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1. INTRODUCTION

The Maritime Archaeology Department of the Western Australian Museum has an active excavation programme, which for the past five years has centred around two Dutch East Indiaman wrecks, the 'Batavia', 1629, [1, 2] and the 'Vergulde Draeck', 1656 [3]. A large number of wrecks from the colonial period (1829-1900) have also been recorded or excavated.

A fair proportion of the artifacts recovered from the wrecks are ceramic materials, including a large amount of stoneware and earthenware as well as a few fragments of Chinese porcelain. The most typical ware recovered is the 'Bellarmine flagon' (Figure 1) of salt-glazed stoneware; 27 were found intact from the 'Vergulde Draeck' and 12 from the 'Batavia'. This paper will discuss our experiences of the problems with both on-site and laboratory conservation that occur with these ceramic artifacts recovered from the sea.

2. ON-SITE CONSERVATION

Due to the isolated position of some of the wrecks lying off the Western Australian Coast, many of the recovered artifacts have to remain on site for up to four months. It is essential that during this storage they are kept in a stable environment. For ceramics, this is simple as they can be kept wet by total immersion in seawater (fresh water being at a premium) to which is added Panicide (20 p.p.m.) to prevent fungus growing. It is essential that the ceramics are not allowed to dry out because the salts which have penetrated the body and glaze of the artifacts will crystallize out and tend to cause mechanical damage.

Any excessive amounts of concretion can be removed by mechanical measures; however, final cleaning is left until full laboratory facilities are available.

One of the problems for the marine archaeologist is the assembly of sherds to determine the type and style of the object and, more important, to check whether all pieces are present. Attempts at using sand baths and clay supports have not proved very successful and the simplest method is to use a temporary adhesive. A nitrocellulose adhesive, which is readily reversible, was first used for this work but proved to be very unsatisfactory. As the ceramic must be kept wet during this work there is a reaction between the water and adhesive creating a white opaque product which was difficult to remove. Also, as the adhesive shrank considerably on drying, the edges of the joined pieces were damaged; the more fragile the ceramic body, the greater the extent of damage. Thus a once-simple break might be changed to a delicate filling and restoration task.

The most satisfactory adhesive for this work is a proprietary PVA adhesive, UHU (manufactured by UHU-Werk H.u.M. Fischer GmbH., D-758 Buhl, Baden, West Germany). This will adhere to wet sherds and does not shrink appreciably on drying. As it retains some slight flexibility it does not cause mechanical damage to the joints. UHU is readily soluble in acetone.

This process can be applied to the three main types of ware found on the wrecks, i.e. earthenware, stoneware and porcelain. Great care, however, must be taken with the earthenware, such as terracotta and majolica ware, as these sometimes have very soft bodies and fragile glazes, and excessive handling will cause damage.

For transportation to the Conservation Laboratory the ceramic artifacts are individually wrapped in polythene to retain a humid environment which will prevent salt crystallization.

3. LABORATORY CONSERVATION

3.1 Storage

As the ceramic objects invariably arrive in large batches, they again have to be stored prior to treatment. In this case, however, the storage can be used to commence the cleaning process by slowly reducing the salt content of the storage solution. It is important that this is not carried out too rapidly by the immediate use of deionized water, as the osmotic pressures set up might cause damage to susceptible glazes. The salt water is therefore gradually diluted during storage until tap water can be used, usually requiring a four-week period. The conductivity of the solution is reduced by this process from 50,000 μmhos to 1,000 μmhos approximately.

3.2 Removal of concretion

Coral growth is prolific in the warm waters off the Western Australian coast and most sherds recovered are coated with some form of encrustation (Figure 2). Those which have lain in close proximity to iron objects are iron-stained and any surrounding concretion is heavily impregnated with iron corrosion products. In the case of earthenwares, this iron-rich concretion is often stronger than the ceramic itself.

The easiest method of removing these concretions is by acid treatment; however, there is always the danger of damaging either the body or glaze. A number of experiments have been conducted to determine whether ceramic materials can withstand chemical cleaning processes. Fragments of two Bellarmine flagons were analyzed by X-ray diffraction techniques before and after cleaning by immersion in dilute acid solutions.

The body of the untreated samples contained as the major phase α -quartz (SiO_2), α -cristoballite (SiO_2) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). There was no evidence of iron or its oxides/hydroxides in the ceramic body. However,

the glazes contained α -quartz as the major component with minor phases of magnetite and lepidocrocite ($\gamma\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), the presence of iron being the important factor. Some samples were iron-stained and these stains and the concretions were analyzed to reveal lepidocrocite and calcite (CaCO_3).

These analyses indicate that although the bodies of the ceramics are quite stable, being composed of chemically stable silicates, the glazes do contain iron oxides which would be susceptible to dissolution by acid treatment. These are lepidocrocite and magnetite, of which the latter would be formed in the reducing atmosphere of the salt-glaze firing. The iron stain/concretion, essentially calcium carbonate and iron oxides, could be removed chemically. The analyses indicate, however, that it would be very difficult to carry out chemical cleaning with acid solutions without damaging the underlying glaze.

Experiments were carried out with the ceramic samples to test the effect of dilute acid treatments. The samples were immersed in 10% hydrochloric acid solution until all gas evolution ceased, in order to remove all calcareous deposits. The duration of this immersion was approximately one hour. The solutions turned yellow, indicative of the dissolution of iron oxides. This occurred even with samples which apparently had no surface iron-staining. The samples were next washed in tap water and then immersed in a 10% solution of oxalic acid for 17 hours to remove iron stains.

Examination of the surfaces of the ceramic samples by stereomicroscope before and after treatment revealed that:

1. All iron staining was not removed from the surface of the ceramics, although they did appear much cleaner and the original colours of the glazes became more evident.
2. Ceramic samples with no iron stain were apparently cleaner but this was due to the lepidocrocite being dissolved from the glaze, making it lighter in colour.
3. Friable glazes were damaged by the acid treatment which caused severe exfoliation.
4. There was no change in the fresh broken surface of a ceramic sample before and after treatment, which was as expected from the analyses of the ceramic bodies.

These results show that hydrochloric and oxalic acid treatments, although removing calcareous concretions, tend to dissolve iron oxides from the glazes of the ceramics and increase their tendency to exfoliation. Such treatments are therefore not recommended for cleaning stoneware with iron-containing glazes. Earthenwares, particularly terracottas, are far more prone to deterioration by acid treatments, as the body is much softer than stoneware and generally has a high iron content.

One of the most useful chemicals for cleaning ceramics is ethylenediaminetetra-acetic acid (EDTA). The choice of the salt, e.g. di-sodium, or tetra-sodium, determines the pH: the lower the valency the lower the pH. Iron is most soluble at pH 4, the calcium salts at pH 13. Therefore a 5% solution of the tetra-sodium salt of EDTA (pH 11.5) can be used for removing calcareous concretions without seriously affecting the iron content of the ceramic. In many cases, iron oxides which are bound in with the calcium salts will be removed when the latter are taken into solution.

Water-softening chemicals such as sodium hexametaphosphate (Calgon) are unsuitable for earthenwares, as the body is softened more readily than the calcareous deposit. They are of use in the final cleaning of stonewares when small particles of concretion need to be removed from abraded glaze areas.

Chemical treatments using dilute hydrochloric and oxalic acids cannot therefore be used for cleaning calcareous deposits from stonewares or earthenwares which contain iron oxides in the ceramic bodies or glazes. They can be used for stonewares and porcelain which are free from iron oxides, and results to date have been very satisfactory.

Our experience has shown that the safest and most satisfactory cleaning techniques are manual. Most calcareous concretion can be removed easily when wet by scraping with a scalpel or similar implement. If the concretion is allowed to dry, however, it becomes much harder, probably by reaction with atmospheric carbon dioxide to form calcium carbonate in a manner analogous to the function of lime in mortar.

In the case of large or very hard pieces of concretion on friable material, a dental burr is used to reduce it to such proportions that it can safely be removed by scraping. Even very friable earthenwares with fragile majolica glazes have been successfully cleaned with such techniques.

3.3 Removal of salt contamination

During storage, the conductivity of the storage solution is slowly reduced to approximately 1,000 μmhos . The ceramics must then be washed further to remove all salt contamination, otherwise salts crystallizing out can damage glazes (Figures 3a & b).

For this stage of the washing process, deionized water with a conductivity of 50 μmhos is used. There are three methods of salt removal: static immersion, flow-through immersion, and agitation-dispersion.

The static immersion process, where artifacts are simply placed in sealed containers of water, is quite slow. Pockets of relatively high conductivity are to be found in the solution immediately surrounding the artifacts; thus the osmotic pressure differential is low and the salt is removed at a slow rate. This technique is used for very friable objects and those with flaking glazes.

The flow-through immersion technique used by Jedrzejewska [4] is more efficient, but very wasteful of deionized water. A much more efficient method, suitable for most of the ceramic artifacts recovered which are in a sound condition, is the agitation-dispersion process. A gentle agitation is effected, which maintains a homogeneous conductivity throughout the solution. Thus an optimum osmotic pressure differential is maintained, which removes the salt at a faster rate.

An apparatus has been devised which suitably agitates the solution in a gentle manner. Old washing-machines of the twin-tub impeller variety can be cheaply and easily modified to suit the requirements. A perspex baffle with several holes drilled in it is placed in front of the impeller and a gentle but uniform agitation of the water

results. The 'spin tub' can also be adapted by removing the spin basket and blocking the resultant hole. The pump outlet tube is extended and placed in the tub, which serves to recycle the water. The machine works best on a half-hour on, hour off cycle. Sturdy plastic-mesh bags are used to contain the sherds and ensure that adequate circulation is possible.

With such apparatus the time taken to bring the conductivity down to an acceptable level, about 150 μ mhos or less, is reduced from months to weeks. Generally, four weekly changes of water are sufficient. An added advantage is that less deionized water is used. Once the salts have been removed the ceramics are allowed to dry.

3.4 Stain removal

At this stage, any stain removal which is necessary is carried out. This is only attempted if the offending stain is a serious disfigurement, obscuring glaze details, or if its removal is necessary for stabilization. It would be pointless to remove every bit of iron stain from every sherd when their assembly is unlikely. Iron oxide stains are removed from wet stoneware by local application of 10% oxalic acid by means of cotton buds. In this way one has control over the reaction, to ensure that no damage is caused. For large stains one must ensure that the piece is well soaked in deionized water, and then cotton wool pads saturated with oxalic acid are applied.

To date we have not been successful in devising a treatment to remove iron stain safely from stoneware and earthenware ceramics which contain iron oxides in the body or glazes. Localized treatment with oxalic acid is partly successful; however, great caution must be exercised during this process.

Following iron-stain removal, the ceramics are returned to the wash tank where they remain until a neutral pH is obtained.

For the black iron-sulphide stains which are frequently found, and for organic stains, hydrogen peroxide at a strength of 10 or 25 volumes is used, depending on the severity of the stain. Several earthenware majolica apothecary jars, which were so badly stained that they appeared quite black, were treated in 25 vol. hydrogen peroxide for up to 36 hours, after which time the original colours could be seen (Figures 4a & b). There is no need for rinsing after hydrogen peroxide treatment.

After being allowed to dry out, the ceramics are assembled and the surfaces consolidated where necessary. As the techniques [5, 6] for these processes are well known, they will be mentioned only briefly.

3.5 Surface consolidation

Some ceramic artifacts suffer from friability or from flaking glazes. In these cases consolidation is necessary. Of the many consolidants available, PVA dissolved in acetone and ethyl acetate, and soluble nylon, are preferred. These can be either brushed or sprayed on, or, if complete impregnation is necessary, objects can be immersed in PVA.

Soluble nylon has the advantage that it is comparatively permeable and other reagents may penetrate its film. It can therefore be used to consolidate a flaking glaze before commencing the desalination process, to ensure that the glaze is not damaged. It has been used with success on some majolica ware apothecary jars, prior to washing and removal of sulphide stains (see section 3.4).

Where glaze fragments have broken away from the ceramic body they are reattached with PVA.

3.6 Repair of broken ceramics

Assembly of broken ceramics, where practicable, follows cleaning and consolidation procedures. It is rare to find all the sherds of a pot, and often only a few pieces are recovered. A sand box is used for holding the sherds during assembly and repair.

For earthenwares, PVA dissolved in acetone and ethyl acetate, or a proprietary PVA adhesive such as UHU, is used. For stoneware and porcelain, epoxy resins are used if all fragments are present. If not, reversible adhesives must be used, as there is always the possibility that the missing fragment will be recovered on a future expedition.

4. CONCLUSION

Ceramic artifacts survive well under the sea, their biggest dangers being from physical damage. Unless correct procedures are carried out when they are recovered, to desalinate and clean the ceramics effectively, then disintegration of the bodies and glazes of the artifacts may result. The necessity of always keeping ceramic objects wet cannot be over-emphasized. Desalination techniques are the most important of the conservation processes for ceramics from the sea and if these are carried out efficiently there will be little likelihood of the artifacts deteriorating further.

The removal of concretion by mechanical means is recommended in preference to the use of chemicals. Iron stains, however, are still causing a problem which will require further research.

REFERENCES

1. Bateson, C., 'Australian Shipwrecks. Vol 1. 1622-1850', Reed, Melbourne, 1972.
2. Edwards, H., 'Islands of Angry Ghosts', Hodder and Stoughton, London, 1966.
3. Green, J., The loss of the Dutch East Indiaman 'Vergulde Draeck' 1656, 'Int. J. Naut. Archaeol. and Underwater Archaeol' 2 (1973) 267-289.
4. Jędrzejewska, H., Removal of soluble salts from stone, in 'Conservation of Stone and Wooden Objects', IIC, London, 1970.
5. Larney, J., Ceramic restoration in the Victoria and Albert Museum, 'Studies in Conservation' 16 (1971) 69-82.
6. Plenderleith, H. J. and Werner, A. E. A., 'The Conservation of Antiquities and Works of Art', Oxford University Press, 1971.

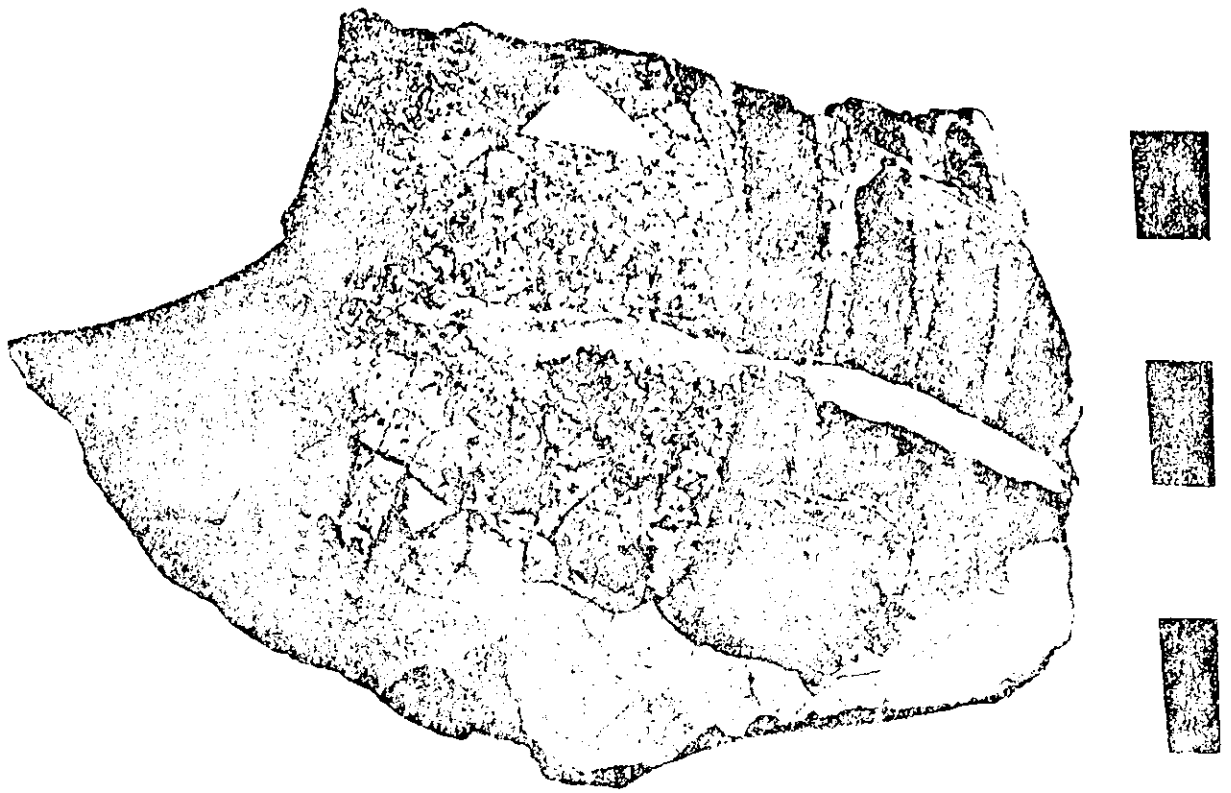


Figure 4a. Majolica ware sherds after salt removal.



Figure 4b. Same group of sherds after bleaching with hydrogen peroxide.

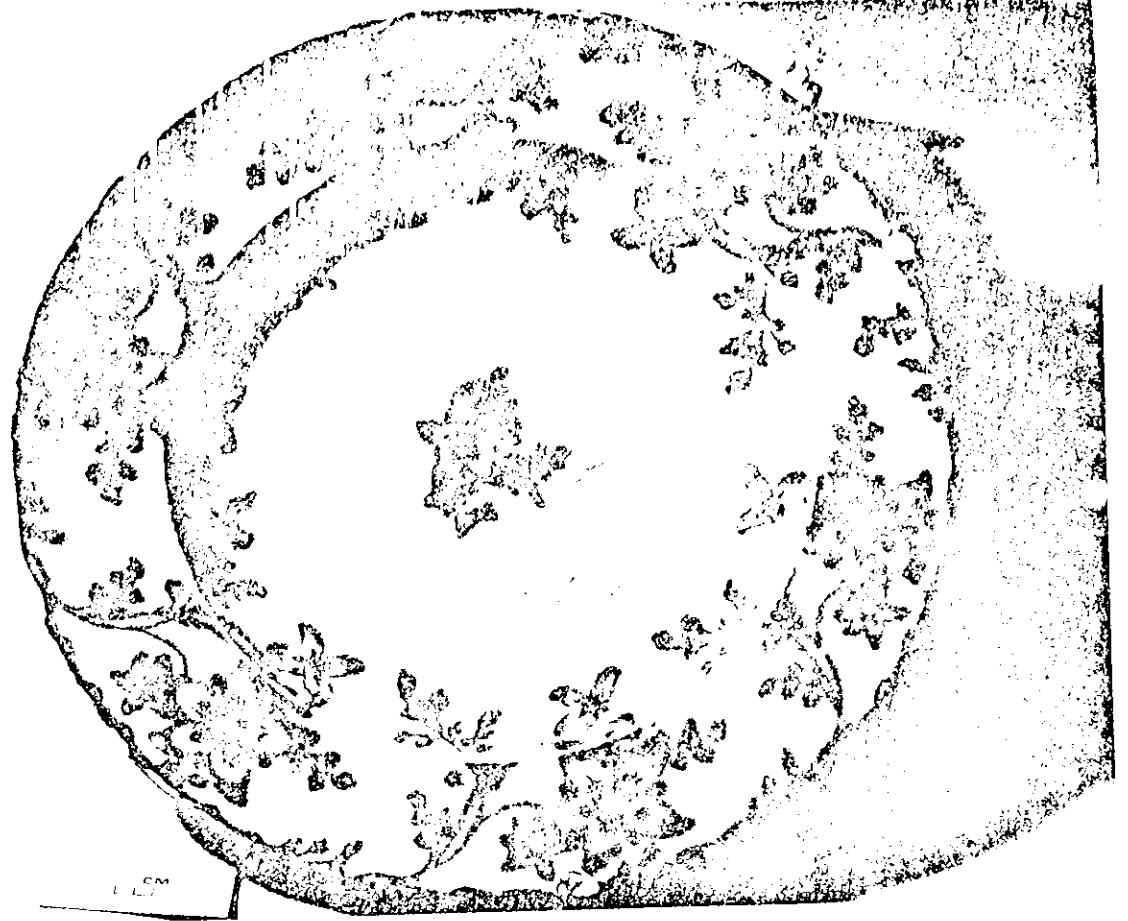


Figure 3a. Colonial porcelain plate showing flaking glaze due to salt crystallization.

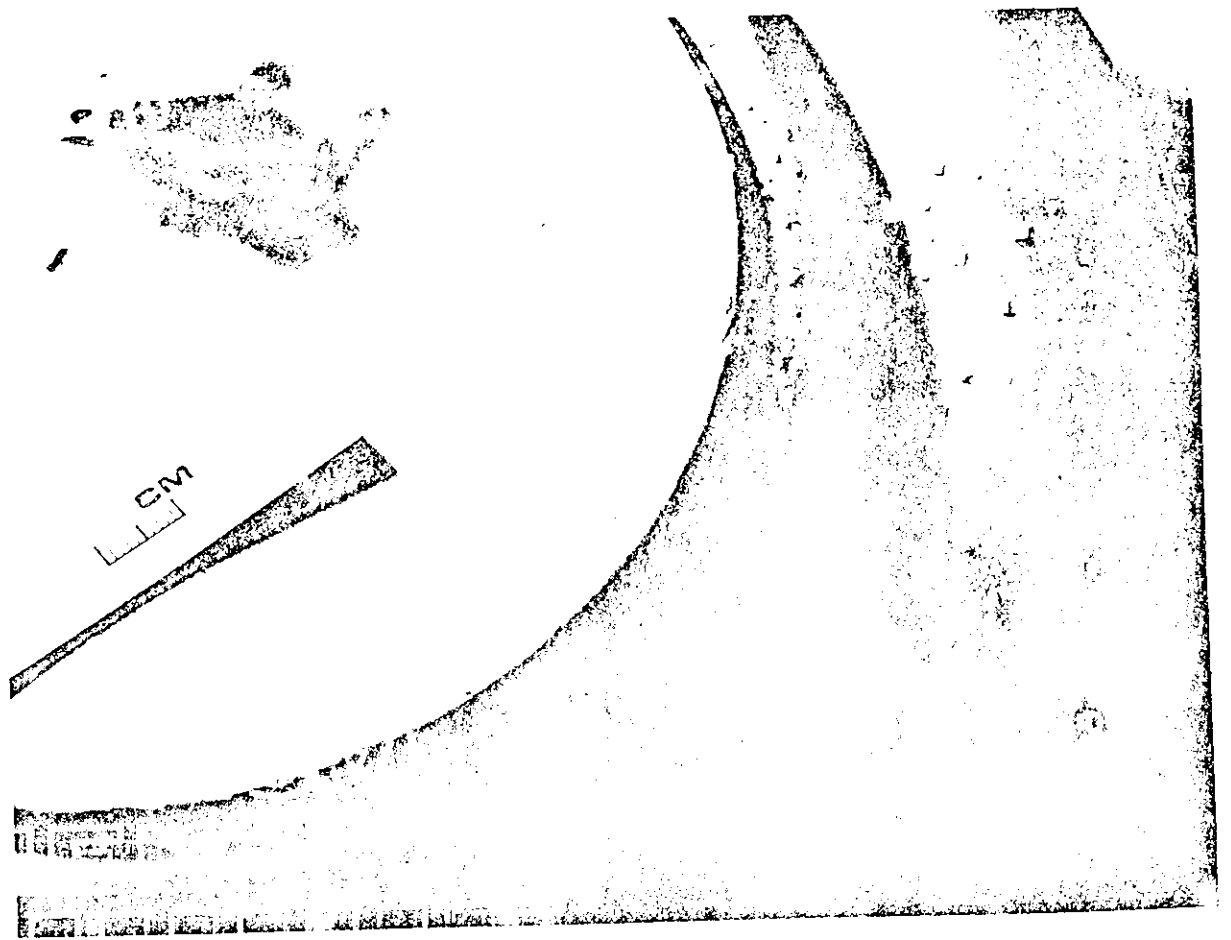


Figure 3b. Reverse side of plate

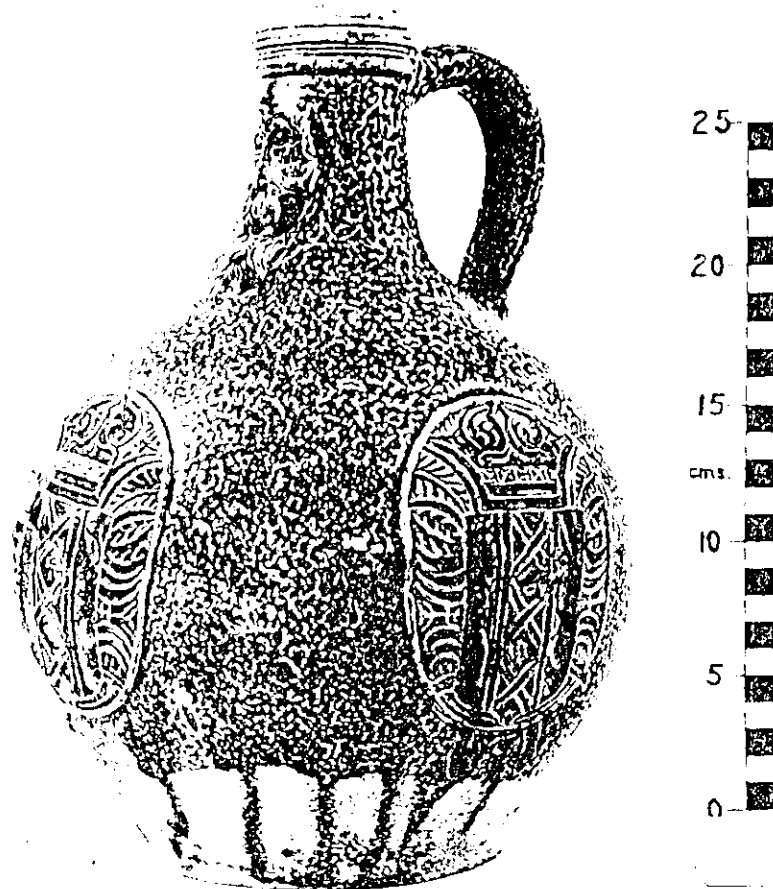


Figure 1. Bellarmine Flagon. Salt-glazed stoneware, with underglaze iron oxide slip and splashes of cobalt blue.



Figure 2. Bellarmine Flagon as recovered, showing coral encrustation.