PROPONTICA
Uluslararası Proponstis Arkeolojisi Dergisi
International Journal of Propontic Archaeology

e-ISSN: 2980-132X, **PROPONTICA**, March 2024, 2 (3): 133-146

Desalination of Underwater Ceramic Cultural Heritage: The Example of Kerpe Underwater Excavation

Sualtı Seramik Kültür Varlıklarında Tuzdan Arındırma: Kerpe Sualtı Kazıları Örneği

Hiranur GÜLTEKİN[1], Serkan GEDÜK[2]

[1]Ankara Üniversitesi, Güzel Sanatlar Fakültesi, Kültür Varlıklarını Koruma ve Onarım Bölümü, Keçiören, Ankara
· **hgultekin@ankara.edu.tr** · ORCİD > 0000-0001-9546-4251

[2]T.C. Kültür ve Turizm Bakanlığı, Kocaeli Müze Müdürlüğü, İzmit, Kocaeli
· **serkangeduk@hotmail.com** · ORCİD > 0000-0002-5747-7251

Makale Bilgisi/Article Information

Makale Türü/Article Types: Araştırma Makalesi/Research Article
Geliş Tarihi/Received: 4 Kasım/November 2023
Kabul Tarihi/Accepted:15 Mart/March 2024
Yıl/Year: 2024 | **Cilt – Volume:** 2 | **Sayı – Issue:** 3 | **Sayfa/Pages:** 133-146

Atıf/Cite as: Gültekin, H., Gedük, S. "Desalination of Underwater Ceramic Cultural Heritage: The Example of Kerpe Underwater Excavation" Propontica, 2 (3), March 2024: 133-146.

Sorumlu Yazar/Corresponding Author: Hiranur GÜLTEKİN

https://doi.org/10.56170/propontica.1386168

DESALINATION OF UNDERWATER CERAMIC CULTURAL HERITAGE: THE EXAMPLE OF KERPE UNDERWATER EXCAVATION

ABSTRACT

Salinity, which is one of the chemical properties of the marine environment, is mixed into seawater due to the dynamic exchange processes between the atmosphere and the hydrosphere and the dissolution of the shells of marine organisms on the seabed. The amount of soluble salts is measured in parts per million (ppm), but in this article, it is measured in parts per thousand (ppt). When soluble salts are not removed by appropriate conservation methods, they crystalize in the pores of artefacts that constitute underwater cultural heritage. These crystals cause physical deterioration in ceramics, which are porous cultural heritage, such as fragmentation from the surface and microscopic cracks. For this reason, the first step in repairing cultural remains recovered from underwater archaeological excavations is to determine the physical properties of the artefacts, such as porosity and salt absorption capacity, as well as the type and amount of salt accumulated in their pores. Thus, the appropriate desalination method can be selected, and estimates can be made on how long the desalination process will take. This paper studied ceramic sherds of Roman and Byzantine amphorae and cooking vessels recovered during underwater excavations in the ancient harbor of Kerpe Bay in Kocaeli, Turkey, in 2022. The aim of the study was to make a preliminary examination for further studies, including instrumental analyses, and to determine the types and amounts of salt deposited on the samples. The samples were desalinated for one month in 200 ml containers with weekly changes of deionized water, and the desalination water was tested to measure salinity and determine the dissolved salt species. Spot tests were used to determine dissolved salts. Sulphate, chloride and carbonate were found in the samples due to these tests. The porosity of the samples was determined by the water absorption method.

Keywords: Underwater Cultural Heritage, Kerpe Underwater Excavations, Ceramic Cultural Heritage, Dissolved Salts, Desalination.

❁❁❁

SUALTI SERAMİK KÜLTÜR VARLIKLARINDA TUZDAN ARINDIRMA: KERPE SUALTI KAZILARI ÖRNEĞİ

ÖZ

Deniz ortamının kimyasal özelliklerinden biri olan tuzluluk, atmosfer ve hidrosfer arasındaki dinamik değişim süreçleri ve deniz dibindeki deniz canlılarının kabuklarının çözünmesi nedeniyle deniz suyuna karışmaktadır. Çözünebilir tuzların miktarı milyonda parça (ppm) olarak ölçülmektedir ancak bu makalede binde parça (ppt) olarak ölçülmüştür. Çözünebilir tuzlar uygun koruma yöntemleriyle uzaklaştırılmadığında, sualtı kültür mirasını oluşturan eserlerin gözeneklerinde kristalleşir. Bu kristaller gözenekli kültür varlıklarından olan seramiklerde yüzeyden parça dökülmesi, mikroskobik çatlaklar gibi fiziksel bozulmalara neden olur. Bu nedenle sualtı arkeoloji kazı çalışmaları sonunda ele geçen kültür kalıntılarının onarımın ilk aşaması; eserlerin gözeneklilik ve tuz emme kapasitesi gibi fiziksel özelliklerinin ve gözeneklerinde biriken tuzun türü ve miktarının belirlenmesidir. Böylece hem uygun tuzdan arındırma yöntemi seçilebilir hem de arındırma sürecinin ne kadar zaman alacağı üzerinde tahminler yapılabilir. Bu çalışmada Kocaeli, Türkiye'deki antik liman Kerpe Körfezi'nde 2022 yılında gerçekleştirilen sualtı kazılarında ele geçen, Roma ve Bizans Dönemine tarihlenen amphora ve pişirme kaplarına ait seramik parçalar üzerinde çalışılmıştır. Çalışmanın amacı; örnekler üzerinde yapılacak analitik analizleri de içerecek sonraki çalışmalar için bir ön inceleme yapmak ve örneklerde biriken tuz türleri ile miktarının tespit edilmesidir. Örnekler bir ay boyunca 200 ml'lik kaplar içerisinde haftalık deiyonize su değişimleri ile tuzdan arındırılmış ve tuzdan arındırma suyu, tuzluluğu ölçmek ve çözünmüş tuz türlerini belirlemek için test edilmiştir. Çözünmüş tuzların belirlenmesi için spot testler kullanılmıştır. Bu testler sonucunda örneklerde sülfat, klorür ve karbonat bulunmuştur. Numunelerin porozitesi su emme yöntemi ile belirlenmiştir.

Anahtar Kelimeler: Sualtı Kültür Mirası, Kerpe Sualtı Kazıları, Seramik Kültür Mirası, Çözünebilir Tuzlar, Tuzdan Arındırma.

❁❁❁

INTRODUCTION

Ceramics are the most frequently recovered in underwater excavation or protected archaeological sites. Ceramics, which were used in ancient times, constitute a dating source for archaeologists with their typology and production technology. In addition, the production techniques of ceramics provide information about the level of technological development of the societies to which they belonged. Therefore, choosing appropriate conservation methods means protecting the information that can be obtained from the materials.

Many factors affect the conservation process and the underwater deterioration of the ceramic. Among all, the physical and chemical properties of the clay and the additives within that for reducing the firing temperature or facilitating the processing are worth noting. For instance, cleaning the biological layers accumulated underwater on any ceramic surface by mechanical methods gives better results for ceramics with low porosity due to their firing at high temperatures[1]. The desalination phase, which is one of the first stages of the conservation practices applied to underwater ceramic finds, is important. The porosity and firing temperature of ceramics are physical properties that affect salt accumulation. As the pore size increases, the amount of water absorbed increases. In ceramics fired at high temperatures, the pores close and shrink. This results in less accumulation of dissolved salts in low-pore-size ceramics such as porcelain[2].

The ‰ ratio of soluble anions and cations that make up the salinity of seawater is called salinity. The elements with concentrations higher than 100 ppm in seawater are chloride, sodium, sulfate, magnesium, calcium, and bicarbonate, also called primary ions. Among these, sodium, magnesium, and calcium are cations (positive ions), while chloride, sulfate and bicarbonate are anions (negative ions)[3].

The deterioration of ceramic artefacts recovered from underwater excavations caused by soluble salts in the seawater is primarily physical. The drying of soluble salts without appropriate desalination processes causes the crystallization of dissolved salts in the sea salt, which, in the end, fills the pores of the artefact. This crystallization may occur on the surface of the artefact during the evaporation of the seawater accumulated in the pores, or it may occur inside the pores. In such a case, the salt crystals accumulated in the pores may create mechanical pressure, resulting in cracks in the artefacts and, in more advanced cases, fractures[4]. Due to the solid physical strength of ceramic artefacts, such fracture deterioration occurs mainly on the surfaces. Micro-cracks and fractures on the surface in the form of a network can cause the loss of particle where the surface layer exfoliates[5]. The extent to which the salts are deposited in pores varies according to the clay structure, which has been investigated experimentally by O'Brien[6]. In recent studies that depend on instrumental analysis, it has been observed that as the pore size of ceramics increases, the amount of salt absorbed increases as well, which results in the overall increase of salt crystallization[7].

The desalination process is carried out in a process that can also be referred to as gradual desalination. The seawater accumulated in the ceramic pores is gradually replaced first with tap water and then with deionized water[8]. This process is prolonged depending on the physical and chemical structure of the ceramic and the amount of soluble salt it absorbs during its underwater stay. Salts in the clay it-

1 Ricca et al. 2021, 11.
2 Du et al. 2019, 8.
3 Morrissey – Sumich 2012, 67-69; Geldiay – Kocataş 2014, 50-55.
4 Pearson 1987, 100.
5 Zornoza-Indart et al. 2011, 255.
6 O'Brien 1990, 393-40.
7 López-Arce et al. 2012, 2041.
8 Pearson 1987, 256-257; İvgin 2021, 83-85.

self and the additives used in ceramic production change the desalination process. For example, calcium is also present in natural clay or substances such as ash used during the manufacturing of ceramics. During the desalination process, there is a risk that the salts contained in the ceramic paste will dissolve and be removed from the ceramic[9].

The ceramic sherds subject to this study were excavated in the summer of 2022 in the harbor of the Black Sea city Kocaeli within the scope of the Archaeological Underwater Excavations in Kerpe Bay (Fig.1). The underwater excavations located in the harbor area of the ancient city of Kalpe have been carried out by the Directorate of the Kocaeli Archaeological Museum since 2020 with the permission of the Ministry of Culture and Tourism. The first results of the research showed the connection of the harbor with the ancient city of Nicomedia and drew attention to its importance in the maritime trade in the Black Sea [10]. The study's sample group was selected among cooking pots belonging to different vessels, where soot residue can be observed in microscopic images and resin residues are charred. This study aimed to determine the samples' porosity and the type of dissolved salt deposited in the pores of the sherds. Studies, including instrumental analyses such as firing temperature determination and dating, are planned to be carried out on the samples. For this reason, the determination of the physical properties and salt types of the samples is intended as a preliminary study for future analyses.

Fig. 1: Exact place of the Kerpe excavation 2022 season (Writers personal archive)

9 Rice 1987, 97.
10 Gedük – Çomak 2022, 12; Gedük – Bilir 2022: 66-95.

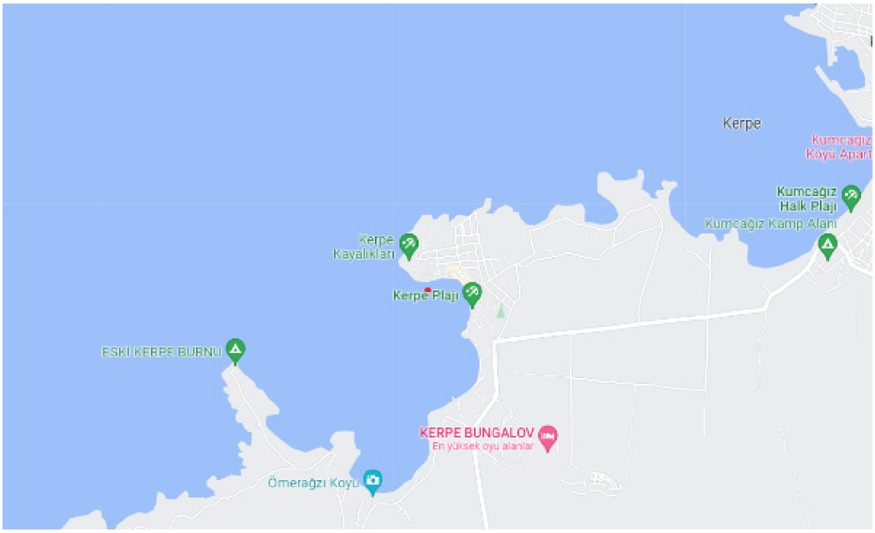


Fig. 2: Location of the Kerpe Bay showing the location of the excavation (Google Maps)

MATERIALS AND METHODS

The proper examination of the effects of the desalination process, according to the physical properties of ceramic clay and the type of soluble salts, was necessary. Thus, the sample group was selected from ceramic pieces that could be completely covered with water when placed in 200 ml containers. Although the sample sizes were kept as equal as possible, each sample had a different weight due to the dough structure. The charred resin residues found on the inner surface of KP22-S22 and KP22-S26 reinforce the idea that the sherds were exposed to high temperatures after production (Fig. 3). Billur Tekkök Karaöz meticulously dated the samples taken from the jugs or cooking pots to the Hellenistic, Roman, Late Roman, Byzantine and Principalities Periods according to the physical characteristics of the ceramics. None of the samples has any joining fragments. The images from the surface and cross-sectional parts of the samples taken with the digital microscope show the clay characteristics of the ceramics and the accumulated soot layer (Fig. 4). The samples were dried without desalination following their excavation and were stored at room temperature within polyethylene bags. Examination by the digital microscope enabled us to observe salt crystals on the ceramic finds (Fig. 5).

The desalination process was carried out with four water changes in 1 month using deionized water, i.e., with changes every 7 days (Fig. 7). *Hanna HI 98319 'Marine' Salinity Meter* was used as the measuring device. The salinity of the deionized water was tested before first use and determined as 0.0 ppt. The average temperature of the water during desalination was 19˚C. The water absorption method was used to measure the porosity (*PA*) of the samples. For this method, small ceramic sherds which were taken from samples weighted with a precision balance (300 gr / 0.001 gr) after dried in oven at 105ºC (*W1*). Pieces were put in 25 ml containers, covered with deionized water, and boiled for 5 hours. After the water inside the containers cooled down at room temperature, ceramic pieces were removed, gently wiped with paper towels, and weighed again (*W2*). For measuring the water-immersed weight, each piece was placed in 25 ml containers without drying and weighted once again with precision balance (*W3*)[11].

$$PA = \frac{W2 - W1}{W2 - W3} X\ 100$$

Fig. 3: Charred resin residues on the inner surface of samples KP22-S19 on the left and KP22-S26 on the right (Kocaeli Museum Archive).

RESULTS AND DISCUSSION

When the ceramic pieces were placed in deionized water at the beginning of the desalination process, air bubbles were observed (Fig. 4). These air bubbles indicated that open pores inside the ceramic were still filled with air. The sudden increase in the measurement taken during the second water change was observed on two consecutive days. The high measurement values taken before the second water change were not observed in the third and fourth measurements (Fig. 7). The sudden increase in the second water change during desalination is an expected situation that has been previously recorded in scientific studies.

11 Rice 1992, 352-353.

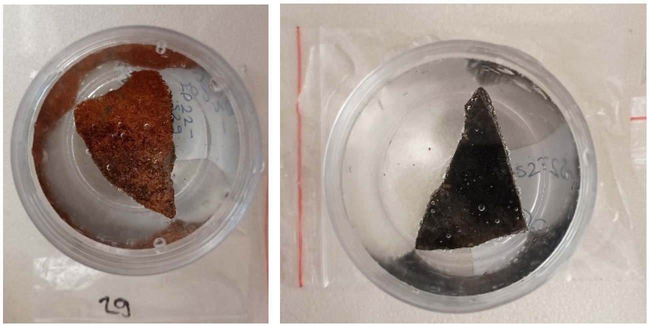


Fig. 4: Bubbles coming inside from ceramic indicate the open pores filled with air. (Kocaeli Museum Archive)

Porosity tests on the samples according to the water absorption method show that the average porosity of the samples is 20%. Samples that have higher porosity are recorded as KP22-S3, KP22-S19, and KP22-S3, which have a porosity of over 25% (Fig. 8).

Determination of the type of soluble salts deposited in the ceramic shards was carried out using spot tests for each sample after one week of desalination. At the end of the one month, the final desalination water was also tested as some types of salts need longer durations to desalinate, as proven by other studies[12]. The manual published by İBB KUDEB (Istanbul Metropolitan Municipality Directorate of Protection Implementation and Supervision) was essential in determining the types of soluble salts[13]. According to the spot test, carbonates were evident in all the samples. This is in line with the results of the previous studies, considering that marine remains were found intensively in the excavation area. None of the samples had nitrates but rather sulphates, except for KP22-S29 and KP22-S30 (Fig. 9). According to previous studies, the presence of sulphates may point to the activity of sulphate-reducing bacteria[14]. However, in our case of the sample group, further studies are needed to determine the existing activity of the sulphate-reducing bacteria.

CONCLUSION

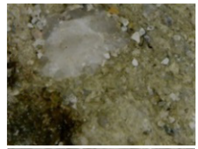
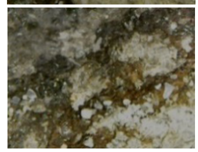
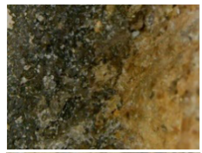
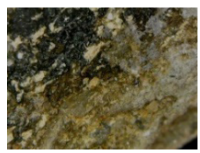
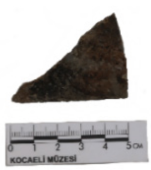
Dating of the pottery from the Kerpe harbor were realized according to their clay structures. According to this dating, the harbor has been in use since the Hellenistic period. Further dating of the pottery via instrumental analysis or comparison with typological classification is a subject for further studies.

12 MacLeod – Davies 1987, 1005-1007.
13 Alkan et al. 2011, 58-60.
14 Montana et al. 2014, 407-408.

Physical tests on the selected samples showed that each had high porosity rates and exposure to high temperatures after production may cause changes in their physical properties. The presence of soot residues on the surfaces of most of the sherds and their classification as cooking vessels further supports this argument. This structure of the sherds indicates that the desalination process may take a relatively long time during conservation. Among the salt species identified by spot tests, carbonates can be considered as usual due to the nature of the excavation area. However, further research is needed to clarify the source of sulfates. Yet, given the level of sulfates in normal seawater, the most likely origin for their occurrence here can be reasoned by the marine environment. Desalination of the ceramics was fast owing to their porosity, and the removal of salts in one month was speedy compared with more than two thousand years of immersion in seawater.

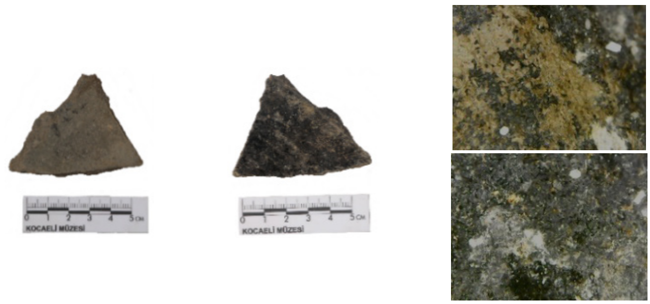
SAMPLE CODE	COLOR of the CLAY	TYPE of CERAMIC	PHYSICAL PROPERTIES of CERAMIC PASTE	PREDICTED DATE
KP22-S3	Grey	Cooking pot	Soft, powdery, small pores	Hellenistic
KP22-S19	Red	Jug	Hard, fragile, without an intense burn mark on the surface	Byzantian
KP22-S21	Yellow	Cooking pot	Hard, fragile, with an intense burn mark on the surface	Period of Principalities
KP22-S23	Red	Cooking pot	Hard, fragile, with an intense burn mark on the surface	Byzantian
KP22-S26	Cream-Yellow	Cooking pot	Hard, fragile, with an intense burn mark on the surface	Roman
KP22-28	Cream-Yellow	Jug	Soft, powdery, small pores	Roman
KP22-S29	Red	Cooking pot	Hard, fragile, with an intense burn mark on the surface	Byzantian
KP22-S30	Grey	Jug	Hard, fragile, without an intense burn mark on the surface	Roman
KP22-S31	Cream	Cooking pot	Soft, powdery, small pores	Late Roman
KP22-S35	Grey	Cooking pot	Hard, fragile, with an intense burn mark on the surface	Byzantian or Period of Principalities

Fig. 5: Information about the sample group of the study.

SAMPLE CODE	INTERIOR SURFACE PHOTO	EXTERIOR SURFACE PHOTO	USB MICROSCOPE IMAGE
KP22-S3			 
KP22-S19			 
KP22-S21			 
KP22-S23			 

KP22-S26

KP22-S28



KP22-S29

KP22-S30

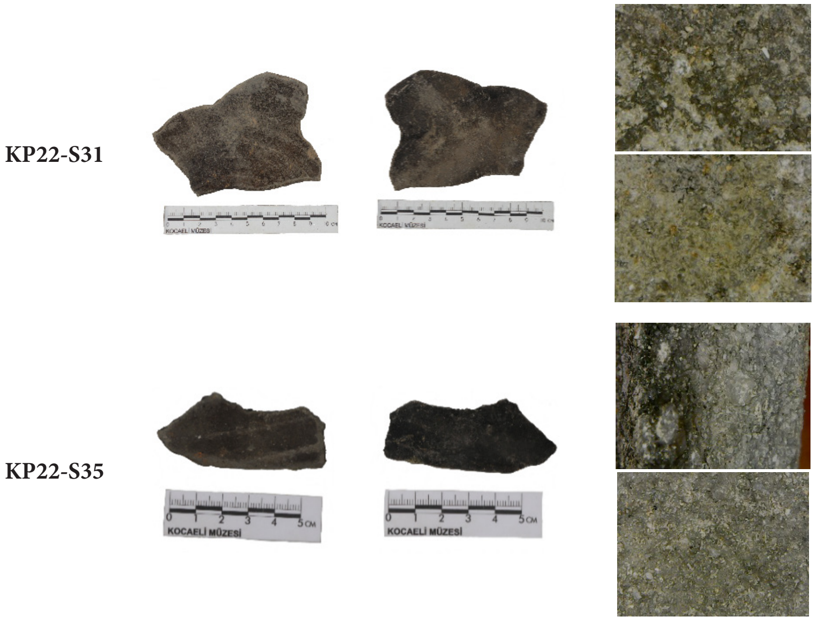


Fig. 6: Digital microscope images of crystallized dissolved salts and clay properties of ceramic samples. (Kocaeli Museum Archive)

SAMPLE CODE	1. water change	2. water change	3. water change	4. water change
	21/09/2023	28/09/2023	06/10/2023	12/10/2023
KP22-S3	0.2	2.6	0.4	0.1
KP22-S19	0.6	1.8	0.3	0.0
KP22-S21	0.3	1.5	0.2	0.0
KP22-S23	0.2	0.9	0.1	0.0
KP22-S26	0.4	2.1	0.2	0.0
KP22-S28	0.5	1.3	0.1	0.0
KP22-S29	0.2	0.4	0.0	0.0
KP22-S30	0.5	2.2	0.3	0.0
KP22-S31	0.4	1.5	0.2	0.0
KP22-S35	0.5	1.8	0.2	0.0

Fig. 7: Desalination schedule before water changes (The unit of measurement is ppt).

SAMPLES	DRY WEIGHT (g)	WET WEIGHT (g)	WATER IMMERSED WEIGHT (g)	POROSITY (%)
KP22-S3	4.7322	5.4320	2.7219	**25.82**
KP22-S19	3.1313	3.5493	1.9013	**25.36**
KP22-S21	4.7340	5.2235	2.7574	**19.85**
KP22-S23	4.1667	4.6862	2.5438	**24.25**
KP22-S26	5.5868	6.3191	3.3542	**24.70**
KP22-S28	4.2270	4.7096	2.5653	**22.51**
KP22-S29	3.2480	3.5983	1.9272	**20.96**
KP22-S30	4.1813	4.7750	2.5517	**26.70**
KP22-S31	5.0937	5.6045	2.9831	**19.49**
KP22-S35	5.0235	5.5186	3.0086	**19.73**

Fig. 8: Porosity of the samples according to water absorption method.

SAMPLES	SULPHATE (SO_4^{2-})	CHLORITE (Cl^-)	CARBONATE (CO_3^{2-})	NITRATE (NO_3^-)
KP22-S3	+++	++	+	-
KP22-S 19	+	-	+	-
KP22-S 21	++	-	+	-
KP22-S 23	+	-	+	-
KP22-S 26	+	-	++	-
KP22-S 28	+	-	+	-
KP22-S 29	-	-	+	-
KP22-S 30	-	-	+	-
KP22-S 31	++	++	+	-
KP22-S 35	+	-	+	-
Desalination water after one-month period	++	+++	+	-

Fig. 9: Types of salt tested from desalination water after one week.

Conflict of Interest

Within the scope of the study, there is no personal or financial conflict of interest between the authors.

Ethics

Regarding the Ethics Committee authorisation; the authors and reviewers of this study have declared that there is no need for Ethics Committee authorisation.

Author Contribution

Design of Study: HG (% 100)

Data Acquisition: HG (% 50), SG (% 50)

Data Analysis: HG (% 100)

Writing Up: HG (% 90), SG (% 10)

Submission and Revision: HG (% 100)

REFERENCES

Alkan et al. 2011, Alkan, N. – Çağıran, E. – Ersan, H. Ö. – Eruş, M., Restorasyon ve Konservasyon Laboratuvarları, İstanbul.

Du et al. 2019, Du, J. – Luo W. – Li N. – Wang, C., "Characterization Of the Micro-Contaminants from the Inner-Body of Kraak Porcelain Excavated from the "Nan'ao I" Shipwreck, The South China Sea", Heritage Science, 7, 1, 1-9.

Gedük – Bilir 2022, Gedük, S. – Bilir, A., "Kerpe Koyu Sualtı Araştırmaları ve Sualtı Kazısı", TINA Denizcilik ve Arkeoloji Dergisi, 18, 66-95.

Gedük – Çomak, 2022, Gedük, S. – Çomak, A., "Nikomedia'nın Karadeniz'e Açılan Kapısı: Antik Kalpe (Kerpe) Limanı", Sosyal Bilimler Araştırma Dergisi (KOUSBAD), 16, 1-14.

Geldiay – Kocataş 2014, Geldiay, R. – Kocataş, A., Deniz Biyolojisi, Bursa.

İvgin 2021, İvgin, İ, "Sualtından Ele Geçirilen Pişmiş Toprak Kültür Varlıklarının Yüzey Temizliği Hakkında Bazı Düşünceler", Journal Of Ceramic Research, SRMK 3, 78-98.

Lopez-Arce et al. 2013, López-Arce, P. – Zornoza-Indart, A. – Gomez-Villalba, L. – Pérez-Monserrat, M. E. – Alvarez De Buergo, M. – Vivar, G. – Fort, R., "Archaeological Ceramic Amphora from Underwater Marine Environments: Influence of Firing Temperature and Salt Crystallization Decay", Journal of European Ceramic Society, 33, 10, 2031-2042.

MacLeod – Davies, 1987, MacLeod, I. D. – Davies, J. A., "Desalination of glass, stone and ceramics recovered from shipwreck sites", In ICOM committee for conservation: 8th triennial meeting, Sydney 1987, 3, 1005-1007.

Montana et al. 2014, Montana, G. – Randazzo, L. – Castiglia, A. – La Russa, M. F. – La Rocca, R. – Bellomo, S., "Different Methods For Soluble Salt Removal Tested On Late-Roman Cooking Ware From A Submarine Excavation At The Island Of Pantelleria (Sicily, Italy)", Journal Of Cultural Heritage, 15, 4, 403-413.

Morrissey – Sumich 2012, Morrissey, J. F. – Sumich, J. L., Introduction to the Biology of Marine Life, Jones & Bartlett Learning.

O'Brien 1990, O'Brien, P., "An Experimental Study of the Effects of Salt Erosion on Pottery", Journal of Archaeological Science, 17, 4, 393-401.

Pearson 1987, Pearson, C., "Deterioration of Ceramic and Stone", Conservation of Marine Archaeological Objects, (ed. Colin Pearson), London, 99-104.

Ricca et al. 2021, Ricca, M. – Camara, B. – Fort, R. – De Buergo, M. Á. – Randazzo, L. – Petriaggi, B. D. – La Russa, M. F., "Definition Of Analytical Cleaning Procedures for Archaeological Pottery from Underwater Environments: The Case Study of Samples from Baia (Naples, South Italy)", Materials & Design, 197/109278, 1-12.

Rice 1992, Rice, P. M., Pottery Analysis: A Sourcebook, The University of Chicago Press, Chicago.

Zornoza-Indart et al. 2011, Zornoza-Indart, A. – López-Arce, P. – Gómez-Villalba, L. S. – Alvarez De Buergo, M. – Fort, R. – Vivar, G. – Bettuzzi, M., "Salt Weathering in Desalinated and Non-Desalinated Ceramic Amphorae from Underwater Marine Environments", Proceedings Of SWBSS, Cyprus 2011, 249-256.