STABILITY OF TREATED ARCHAEOLOGICAL IRON: AN ASSESSMENT

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Abstract—Various desalination methods had been used in the past to treat a large collection of archaeological iron objects. In order to establish whether desalination treatments had been effective, the condition of the objects was assessed and the data analyzed using statistical methods. It was found that objects which had been treated using desalination methods were less likely to re-corrode, and the conclusion was that the development of more effective techniques of chloride removal would be useful.

1 Introduction

Do treatments intended to reduce the level of chloride in archaeological iron delay the onset of re-corrosion, make no difference, or even hasten it? Laboratory experiments seem to show that if the amount of chloride in contact with iron is sufficiently small then aggressive corrosion will not occur, even at high relative humidity [1, 2]. The conclusion from some studies of desalination methods, however, has been that it was the degree to which the object was mineralized which determined the fate of the object, and not the method of treatment [3, 4]. Artifacts themselves usually consist of complex metal/corrosion systems, and their behaviour during normal handling and storage may be very different from that of experimental samples in accelerated ageing tests.

In the study described below the present condition of artifacts treated some years ago, using different techniques of chloride removal, was assessed. It was hoped to gain some indication as to whether treatments had been successful, or whether it would be more useful to adopt, in future, a different method of inhibiting corrosion, such as permanent storage in the absence of moisture.

2 The sample

During the years 1969 to 1977 a large number of iron objects from excavations in Winchester, England, was treated. These excavations had taken place between 1961 and 1971. There was a variety of soil conditions: aerobic, anaerobic but not waterlogged, and truly waterlogged. Objects of all periods were recovered, and their condition varied from totally mineralized to lightly corroded. Not all objects from each context were conserved, so it has been possible to compare the present condition of those conserved with that of very similar unconserved ones. Whether treated or not, all the material was stored and handled in the same way. All treatment was carried out by or supervised by one of the authors, and there are adequate records (available in the archive of the Winchester City Museums).

2.1 *Storage conditions*

Most of the objects were kept in paper or polyethylene bags grouped inside cardboard boxes. The most fragile ones were packed individually in plastic or cardboard boxes. Packaging was not acid-free.

Until 1980 the store was an attic room in which temperature and relative humidity fluctuated widely, generally from 10° to 30°C and from 30% to 70% relative humidity, but with occasional higher peaks. The objects were frequently removed from the store and from their packaging during work on the publication programme; both treated and untreated items were therefore subjected to a fairly severe test. In 1980 the collection was moved to a purpose-built store in which conditions are held at 20°C, 40% RH.

2.2 *The conservation programme*

The conservation programme was organized in parallel with study and publication, so objects were selected for treatment according to type of artifact, not by condition or date of excavation. Thus a random selection of objects from different soils, excavated at different dates, was in treatment at any one time. The period between excavation and treatment varied widely, from 0 to 20 years (see section 4.1.2).

2.3 *Treatments used*

All treatments were based on the assumption that the re-corrosion of archaeological iron is promoted by the presence of soluble chloride salts, and that removing these or at least reducing their concentration will make further corrosion less likely. All treatments were continued until no chloride could be detected in the wash water, using the silver nitrate test. The concentration detectable in solution at the end point is likely to have been <5 ppm [5].

Some of the techniques used have not been published fully. In others, the procedures used may vary from the published descriptions. Details are given below when they are not otherwise available.

At the start of the programme, in 1969, the only treatments in common use were electrolysis and boiling.

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Table 1 Numbers of objects desalinated

Technique	*Year* *'68*	*'69*	*'70*	*'71*	*'72*	*'73*	*'74*	*'75*	*'76*	*'77*	*'78*	*'79*
Electrolysis	15	13	8	1	1	4	6	3	16	1	4	
Boiling				1		9	5	4	4	1	2	3
Ionophoresis			7	7	7	4	3	1				
Circulation bath									9	39	2	
Steaming											18	
Soaking												8

2.3.1 Electrolysis [6, p. 285]
Procedure used: sodium carbonate electrolyte, stainless steel anode. Electrolysis was usually continued for three weeks. The object was then boiled three times in distilled water, which was tested for chloride.

Electrolysis was the only treatment in which corrosion was completely removed from the metal. In all the other techniques described below the intention was to leave the corrosion layer intact, since it often contained details of the object's shape, non-ferrous metal decoration or plating, replaced organic components, etc.

2.3.2 Boiling [6, p. 291]
Procedure used: the object was mechanically cleaned and then boiled in changes of distilled or deionized water. It was dried out at the end of each day.

Both electrolysis and boiling had serious disadvantages. The former is a drastic treatment, and can only be used for lightly corroded objects in which the corrosion layers contain no important detail. Boiling was very time-consuming and objects were easily damaged during the process, both physically and by fresh corrosion.

2.3.3 Ionophoresis [7, 8]
Procedure used: electrolyte, 5% sodium benzoate (a corrosion inhibitor for ferrous metals) at room temperature; stainless steel electrodes. A low current was passed through the electrolyte in which the objects were suspended, in order to attract ions, including chloride, towards the appropriate electrode. Objects were removed and boiled individually to test for chloride.

This method was adopted for the treatment of most artifacts. Although damage to the objects was reduced, it took between one and ten months for chloride concentrations to fall below detection level. In some cases it was found to be quicker to complete the treatment by boiling in the usual way.

It was felt that raised temperatures resulted in shorter treatment times, and in due course a technique (2.3.4) using continuous washing at temperatures close to boiling, combined with chloride removal, was developed by John Cross, at the Department of the Environment Ancient Monuments Laboratory.

2.3.4 Circulation bath
Procedure used: cleaned objects were placed in a circulation bath maintained at approximately 90°C. Chloride and other soluble salts were removed from soak water by circulating it through an ion-exchange resin (Amberlite MB–1). It took from four to seven months to complete the treatment. The water became well oxygenated as a result of the circulation process, and 'flash rusting' was a serious problem, frequently clogging up the circulating system.

All the washing methods described so far were based on the premise that soluble chloride salts in the object were removed faster if the concentration of salts in the soak water was kept at a minimum. In 1978 North and Pearson published their review of soaking methods [9] and concluded that the concentration of salts in solution outside the iron was normally too low to affect the rate of diffusion from the core to the outside of the object. If length of soaking time was the determining factor in chloride removal then it was obviously more convenient, cheaper and less damaging to the object simply to soak it. At the same time, however, chloride removal using steam was being developed at the Parks Canada Laboratory. These developments came at the end of the programme, so only one small batch of iron objects was treated in each of these ways.

2.3.5 Steaming
Procedure used: the objects were placed above water level in a domestic pressure-cooker containing deionized water and steamed at 15lb pressure during working hours. At the end of each day, the deionized water used was tested for chloride, and the objects were removed and dried. The basis of the method was that steam would penetrate the pores of the corrosion, and the constant supply of freshly condensing water would rapidly remove soluble chloride as it ran out, but after two months chloride levels were still high, and the objects were flaking and visibly corroding. The treatment was discontinued.

2.3.6 Soaking
Procedure used: groups of objects were placed in sealed polyethylene boxes, containing 5% sodium benzoate in deionized water, and kept at 50°C. The

solution was changed every 3–4 weeks, and tested for chloride. The objects had started treatment in the circulating bath but it still took two months for chloride levels to fall to undetectable levels. The sodium benzoate appeared to dissolve away surface corrosion in places where there was only a thin layer over the metal.

2.3.7 Coatings, consolidants and adhesives

Some objects had been consolidated immediately after excavation with 10% PVAc solution. This was removed by soaking the objects in changes of acetone before they were treated. Very fragile objects, and those with non-ferrous decoration contained within the corrosion layer, were usually consolidated after corrosion removal by vacuum impregnation with Araldite AY103/HY951, a low-viscosity epoxy resin. Objects which had broken because of fresh corrosion or mechanical damage were adhered with Araldite two-pack resin. Desalination treatment followed consolidation or repair, and impregnation did not appear to result in lower levels of chloride in the soak water. After chloride removal all objects, both consolidated and unconsolidated, were lacquered, usually by dipping, with Ercalene, a proprietary cellulose nitrate lacquer. Wax was not used at all.

2.3.8 Inspection and assessment

The treated objects were mostly inspected during two days in 1982, with a return visit in 1983 to inspect more objects and to check some points. The statistical assessment includes an allowance for the additional year since treatment.

Each treated object was inspected and listed. If there was the slightest sign of instability, other than simple mechanical breakage, an object was counted as unstable. As a control, for every treated object inspected, an untreated object excavated from the same site at the same time was also looked at.

3 Statistical comparison of different treatments

3.1 Data

The following information was available for each of 210 iron objects:

(a) date of excavation,
(b) date of treatment,
(c) method of treatment (one of the treatments in section 2.3, each with or without Araldite),
(d) whether object was still stable in the base year (1982).

For comparison, (a) and (d) were available for 148 untreated objects.

3.2 Model

As a first approximation, simple negative exponential models were fitted to the data, both overall and for individual treatments. These models are based on the assumption that the probability of a stable object becoming unstable within the next year depends *only* on the method of treatment, and not on (i) how much time has passed since treatment, (ii) the length of the interval between excavation and treatment, or (iii) the condition of the object before treatment.

Assumption (i) is reasonable in the absence of any evidence for positive or negative ageing. The need for assumptions (ii) and (iii) could be avoided by using a carefully balanced and randomized experimental design, i.e. by ensuring that the relative numbers treated in different ways were the same from year to year, and by allocating objects to treatments randomly. The second requirement, for random allocation, was met informally by the way of assigning objects to treatments (4.1), but the first was not, because different methods of treatment were introduced at different dates (see Table 1). Assumption (ii) must therefore be invoked, with the warning that if it does not hold, the more recent treatments may suffer an unfair comparison with the earlier ones. The contrasts between individual recent treatments and 'no treatments' may in this case not reflect the full benefit that could have been gained had the objects been treated immediately.

However, the models do appear to fit the data reasonably well, so that broad comparisons between treatments can (with some caution) be made without recourse to more complex models. It is probable that better fits could be achieved with more practically realistic, but statistically more complicated and less tractable, models. A printout of the data is available on request to anyone wishing to examine alternative models.

3.3 Method

The models used are 'single-parameter' models, i.e. their behaviour is completely specified by one parameter, either the 'half-life' of the objects (the time taken for half of them to become unstable) or the probability 'p' that any one object will become unstable within a year. These two parameters are related and each can easily be calculated from the other.

The method of maximum likelihood estimation (mle) was used to estimate the parameter 'p' and hence the half-life for each treatment individually, for all treatments together and for the untreated objects. Such estimates are, however, of little value unless some likely margin of error can be attached to them. Conventionally, this is expressed in terms of their standard deviations (sd). In this instance, standard deviations were not calculated because, firstly, their value is limited because the distributions are very skew and confidence intervals difficult to obtain, and, secondly, the calculation is extremely complicated. As well as the best estimate of the half-life, a range of

Table 2 Numbers of treated and untreated objects, and numbers still stable in 1982

Treatment	*With Araldite*						*Without Araldite*					
	Treated	*Stable*	*'p'%*	*Half-life Estimate*			*Treated*	*Stable*	*'p'%*	*Half-life Estimate*		
				Min		*Max*				*Min*		*Max*
Boiled	15	15	0	∞	∞	∞	16	5	16	3	6·5	12
Circulated	44	36	4	12	26	60	6*	4	7·5	4	13	35+
Electrolyzed	—	—	—	—	—	—	75	46	5	13	21	30+
Ionophoresised	11	9	2	13	50	150+	19	13	5·5	13	18	75
Soaked	8*	7	4	8−	25	75+	—	—	—	—	—	—
Steamed	13	5	21	3	5	12	5*	3	12	4	8·5	24+
All	91	72	4	16	25	40	119	71	5·5	13	18	25
Untreated	—	—	—	—	—	—	148	28	11	8	9	11

This table includes the estimated value of 'p' and the half-life, together with upper and lower limits for the latter ('min' and 'max' columns; see Appendix for details). In the 'min' column, '−' indicates that the limit is less than the value shown, while in the 'max' column '+' indicates that the limit is greater than the value shown. '*' indicates that the figure is too small to yield reliable results.

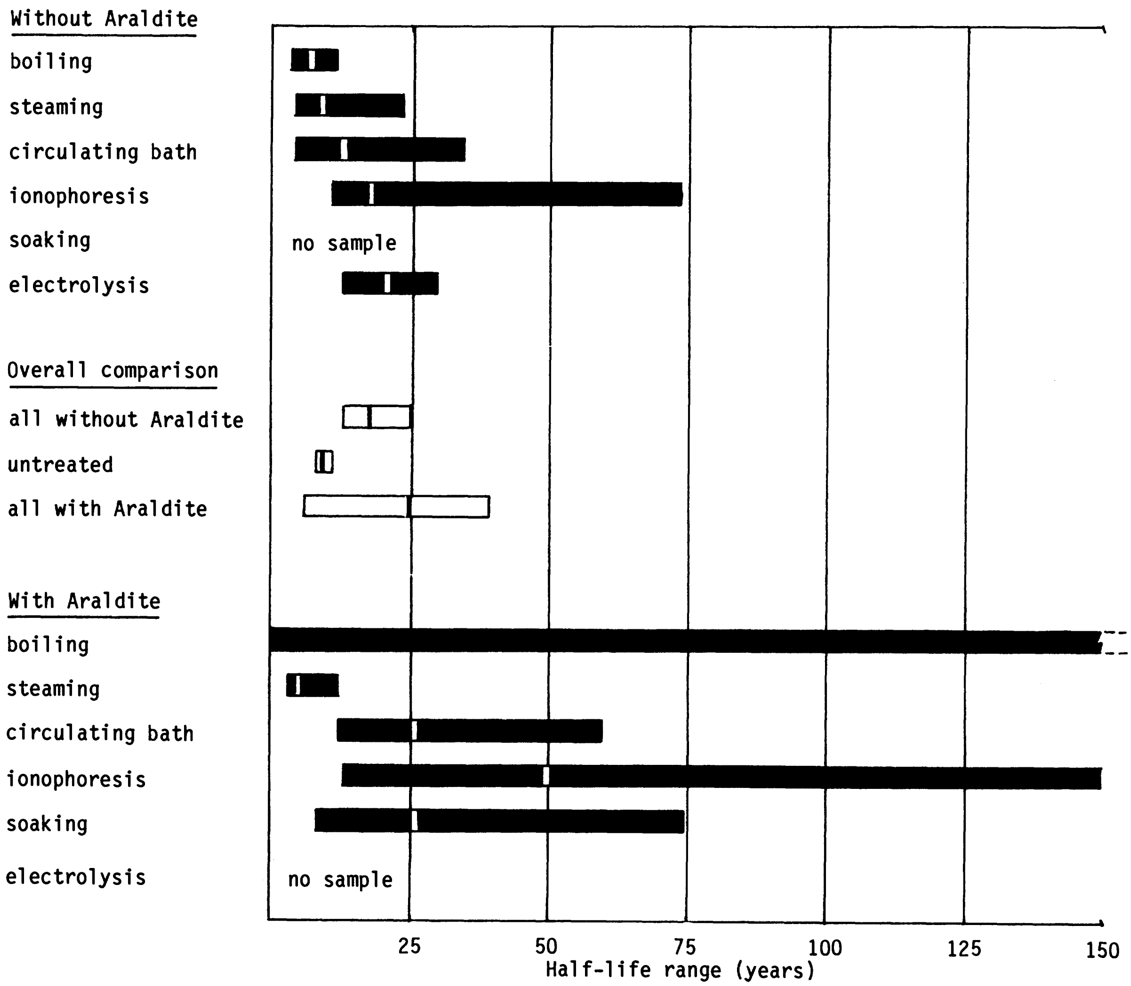

Figure 1 Half-lives of treated archaeological iron. Ends of bars show 'minimum' and 'maximum' values; central lines show 'best' estimates.

estimates consistent with the data (at a predetermined significance level) was computed.

3.4 Results

It is clear (Table 2, Figure 1) that treatment does improve the life expectancy of the objects: the half-life is increased from 8–11 years to 13–25 years (without Araldite) or 16–40 years (with Araldite). It appears that treatment which included Araldite was more successful than treatment which did not, but this cannot be stated with certainty because the experiment was not balanced, i.e. some treatments were always accompanied with Araldite and some never were. However, looking at treatments individually as well as overall, there does seem to be an improvement.

Turning to the individual treatments, there are no significant differences between them except for boiling and steaming. Steaming is markedly worse than the other treatments: apparently worse than no treatment at all, though the difference between steaming and no treatment is not statistically significant. Boiling without use of Araldite is also markedly worse than other treatments but, paradoxically, boiling with use of Araldite appears best of all, with no unstable objects.

A subjective examination of the residuals (i.e. the differences between the predicted and actual numbers of stable objects) suggested that objects which had been treated soon after excavation tended to survive better than those that had to wait longer. This finding is in line with 'common-sense' expectations and, if confirmed, would tend to invalidate assumption (ii) (3.2), making comparisons between the different treatments difficult under the simple models used. However, the outcome of a more formal examination was inconclusive.

3.5 Summary

These data, although not the outcome of a controlled experiment, yield useful information on the survival of iron objects after various treatments. Most methods appear approximately to double the expected half-life; used in conjunction with Araldite, a trebling of the half-life could be predicted for them. There appears to be little difference between the methods, except for steaming, which appears markedly worse than the others, and boiling, which also appears worse unless Araldite is used.

4 Discussion

Although no detailed experimental work has been carried out, it is possible to consider how the variations found in the stability of the iron may have been brought about by the different treatments.

4.1 Variations in the samples

We have noted that degree of mineralization and the time-lapse between excavation and treatment may affect the results independent of the effects of the treatment.

4.1.1 Degree of mineralization

Were some treatments considered more suitable than others for objects with no metallic core? The occurrence of these objects in the data would influence the results, since they cannot corrode further. It is not possible to be sure from examination of its radiograph alone whether or not an object has a metallic core remaining, and the only treatment in which degree of mineralization determined the selection of objects was electrolysis, since it is only suitable for lightly corroded objects. Otherwise, objects were selected for the various washing treatments because of the presence of surface detail or non-ferrous metal.

4.1.2 Time between excavation and treatment

Table 3 shows the data for time-lapse from excavation to treatment. If time from excavation to treatment affects results, then more recent treatments, for which objects had to wait longer, would show as less effective than they really were. The statistical analysis shows them as being slightly more effective; perhaps they are, in fact, better still. However, the marked difference in effectiveness between steaming and soaking—techniques which were in use at about the same time—suggests that time between excavation and treatment is not necessarily the main factor influencing the results.

Table 3 Time-lapse from excavation to treatment

Technique	*Years from excavation to treatment*																				
	0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*	*20*
Electrolysis	4	4	1		2	4	5	35	4	6	2		1	1		1					
Boiling			1	5	2	6	3	3	1		4	1	1							1	2
Ionophoresis	1		1	2	4	2	4	1	4	10											
Circulation bath							14	6	10	7	5			5	2						
Steaming								5	4	2	3	1	1	1		1					
Soaking									3		1			2		1			1		

4.1.3 Effects of coatings and consolidants

The effects of coatings and consolidants were considered separately, and the conclusions have been published elsewhere [10]. The PVAc and cellulose nitrate lacquer appeared to have had no effect on the objects' stability and have been ignored. The epoxy resin consolidant did appear to have an effect, however, and this has been included in the assessment of the data.

Each batch, then, consisted of a random mixture of objects, excavated between 0 and 20 years previously, their condition varying from totally mineralized to scarcely corroded, some of them already showing re-corrosion, some of them pre-consolidated. Although comparisons of treatments based on the assessment of individual objects would be impossible, we think that the numbers of objects are large enough and the batches themselves likely to have been sufficiently comparable to allow the effects of desalination to be distinguished from those of other factors.

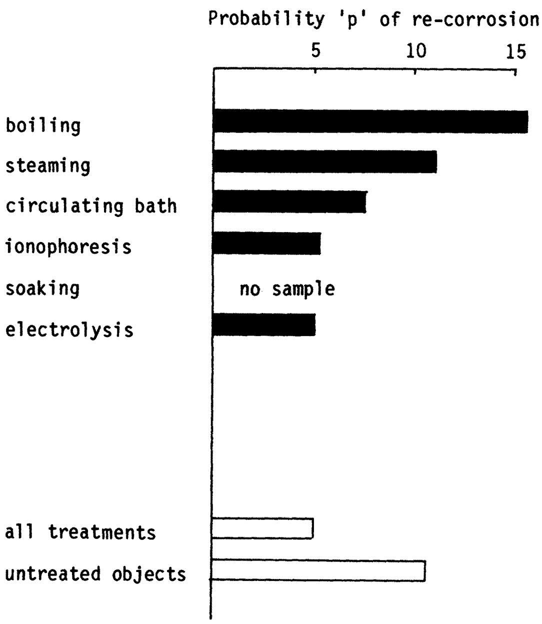

Figure 2 Probability 'p' that a treated object will corrode in any given year. Values are for 'without Araldite' objects.

4.2 Effects of treatments

The effects of desalination may best be seen by considering 'without Araldite' objects alone (Figure 2).

The poor performance of steaming is entirely as expected, since the objects were deteriorating visibly even during treatment. The reason for the negligible effect of boiling might be the comparatively short time the objects spent in water.

Of all the treatments, electrolysis is the one likely to have removed the greatest proportion of the chloride contained in the corrosion. It does, however, leave a deeply etched metal surface, which presents an enormous area for re-corrosion, and this may be why electrolysis was not found to be the most effective of the treatments.

The relative success of ionophoresis may be partly due to the corrosion inhibitor, sodium benzoate, used as the electrolyte. That chloride removal itself may be effective is suggested by comparing the results of the circulating bath, in which deionized water alone was used, with those for untreated objects.

On the whole, the treatments which employed the longest soaking times seem to have been the more effective.

The apparent benefits of epoxy resin impregnation should be considered carefully. Firstly, it will presumably make the objects physically stronger, so that re-corrosion at the metal core will take longer to force off flakes of corrosion. Secondly, fragile objects requiring consolidation are likely to include a high proportion of totally mineralized, and therefore more stable, ones. However, epoxy resin is more likely than PVAc or cellulose lacquer to perform well as a protective coating [10], and it may, in fact, be delaying the onset of corrosion.

Epoxy resin must be considered as completely irreversible in this application. Since it can only be made to swell and soften, not dissolve, it would be impossible to remove it from the pores of the corrosion. However, its short-term effects appear to be beneficial, and its use may be justified for very fragile objects which are likely to be handled. Experience has shown it to have certain practical advantages, not least that it can be used before or during mechanical cleaning, when other consolidants such as Paraloid B72 or polyester resin tend to smear and make corrosion removal much more difficult

5 Conclusions

Even though they must be interpreted with caution, the results of the survey suggest that treatments which aim at chloride removal make the re-corrosion of archaeological iron somewhat less likely. Watkinson concluded that desalination treatments do not affect the stability of iron objects, but he assessed stability in extreme conditions: 90% RH for nine months [3]. The results from the present study do not conflict with this, since they show only that, in conditions of lower but fluctuating humidity, desalination treatments tend to extend the period of time before objects re-corrode.

There is a further point: for the purposes of statistical analysis, objects were noted as 'stable' or 'unstable'. At the time of the inspection, however, it was very clear to us that treated artifacts were in much better condition than untreated ones. Most of the latter had split and flaked to the point of disintegration, while those treated ones which were noted as 'unstable' mostly had no more than a small detached flake or two.

There are indications that some treatments are more effective than others. It has not been established what factors determine this, but length of soaking-time may be one. The development of more effective methods of washing, such as chemical reduction using alkaline sulphite, or soaking in amine solutions, is therefore to be encouraged and welcomed.

Appendix

For a number of values of the half-life on either side of the estimated value (typically from one-third to three times the half-life), the expected numbers of stable objects were calculated. These values were compared with the actual values in two ways: (i) using a chi-squared test on values for individual years and (ii) testing the total number of stable objects, using a Normal approximation to the Binomial distribution. The value of the half-life was rejected if either test failed at the 1% level.

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Résumé—Différents méthodes de désalination ont été utilisées dans le passé pour traiter une grande quantité d'objets archéologiques en fer. Afin d'établir si ces traitements ont été efficaces, l'état de conservation des objets a été évalué et les différentes données les concernant analysées par des méthodes statistiques. On a constaté que les objets qui avaient été traités par désalination ont moins tendence à se recorroder et l'on a conclu que la mise au point de méthodes plus efficaces pour l'enlèvement des chlorures serait utile.

Auszug—In der Vergangenheit wurden verschiedene Entsalzungsmethoden angewendet, um eine große Sammlung archäologischer Eisenobjekte zu behandeln. Um zu bestimmen, ob Entsalzungsbehandlungen wirksam waren, wurde der Zustand der Objekte ausgewertet und die Daten unter Anwendung statistischer Methoden analysiert. Es wurde festgestellt, daß Objekte, die unter Anwendung von Entsalzungsmethoden behandelt worden waren, weniger Tendenz für eine erneute Korrosion zeigten, und die Schlußfolgerung war, daß die Entwicklung wirksamerer Techniken der Chloridentziehung nützlich sein würden.