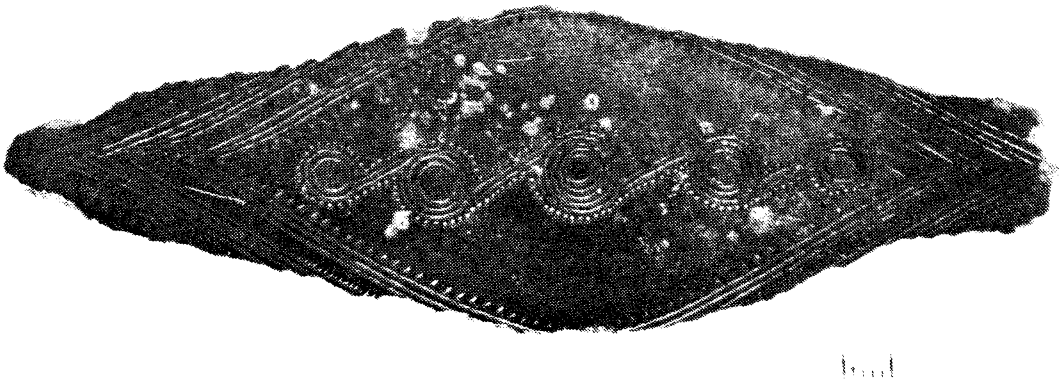


Figure 3. Effectiveness of chemical treatment in cleaning of corrosion pits on KBS 25. ○ = mean value, ● = median value.

Fig. 4 Photos of ornamentation on Bronze-Age fibula, KBS 43.

Below in slightly more natural size. At left, magnification 20 x.



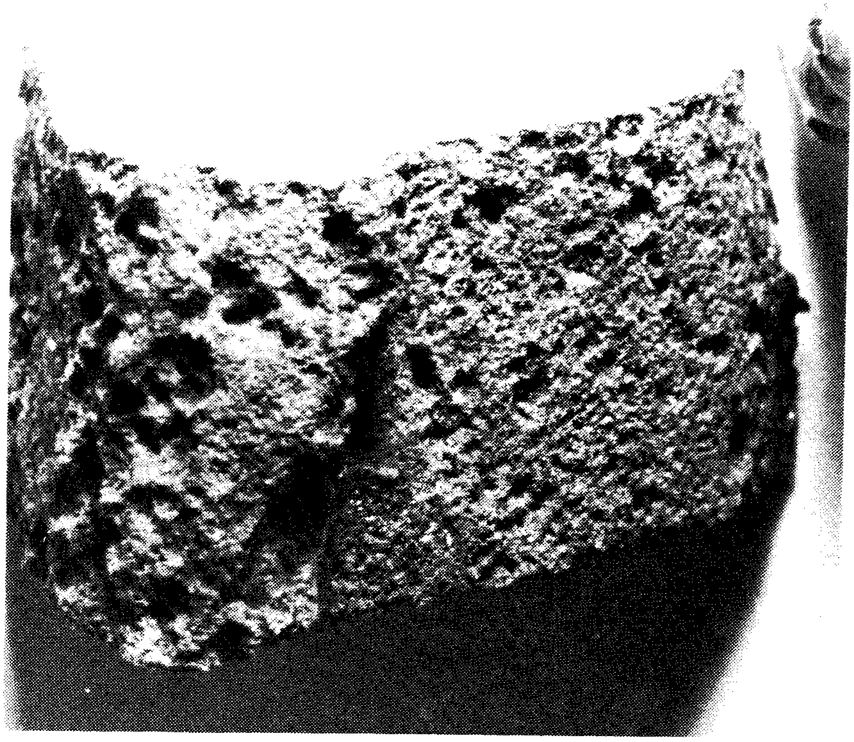


Fig. 5. Photo of the native copper lump KBS 48, magnification 4.5 x.

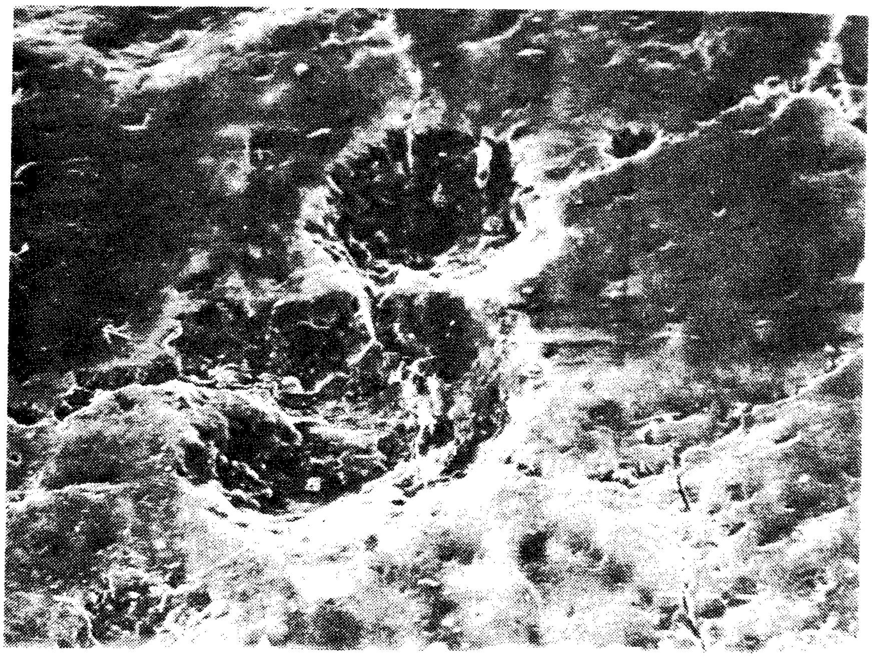


Fig. 6. Corrosion pits from a razor from the Bronze Age, photographed through a SEM-microscope. Magnification about 300 x.

Pitting corrosion on archaeological bronzes - an archaeological comment

By Jozef Saers.

The objects that have been studied for the purpose of this report and which belong to the Bronze Age can all be dated as at least probably belonging to one of the six periods of the Bronze Age. Schematically, these periods span 200 years each, with the Bronze Age beginning in about 1600 B.C. and ending at the beginning of the Iron Age in 400 B.C. When the material is arranged in this fashion, it is possible to see the difference between the early and late Bronze Age in an interesting manner.

During the early Bronze Age, the rest of Europe was also completely dependent on bronze, switching to iron for their implements during the course of the late Bronze Age. In Scandinavia, however, bronze continued to be used for this purpose.

In the analyses of table 2 presented in table 13, it can be seen that the arsenic content of bronze steadily declines during the early Bronze Age, while it is highly variable during the late Bronze Age, as if old bronze had been remelted. The slightly lower tin contents of bronze during the late Bronze Age also indicate this, and in addition show large variations during period V. The remelting of scrap bronze is not the only explanation, however. It is also reasonable to postulate a change in metallurgical knowledge and in ores available. The iron content of bronze is consistently lower during the late Bronze Age, whereas vismuth increases while lead shows a tendency to cluster around two peaks, one at levels around 0.1% and one at levels of more than 1%. Silver shows an analogous evolution, with low levels during periods II-III, higher levels during period IV, and during period V high levels separated from a cluster of levels as low as during the early Bronze Age. Finally, in period VI, these two groups blend into an intermediate group. The middle Bronze Age exhibits the highest zinc contents in this material, while only contents below 0.01% are found in periods I and VI. In this respect, the most recent Bronze Age differs from what is later found during the first two centuries of the early Roman Iron Age, when zinc contents of around 10% are found in Sweden, Poland and the Roman Empire (Saers 1982, p. 60). A general review of the alloys is provided in Oldeberg (1976, p. 47 ff.). The Swedish bronzes follow the same trend as the European bronzes during the early Bronze Age, with the exception of Greece, judging from data presented in SAM 2.2, table 11.

By chance, three previously analyzed bronzes were included among the bronzes subjected to analysis this time. They are published in Oldeberg (Oldeberg 1976, p. 122). There, KBS Nos. 4, 4y and 32 have been given analysis numbers 109, 72 and 56, respectively. These analyses previously performed by AB Analytica agree with those done now insofar as the contents for the different elements all fall into the same or immediately adjacent groups in the grouping used above. In KBS 4 and 4y, however, silver, tin, arsenic and iron deviate more, probably due to in -homogeneities in the material. They belong to the oldest bronzes and can be regarded as examples of the difficulties encountered by the first bronze craftsmen.

If the material is broken down according to context of find, i.e. the environment in which they were preserved, an indication is obtained that pitting corrosion is least when the objects are allowed to lie in a stone cist protected by an earth barrow, i.e. like in a small cellar, before the earth has seeped into the cist. They are less protected in a cairn, where they are exposed to air and all the forces of the weather in the form of rain and frost. The bronzes exposed to the greatest damage are those placed in an urn and buried a decimete or two down in the soil. The tendency that points towards this conclusion is weak and can best be seen in the value of the deepest pit (G) in table 8, compilation in table 13, and of the standard deviation (s).

If the time factor is also taken into account, the mean diameter of measured pits shows a consistent tendency towards being larger the older the material is. This tendency seems to be relatively independent of the preservation environment. This provides a reminder of how complex the phenomenon of corrosion is. Unfortunately, the material is too small to permit any further conclusions to be drawn, for example how the composition of the alloy has influenced corrosion.

Addendum

While the text was being translated it was discovered that bronzes with a larger silvercontent, i.e. over 0.05% and with a lower nickelcontent, i.e. below 0.30% were the least corroded, independent of their belonging to the early or the late bronze age.

References

Oldeberg, A	1976	Die ältere Metallzeit in Schweden II. Stockholm.

Saers, J	1982	Statistische Auswertung der Analysergebnisse, in Blumbergs, Z: Bronzebuckelchen als Trachtzier, Thesis and Papers in North-European Archaeology 12, Stockholm
SAM 2, Junghaus, S Sangmeister, E und Schröder, M	1968	Kupfer und Bronze in der frühen Metallzeit Europas. Berlin.

Table 1. Primary archaeological data for objects from Group A

KBS No.	SHM No.			Object	Circumstances of find	Period
1				razor	stray find	V
2				razor	stray find	V
3	1374 :4	Sk	Sjörup parish, Vallöse	socketed axe	stray find	IV
4	2548	Sk	between Skegrie and Tomarp parishes	2 flanged axes, 1 chisel	hoard, found under large stone	I
5	2791 :330	Sk	Eastern Nöbbelöv parish, Gislöv (Lundh collection)	razor	from gravel pit	II
6	5990	Sk	Nöbbelöv parish, Simris	belt box	stray find	II
7	3765	Sk	Solberga parish, Torsjö	socketed axe	stray find	II
8	6150 d	Sk	Simris parish, Simris village	razor, fragment	in a barrow	V
9	8755	Sk	Stoby parish	razor	loose find	V
10	8762 :14	Sk	near Simrishamn	razor, fragment	loose find	II
11	8762 :48	Sk	near Simrishamn	part of sword	stray find	V
12	9822 :742	Sk	Smedstorp parish	socketed axe	stray find	IV
13	11094	Sk	Rörum parish	socketed axe	stray find	V
14	11974 :6	Sk	district of Simrishamn	razor	in a stone cist	III
15	17890 :7	Sk	Skivarp parish, Varbacka	scythe	in clay jar in cemetery at gravel pit	VI
16	17890 :12	Sk	Skivarp parish, Varbacka	razor	in stone cist in cemetery at gravel pit	VI
17	21266	Sk	Skivarp Öremölla 16	razor	in clay jar in cemetery at gravel pit	V
18	6969 :3	Sk	Hofterup parish	flanged axe	in waterlogged and stony soil	II
19	7532 :77	Bo	Tossene parish, stora Gistad soldier's cottage	knife	stray find	IV
20	28871:216	Up	Järfälla parish, Veddesta 2:1 ancient monument, reg nr 216,F3	neck ring	in cairn with earth fill	VI
21	7775	Ög	Norrköping, Vikbolandet	socketed axe	stray find	V
22	7870:127,128	Vg	Berg parish	razors	stray find	IV
23	2471	Ha	Ljungby parish, Höstena	razor	in a stone cist in a barrow	V

24	4840:2	Vg	Friggeråker parish, No.26, Bissgården	razor	in cist in cairn	V
25	9170:1233	Up	Skogs-Tibble parish	socketed axe	in a pasture	V
26	22775	Vm	Västerås, Tunbyvägen 74	3 saw blades	among fire-cracked stones on a hill	II
27	2918	Sk	Glumslöv (A.Bruzelius collection)	sword	from gravel pit	III
28	15078:4	Sm	Barkaryd parish, Hafrida	rapier	at bottom of cairn	II
29	8923 B	Sm	Gårdby parish, Hultet	rapier	in stone cist in cairn	III
30	8923 B	Sm	Gårdby parish, Hultet	razor, 2 parts	in stone cist in cairn	III
31	9410:17	Sm	Öjaby parish, Lunnaby	spear	in stone cist in cairn	III
32	17343:144f	Ög	Kvarsebo parish, Östanå	flanged axe	stray find	I
33	5560:60	Ög	Rök parish, Eveboda	rapier	in barrow	II
34	14736	Ög	Skeppsås parish, Alnäs Västergård	awl	in stone cist in cairn	II
35	25389:34	Up	Bälinge parish, Högsta	razor	in round stone barrow on a ridge	III
36	9716	Up	Knutby parish, Kumla	socketed axe	stray find	VI
37	15787:9	Sö	Frustuna parish, Hållsta	socketed axe	stray find	V
38	26138	Sö	Grödinge parish, Sibble 2:3	scythe	north of burial mound	II
39	7591:19	Vg	Gökhem parish	sword	in cairn	III
40	7216	Vg	Varnhems parish, Ryttargården	spear	purchased, probably grave find	II
41	4125	Sk	Österlöv parish	razor	in clay pot in barrow	V
42	28516:14 62	Go	Lärbro parish, St. Vickers 1:77	fibula	in cist in cairn	IV
43	16149	Go	Västkinde parish, Gjellings	fibula	hoard under a flat stone in a field	III
44	7331:538	Ha	Abbilds parish, Hjuleberg	part of knife	stray find	III
45	18965:1	Ha	Eftra parish, Skällentorp 8:9	razor	in clay jar in cemetery	IV
46	8344:b	Ha	Eldsberga parish, Flädje	razor	in cist in barrow	IV
47	2598		Denmark	knife	stray find	III

Table 2. Chemical analysis data for objects from Group A and Group E

ANALYTICA AB

ANALYSINTYG

KBS
REG. NR 14.573
BESV. DEN
ANK. 28 MAJ 1982
HANDL. LW
DELG. H Brene
BRAGA

Client Svensk Kärnbränsleförsörjning AB
Att: Lars Weerme
Box 5864
102 48 STOCKHOLM

Object

Certificate No. 82-28550 Date 1982-05-26

Sample dark

Metal assays of archaeological specimens.

		% Cu	% Sn	% As	% Ni	% Fe	% Pb	% Ag	% Zn	% Bi
KBS	1	86	9.9	0.07	0.21	0.03	0.07	0.01	<0.01	<0.01
	2	85	6.6	0.34	0.55	0.02	1.7	0.37	<0.01	<0.01
	4	80	10	2.4	0.22	0.04	0.05	0.73	<0.01	0.05
	4(y)	84	8.1	3.0	1.9	0.02	0.10	0.21	<0.01	<0.01
	4(M	86	8.9	0.18	0.12	0.18	<0.05	0.03	<0.01	<0.01
	6	82	9.5	0.19	0.26	0.05	0.09	0.02	<0.01	<0.01
	8	88	0.8	0.70	1.5	0.01	0.29	0.43	0.02	<0.01
	10 I	81	11	0.25	0.52	0.10	0.12	0.02	<0.01	<0.01
	10 II	74	9.3	0.26	0.43	0.10	0.12	0.02	<0.01	<0.01
	11	59	8.0	0.29	0.27	0.02	0.18	0.03	0.01	<0.01
	15	85	4.5	0.29	0.36	0.04	1.4	0.39	<0.01	0.02
	16	85	4.5	0.47	0.32	0.02	2.4	0.10	<0.01	0.06
	17	86	12	0.08	0.23	0.02	<0.05	0.03	<0.01	<0.01
	18	77	12	0.14	0.31	0.03	<0.05	0.01	<0.01	<0.01
	19	89	9.5	0.28	0.32	0.04	0.38	0.11	<0.01	<0.01
	20	81	15	0.03	0.07	0.03	<0.05	0.04	<0.01	<0.01
	21	87	1.8	0.52	0.47	0.02	1.1	0.37	<0.01	<0.01
	22	85	5.4	0.60	0.42	0.01	0.22	0.34	<0.01	0.02
	23 I	83	6.3	0.13	0.21	0.02	<0.05	0.03	<0.01	<0.01
	23 II	89	4.7	0.09	0.20	0.01	<0.05	0.03	<0.01	<0.01
	24	92	2.8	0.33	0.41	0.01	1.1	0.28	<0.01	<0.01
	25	81	4.3	0.90	0.37	0.03	0.22	0.47	0.02	0.02
	26aI	85	9.2	0.33	0.49	0.05	<0.05	0.03	<0.01	<0.01
	26aII	86	10	0.32	0.48	0.06	0.06	0.02	0.01	<0.01
	26b	88	8.6	0.23	0.44	0.05	0.13	0.04	<0.01	<0.01
	26c	82	11	0.28	0.48	0.05	<0.05	0.02	<0.01	<0.01
	27 I	77	9.6	0.02	0.03	0.14	0.42	0.06	0.08	<0.01
	27 II	78	10	0.03	0.03	0.28	0.41	0.05	0.05	<0.01
	28	78	10	0.12	0.23	0.04	0.26	0.03	0.01	<0.01
	29	83	12	0.20	0.44	0.26	0.16	0.02	0.01	<0.01
	30	81	11	0.23	0.54	0.07	0.09	0.02	0.01	<0.01
	31	84	8.7	0.13	0.32	0.09	0.11	0.02	0.03	<0.01
	32	79	9.4	0.23	0.23	0.10	<0.05	0.01	<0.01	<0.01
	33	83	12	0.15	0.24	0.01	0.17	0.02	<0.01	<0.01
	34	82	9.2	0.68	0.54	0.05	<0.05	0.01	<0.01	<0.01
	35	82	10	0.18	0.41	0.01	0.09	0.02	<0.01	<0.01
	36	84	6.3	0.20	0.27	0.79	0.37	0.19	<0.01	<0.01
	37	80	9.0	0.10	0.24	0.19	<0.05	0.02	<0.01	<0.01
	38a	82	11	0.17	0.48	0.20	0.13	0.02	0.03	<0.01
	38b	86	9.3	0.20	0.50	0.04	0.10	0.03	0.04	<0.01
	39	83	13	0.24	0.49	0.39	0.10	0.01	0.02	<0.01
	40	83	12	0.08	0.11	0.16	<0.05	<0.01	<0.01	<0.01
	41	92	2.8	0.64	0.44	0.01	0.10	0.44	<0.01	0.01
	42	89	5.1	0.91	0.53	0.01	0.08	0.31	0.04	<0.01
	43	83	10	0.08	0.36	0.01	0.09	0.03	0.02	<0.01
	44	82	9.5	0.14	0.26	0.04	0.14	0.02	0.01	<0.01
	45	89	3.4	0.77	0.41	0.03	0.15	0.33	0.03	0.02
	46	84	5.7	0.69	0.39	0.02	0.09	0.31	0.06	0.02
	47	80	13	0.16	0.28	0.06	0.27	0.04	0.03	<0.01
	48	98	<0.1	<0.01	<0.01	0.04	<0.05	<0.01	<0.01	<0.01

Approx. 5 mg of sample was dissolved in a mixture of 1 ml H_2O, 150 /ul of a solution containing fluoboric acid HBF_4, nitric acid HNO_3 and 1% tartaric acid $C_4H_6O_6$ in proportions of 1:2:1, plus 300 /ul HNO_3.[x)] The sample was then diluted to 25 ml. Arsenic and vismuth were analyzed by means of the hydride generation technique, other metals by means of atomic absorption spectrophotometry, flame method.

[x)] According to W.J. Price: Spectrochemical Analysis by Atomic Absorption, page 204.

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Table 3. Primary archaeological data for coin objects from Group B

KBS No.	Weight of coin after cleaning grammes	Diameter of coin, cm	Find data
48	7.8	2.9	Forgery, probably from 18th century
49	9.0	2.5	Tin-containing, Hadrian era, 1st century A.D.
50	4,9	1.9	Relatively pure copper, 200 A.D. In very poor condition
51	4.6	1.9	350 A.D.
52	9.7	2.4	200 B.C.

Table 4. Chemical analysis data for objects from Group B and Group C and corrosion products from Group A.

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ÅNGSVÄGEN 4 · BOX 3 191 21 SOLLENTUNA · SWEDEN

CERTIFICATE OF ANALYSIS

Client	Svensk Kärnbränsleförsörjning AB Att. Lars Weerme Box 5864 102 48 STOCKHOLM	Certificate No. 82-28639	Date 1982.06.09
Object			

Sample dark   Metal assays of archaeological specimens

		% Cu	% Sn	% Pb	% Fe	% Ag	% Ni	% As	% Zn	% Bi
KBS 48		99	<0.1	<0.05	0.18	0.01	0.25	<0.01	<0.01	<0.01
KBS 49		99	<0.1	0.36	0.02	0.03	<0.01	0.05	0.11	<0.01
KBS 50		88	1.3	2.7	0.01	1.4	0.06	0.05	0.03	<0.01
KBS 51		95	1.1	2.0	0.09	0.65	0.15	0.80	<0.01	0.09
KBS 52		84	8.9	0.09	0.06	0.03	0.07	0.46	0.06	<0.01
KBS 53		96	<0.1	0.07	0.27	0.01	0.01	0.22	0.03	<0.01
KBS 54		97	<0.1	0.01	0.06	0.06	<0.01	<0.01	0.02	<0.01
KBS 55		96	0.75	0.02	0.08	0.10	0.04	0.11	<0.01	<0.01
KBS 30	corr.prod.	7.5	30	0.21	0.43	0.06	0.14	0.28	<0.01	<0.01
KBS 35	-"-	16	19	0.25	0.24	0.06	0.27	0.20	<0.01	0.02
KBS 43	-"-	23	19	0.25	0.41	0.10	0.25	0.07	0.02	<0.01
KBS 46	-"-	36	3.4	<0.05	0.23	0.03	<0.01	0.84	<0.01	<0.01

ANALYTICA AB

M.Merseburg

KBS
REG. NR 14.573
BESV. DEN
ANK. 10 JUN 1982
HANDL.
DELG.
BILAGA

Table 5. Observations on metal fragments in Group C.

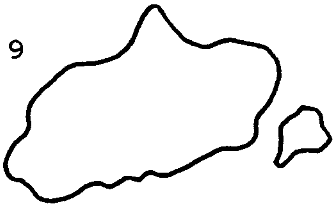
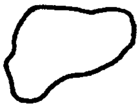
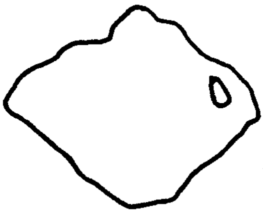
KBS No.	Find No. according to Lindeberg 1973	Weight, grammes	Appearance, scale 1:1.	Fragment's condition before chemical cleaning.
53	42	1.9		On one side a reddish brown coating, on the other side a black coating of corrosion products.
54	45	1.2		Reddish-brown-black coating on both sides.
55	7	2.7		Reddish-brown+black+light green coating of corrosion products. One through hole, metal thickness about 0.3 mm.

Table 6. Chemical analysis of some objects and their corrosion products from Group A

KBS No.	Appearance of corrosion product.	Percentage composition							
		Cu		Sn		As		Ni	
		Metal	Corr. prod.	Metal	Corr. prod.	Metal	Corr. prod.	Metal	Corr. prod.
30	green	81	8	11	30	0.2	0,3	0,5	0,1
35	greenish-brown	82	16	10	19	0,2	0,2	0.4	0,3
43	black-brown	83	23	10	19	0.1	0,1	0,4	0,3
46	porous, light green	84	36	6	3	0,7	0,8	0.4	0,0

Table 7. Importance of pretreatment for denuding of corrosion pits.

Pit depth is given in mm after the different washings. x = mean value, s = standard deviation, M = median value, n = number of measured pits, m = mean diameter of pits, F = pit frequency per 0.25 cm^2.

Object No. KBS		Untreated	EDTA	EDTA	EDTA+ NH_3	EDTA+ NH_3	EDTA+ NH_3+ evac.
25	$\bar{x}$	0,22	0,30	0,29	0,36	0,43	0,36
	s	0,23	0,21	0,17	0,15	0,24	0,14
	M	0,13	0,26	0,23	0,37	0,40	0,33
	n	26	19	22	25	21	34
	m	0,4					
	F	1-10					
21	$\bar{x}$	0,18			0,18	0,18	0.18
	s	0,05			0,04	0,06	0.04
	M	0,17			0,19	0,18	0,19
	n	12			12	20	17
	m	0,2					
	F	1-10					
10	$\bar{x}$	0,09	0,15				0,18
	s	0,04	0,04				0,04
	M	0,08	0,16				0,20
	n	10	10				17
	m	0,6					
	F	1-10					

Table 8. Pitting corrosion data for objects from Group A.

$\bar{x}$ = mean measured pit depth in millimetres
s = standard deviation, G = maximum pit depth in millimeters
F = pit frequency in number of pits per 0.25 cm^2,
m = mean diameter of measured pits in millimeters.

KBS No.	Domain 1					Domain 2				
	$\bar{x}$	s	G	F	m	$\bar{x}$	s	G	F	m
1	0,22	0,12	0,41	1-10	0,4	0.16	0,04	0,23	10	0,2
2	0,13	0,08	0,32	1-10	0,3					
3	0,14	0,09	0,26	1-10	0,4					
4	0,10	0,02	0,14	>10	0,6	0.10	0.03	0,19	1-10	0,5
5	0,19	0,12	0,38	1-10	0.4					
6	0,08	0,02	0,13	>10						
7	0,19	0,06	0,25	>10	0,4					
8										
9	0,08	0,01	0,09	1-10	0.4					
10	0,15	0,04	0,22	1-10	0,6					
11	0,20	0,03	0,25	10	0,6	0,21	0,03	0,26	10	0,6
12	0,21	0,06	0,29	1-10	0,4					
13	0,05	0,01	0,06	<1						
14	0,06	0,02	0,08	>10	0,4					
15										
16	0,07	0,01	0,28	1-10	0,3					
17										
18				<1	0,7					
19	0,30	0,14	0,60	1-10	0,3					
20				>10	0,7					
21	0,18	0,04	0,25	1-10	0,2					
22	0,30	0,11	0,57	1-10	0,3					
23	0,24	0,03	0,28	10	0,4	0,23	0,03	0,27	1-10	0,6
24	0,55	0,13	0,74	1-10	0,3					
25	0,36	0,17	0,88	1-10	0,3	0,34	0,10	0,56	1	0,2
26a	0,30	0,06	0,40	1-10	0,8	0,24	0,06	0,32	1-10	0,7
26b	0,20	0,04	0,26	1-10	0,6					
27	0,16	0,06	0,25	1-10	0,9	0,15	0.05	0,25	1-10	0,9
28				<1						
29	0,40	0,02	0,42	1	1,0	0,39	0,01	0,40	1-10	0,7
30	0,29	0.08	0,41	1-10	0,9					
31				<1						
32	0,87	0,27	1,24	<1	2,0					
33	0,33	0,09	0,57	1-10	0,9	0,46	0,23	0.96	1-10	1,0
34	0,22	0.06	0,37	1-10	0,8					
35				<1						
36										
37	0,85	0,20	1,05	<1	3,0					
38	0,55	0.05	0,61	<1	1,0					
39	0,62	0,04	0,68	1-10	0,9					
40	0,20	0,08	0,32	1-10	0,8					
41	0,48	0,10	0,63	1-10	0.5					
42	0,30	0,16	0,58	<1	0,3					
43	0,71	0,07	0,84	1-10	2.0					
44	0,48	0,12	0,60	1-10	1,1	0,23	0,04	0,30	1-10	1,0
45	0.18	0.06	0,26	1-10	0,5					
46	0,37	0,11	0,54	1-10	0,4					
47	0,28	0,05	0,33	1-10	0,7					

Table 9. Pitting data for objects from Group B.

KBS No.	$\bar{x}$	G	F	m	Notes
48	0,44	0,52	>10	0,8	Reddish-brown corrosion coating. Inscription corroded, but readable.
49	0,20	0,31	>10	0,5	Dark reddish-brown corrosion coating. Sponge-like surface with small pores, inscription barely legible.
50	0,10	0,12	1-10	0,5	Badly degraded. Small number of shallow pits.
51	-	-	-	-	No measurable pits. Greyish-brown coating with some light-green corrosion products in inscription indentations. Slightly corroded.
52	-	-	-	-	Extensive general corrosion, but no measurable pits. Thick reddish-brown plus yellow coating covering inscription.

Table 10. Pitting data for objects from Group C.

KBS No.	$\bar{x}$	G	F	m	Notes
53	-	0,09	1-10	0,3	Find No. 42 according to Lindeberg 1973. Only general corrosion in the form of small round pits.
54	-	0,07	>10	0,3	Find No. 45 according to Lindeberg 1973. Only general corrosion in form of many small round and shallow pits.
55	-	-	1-10	-	Only general corrosion. Find No. 7 according to Lindeberg 1973.

Table 11. Semi-quantitative estimate of elements from objects in Group A.

Analysis method used: X-ray fluorescence.

Object	Elements									
No. KBS	Sn	Ni	Fe	Zn	Al	Si	S	Cl	As	P
1	++	-	+	-	+	+	+	-	-	-
2	++	+	-	-	+	+	+	-	-	-
4	++	+	+	-	+	+	-	+	-	-
6	++	+	+	-	+	+	-	-	-	-
8	++	+	+	-	+	+	-	+	-	-
10	++	+	-	-	+	+	+	-	-	-
11	++	+	+	-	+	++	-	+	-	-
15	++	-	++	-	+	-	+	-	-	-
16	+	++	++	+	++	+	-	-	-	-
17	++	-	-	-	+	+	-	+	-	-
18	++	+	+	-	-	++	-	-	-	-
19	++	+	-	-	-	+	+	-	-	-
20	++	+	-	-	-	+	-	-	-	-
21	+	+	+	-	-	+	-	+	-	-
22	++	+	-	-	+	+	-	-	-	+
23	+	++	+	+	++	+	-	-	-	-
24	+	+	-	-	-	+	-	-	-	-
25	+	+	+	-	+	-	-	-	-	-
26a	+	++	+	+	++	-	-	-	-	-
26b	++	+	-	-	+	+	-	-	-	-
26c	++	+	+	-	-	+	-	+	-	-
27	++	-	-	-	-	+	-	-	-	-

Table 12. Comparison between different pit data from objects from Group A and the native copper in Group E.

Object	Pit frequency, number of pits per 0.25 cm^2.	number of individual measurements	$\bar{x}$ mm	m mm	G mm
Group A	1	9	0,5	1,3	0,7
- " -	1-10	26	0,3	0,6	0,4
- " -	10	7	0,2	0,5	0,2
Group E	10	1	0,1	1,0	0,4

Table 13. Comparison between pits from cast and forged objects from Group A.

Treatment	KBS No.	$\bar{x}$ Mean pit depth mm	Standard deviation mm	G, maximum pit depth, mm	F, number of pits per 0.25 cm^2	m, mean diameter, mm
Cast	32, 37	0.86	0.24	1.15	< 1	2.5
"	3, 21, 25, 40	0.22	0.10	0.42	1 - 10	0.4
"	4, 7, 12	0.17	0.04	0.21	> 10	0.5
Forged	42	0.30	0.16	0.58	< 1	0.3
"	2, 5, 9, 10, 16, 19 22, 24, 30 41, 45, 46	0,27	0.09	0.43	1 - 10	0.4
"	14, 23	0.15	0.03	0.16	> 10	0.4

Table 14. Overview of analysis values

Period

	%	I	II	III	IV	V	VI
Cu	90					2	
	84	2	4	1	5	6	3
	75	2	10	9		3	1
	60						
	37					1	

Period

	%	I	II	III	IV	V	VI
Fe	0,63						1
	0,25			2			
	0,16	1	2	1		1	
	0,10	1	2	1			
	0,06		1	3			
	0,04	1	7	1	1		1
	0,02	1	1		2	7	2
	0,01		1	2	2	4	

Period

	%	I	II	III	IV	V	VI
Bi	0,06						1
	0,04						
	0,03						
	0,02				3	1	1
	0,01					1	
	-	4	14	10	2	10	2

Period

	%	I	II	III	IV	V	VI
Sn	10	1	8	7		1	1
	6,3	3	6	3	1	5	1
	4,0				3	2	2
	2,5				1	2	
	1,6					1	
	1,0						
	0,6					1	

Period

	%	I	II	III	IV	V	VI
Pb	1,6					1	1
	1,0					2	1
	0,63						
	0,40			2			
	0,25		1	1	1	1	1
	0,16			2	1	2	
	0,10	1	5	3	1	1	
	0,06		3	2	2	1	
	-	3	5			4	1

Period

	%	I	II	III	IV	V	VI
Ni	1,59	1					
	1,0					1	
	0,63						
	0,40		8	3	3	4	
	0,25		2	4	2	2	3
	0,16	2	1	1		5	
	0,10	1	1				
	0,06						1
	0,04						
	0,03			2			

Period

	%	I	II	III	IV	V	VI
As	2,51	1					
	1,59	1					
	1,0	1	1				
	0,63		1		3	3	
	0,40				1	1	1
	0,25		5		1	3	1
	0,16	1	5	4			1
	0,10		1	3		2	
	0,06		1	1		3	
	0,04						
	0,03			1			1
	0,02			1			

Period

	%	I	II	III	IV	V	VI
Ag	0,40	1				3	
	0,25				4	2	1
	0,16	1					1
	0,10				1		1
	0,06			1			
	0,04		1	2			1
	0,03	1	3			5	
	0,02		7	6		1	
	0,01		2	1		1	
	-	1	1				

Period

	%	I	II	III	IV	V	VI
Zn	0,08			1			
	0,06				1		
	0,04		1	1	1		
	0,03		1	2	1		
	0,02			2		2	
	0,01		2	3		1	
	-	4	10	1	2	9	4

The numbers give the number of analyses, the scale has the interval $\sqrt[5]{10}$ for copper subtracted from 100%. Lower class limit given.

$\bar{x}$	A	B	C	D
0,04	2			
0,08				
0,16	1	1	2	1
0,32	2		3	1
0,64				

s	A	B	C	D
0,01	1			
0,02	2		1	
0,04		1	1	1
0,08	2		2	1
0,16			1	

G	A	B	C	D
0,0	1			
0,1				
0,2	2	1		1
0,4	2		5	1
0,8				

m	A	B	C	D
0,1				
0,2	1		2	
0,4	3	1		2
0,8	1	1	3	
1,6				

Period

m	I	II	III	IV	V	VI
0,1						
0,2				3	4	1
0,4	1	5	3	4	5	1
0,8		3	7	1	1	
1,6	1		1			

Lower class limit given. For each increment the difference to the next increment is doubled. The numbers give the number of analyses.

A = stone cist in barrow
B = soil-mixed cairn
C = cairn
D = urn grave

x = mean measured pit depth in mm
s = standard deviation
G = maximum pit depth in mm
m = mean depth of measured pits in mm

LIST OF KBS's TECHNICAL REPORTS

1977-78

TR 121 KBS Technical Reports 1 - 120.
Summaries. Stockholm, May 1979.

1979

TR 79-28 The KBS Annual Report 1979.
KBS Technical Reports 79-01--79-27.
Summaries. Stockholm, March 1980.

1980

TR 80-26 The KBS Annual Report 1980.
KBS Technical Reports 80-01--80-25.
Summaries. Stockholm, March 1981.

1981

TR 81-17 The KBS Annual Report 1981.
KBS Technical Reports 81-01--81-16
Summaries. Stockholm, April 1982.

1983

TR 83-01 Radionuclide transport in a single fissure
A laboratory study
Trygve E Eriksen
Department of Nuclear Chemistry
The Royal Institute of Technology
Stockholm, Sweden 1983-01-19

TR 83-02 The possible effects of alfa and beta radiolysis
on the matrix dissolution of spent nuclear fuel
I Grenthe
I Puigdomènech
J Bruno
Department of Inorganic Chemistry
Royal Institute of Technology
Stockholm, Sweden January 1983

TR 83-03 Smectite alteration
Proceedings of a colloquium at State University of New York at Buffalo, May 26-27, 1982
Compiled by Duwayne M Anderson
State University of New York at Buffalo
February 15, 1983

TR 83-04 Stability of bentonite gels in crystalline rock - Physical aspects
Roland Pusch
Division Soil Mechanics, University of Luleå
Luleå, Sweden, 1983-02-20

TR 83-05 Studies in pitting corrosion on archeological bronzes - Copper
Åke Bresle
Jozef Saers
Birgit Arrhenius
Archaeological Research Laboratory
University of Stockholm
Stockholm, Sweden 1983-01-02

TR 83-06 Investigation of the stress corrosion cracking of pure copper
L A Benjamin
D Hardie
R N Parkins
University of Newcastle upon Tyne
Department of Metallurgy and Engineering Materials
Newcastle upon Tyne, Great Britain, April 1983

TR 83-07 Sorption of radionuclides on geologic media - A literature survey. I: Fission Products
K Andersson
B Allard
Department of Nuclear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-01-31

TR 83-08 Formation and properties of actinide colloids
U Olofsson
B Allard
M Bengtsson
B Torstenfelt
K Andersson
Department of Nuclear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-01-30

TR 83-09 Complexes of actinides with naturally occurring organic substances - Literature survey
U Olofsson
B Allard
Department of Nucluear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-02-15

TR 83-10 Radiolysis in nature:
Evidence from the Oklo natural reactors
David B Curtis
Alexander J Gancarz
New Mexico, USA February 1983