Material selection of high-level nuclear waste storage canisters: Lessons from archaeometallurgy

Archaeometallurgical studies on ancient Indian copper can provide valuable insights in a very important modern technological application, namely high-level nuclear waste storage. The basic philosophy of high-level nuclear storage will be briefly addressed before outlining the utility of copper in the overall storage scheme. It is important to distinguish between short-term and long-term storage of high-level nuclear wastes. During the short-term storage period (which is usually 30 to 50 years but may also extend up to several hundreds of years in certain cases), the spent fuel, after appropriate processing, is allowed to cool down to temperatures adequate for subsequent underground repository storage. In case of long-term nuclear waste storage, the waste has to be stored for periods exceeding 100,000 years in order to allow for complete radioactive decay of the dangerous radioactive species still present in the waste. Of course, we understand that the nuclear waste is first immobilized by incorporation of the waste in a glassy matrix.

The nuclear waste has to be placed in suitable storage canisters for both short- and long-term storage. While the canisters will be free from environmental degradation (i.e. corrosion-related processes) on the inside surface which is in contact with the immobilized nuclear waste, they will, however, be subject to corrosion on the environmental side. In the case of canisters for short-term storage, the environment that would be ‘seen’ by the canister would be atmosphere. In this application, the material of construction of the canister must be capable of withstanding atmospheric corrosion. In this regard, the benefits of applying phosphoric irons are readily apparent because of their excellent atmospheric corrosion resistance. A good example of archaeological analogue providing supporting validation is the example of the 1600-year-old corrosion-resistant Delhi Iron Pillar[1], a classic example of phosphoric iron construction, which has withstood atmospheric corrosion due to the formation of a protective passive film on the surface[2].

In contrast to short-term storage, long term nuclear waste storage must essentially involve storage in deep underground repositories because the time frame involved is much longer. The design life is a minimum 100,000 years. The environment to which the long-term nuclear waste storage canisters will be exposed to will depend upon the storage philosophy adopted by the respective nuclear waste producing countries. For example, the American plan consists of storing the long-term wastes encased finally with a 20 mm-thick canister constructed out of a Ni-based alloy called Alloy 22 (56Ni–22Cr–13.5Mo–3W–3Fe). A 50 mm-thick type 316NG stainless steel inner container will provide the necessary structural integrity. These canisters will be stored in depository caves dug into the Yucca Mountain in Utah[3]. On the other hand, the Finnish and Swedish design of spent nuclear fuel package calls for packing the spent fuel in a canister made of spheroidal graphite cast iron, with an outer shield made of copper. The copper shield is responsible for the corrosion protection of the canister[4].

The design thickness of the wall of the storage canister is an important design parameter and this will be primarily based on the maximum corrosion allowance of the selected material in disposal conditions. Considering copper as candidate canister material, the corrosion rates measured in weight loss coupon tests of relatively short duration (7 days) in bentonite clay environment are of the order of 2 μm/year[4]. This corrosion rate would indicate a lifetime of roughly 2500 years for a designed wall thickness of the copper shield of about 50 mm, assuming that the corrosion products on the surface do not protect the material against further corrosion. This is clearly lower than that required for a life of 100,000 + years. A far bigger problem confronts corrosion scientists because the actual condition of the material after long-term exposure is not known and neither is it possible to obtain such data by laboratory testing alone.

It is in this context that archaeological copper analogues can be very useful in understanding and validating theoretical models for long-term corrosion of copper in burial conditions. For example, archaeometallurgical studies on ancient Indian copper samples[5,6], of conservative age of more than 3000 years, provide valuable information about long-term corrosion of copper in soil conditions. Microstructural analysis of ancient Indian copper samples indicated that the degree of corrosion was not severe and moreover, stress corrosion cracking was not evident from the surfaces of the samples. The corrosion product layer was adherent on the surface and this resulted in much lower corrosion rates than anticipated from short-term laboratory studies. The incursion of corrosion products into the matrix appeared to occur along grain boundaries of the underlying matrix. The intergranular nature of corrosion attack is understandable because of the higher-energy state of material at these locations. Nevertheless, it is also important to note that the incursion of corrosion products along the grain boundaries was not deep enough to warrant the use of the term pitting to describe this kind of environmental corrosion. A complementary conclusion is the lack of any environmentally induced cracking in these materials. This is understandable because dangerous chloride ions were not present in the soil environment to which the coppers were exposed to. This was also verified by the absence of chlorides in the X-ray diffraction (XRD) patterns obtained from the surface patina[5,6]. Therefore, in the environments where chloride ions are excluded, microstructural investigations on archaeological Indian copper prove that there is no danger of stress corrosion cracking.

The question would then arise whether the data obtained for ancient Indian copper will apply for modern copper. Electrochemical polarization studies conducted on ancient Indian copper samples[5,6] clearly established that the coppers were electrochemically similar. The major difference between the samples was the presence of second phase inclusions in the case of the archaeological Cu samples. Against the anticipation that the presence of second phase inclusions would deleteriously affect corrosion rates, electrochemically measured corrosion rates in 3.5% NaCl solution of Chalcolithic Cu sample (175 μm/y) and OCP Cu sample (185 μm/y) were only marginally higher than that of modern Cu (55 μm/y)[6]. These data co-relate well with the published corrosion rate for Cu in seawater (25–127 μm/y). In the case of archaeological coppers, the second phase slag particles appear to have slightly enhanced the dissolution tendencies, which could probably be due to galvanic coupling action of the Cu matrix with the slag inclusions. It is to be noted that the sulphides are electrically conducting and they aid in the establishment of local galvanic cells. The effect of the inclusions was not significant because the volume fraction of inclusions was relatively low and, moreover, they were not interconnected but widely dispersed.

As the electrochemical behaviour of ancient coppers is almost similar to that of modern copper, it implies that ancient and modern Cu samples are almost similar chemically. As the ancient Indian copper samples have successfully withstood corrosion under *unplanned* soil burial conditions for such a long time, it indicates that modern-day *planned* burial of copper must also behave similarly. The corrosion of copper exposed to the soil environment will be the critical factor. As ancient Indian copper has proved that it can withstand corrosion in Indian soil conditions over a long period of time, it must be seriously considered as the material of construction of outer canisters for long-term underground storage of nuclear wastes.

Additionally, information about long-term corrosion processes can be also obtained from characterization of surface patina on ancient Indian coppers. This will help in validating long-term corrosion models. For example, XRD patterns obtained from the surfaces, as a function of depth, help in understanding the sequence of formation of corrosion products. The results of XRD analysis conducted on ancient Indian copper[6] revealed that the first product to form was cuprite, followed by the formation of sulphates and oxysulphates, due to the presence of S in the environment.

A significantly large amount of ancient Indian copper objects are presently locked up in Indian museums and archaeological storerooms, waiting to be analysed. The interaction and co-operation of people skilled in metallurgical knowledge with archaeologists will greatly benefit in creating a knowledge database on ancient Indian copper. This will aid in material selection of high-level nuclear waste storage canisters.

1. Balasubramaniam, R., *Curr. Sci.*, 2002, **82**, 1357.
2. Balasubramaniam, R., *Corros. Sci.*, 2000, **42**, 2103.
3. Dunn, D. S., Pensad, O., Brossi, C. S., Cragnolin, G. A., Sridhar, N. and Ahn, T. M., In Proceedings of the International Workshop on Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems (eds Feron, D. and Macdonald, D. D.), European Federation of Corrosion Publications, Number 36, The Institute of Materials, Minerals and Mining, London, 2003, pp. 261–279.
4. Rosborg, B., Karnland, O., Quirk, G. and Werme, L., *ibid*, pp. 287–304.
5. Laha, T., Shankar, J., Balasubramaniam, R., Prabhakar, V. N., Sharma, D. V. and Banerjee, D., *Indian J. Hist. Sci.*, 2002, **37**, 321.
6. Srivastava, A. and Balasubramaniam, R., *Bull. Mater. Sci.*, 2003, **26**, 593.

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Do lichens still grow in Kolkata City?

Kolkata is India's largest metropolis. It is one of the fastest growing cities in eastern India. During the last few decades it has become overcrowded by the population explosion. Increased urbanization, industrialization and heavy vehicular traffic have resulted in deterioration of air quality in the city. Lichens among the plant group have long been recognized as sensitive indicators of environmental condition. The decline of lichens around the city centre due to air pollution is well studied throughout the world[1]. Lichens show their sensitivity to air pollution in different ways such as decline in diversity, absence of sensitive species and morphological, anatomical and physiological changes[2]. Thus to get an idea about the change of lichen diversity in relation to the increased urbanization in the Kolkata, a field survey was attempted both in and around Kolkata and Howrah (Indian Botanic Garden (IBG)) cities. The collection was made in the same localities from where earlier records of the lichens were available.

The identification of specimens revealed the occurrence of 25 species of lichens belonging to 11 genera and 10 families. Among the different localities, IBG exhibits the maximum diversity of lichens represented by 15 species. The boundary areas of Kolkata city have scarce growth of few lichens, while the heart of the city is devoid of lichens[3].

Das *et al.*[4] during 1986 studied the frequency of lichens in 25 streets of Kolkata ('Calcutta') city in relation to traffic load and reported the occurrence of only *Parmelia caperata*, a pollution-tolerant species on the trees in the streets. Frequency of occurrence of lichens from 13.4% to 93.3% on roadside trees withstanding a traffic load of 23.6 to 0.4 vehicles per minute was reported. However, in the present study it has been noticed that no tree vegetation exists in the streets. The few avenue trees that were present on the roadside do not host lichen growth.

The available oldest record of lichen collection in IBG belongs to Kurz, who made intensive lichen collection in the year 1865, out of which 53 species (19 new) for Kolkata were described[5]. During the sixties of the last century, Awasthi attempted to recollect one of the endemic, monotypic taxon (*Pyrgidium bengaliense* Krempelh.) in the type locality (IBG) on the same habitat (bark of *Ravenela madagascariensis)* but had been unsuccessful[6]. The comparison of the present lichen flora of IBG with the situation around 1865 clearly exhibit the extent of the loss of lichen flora in the area. The present record of lichens will provide a basis for further (experimental) research concerning the influence of air pollution and urbanization on the lichens.

The perceptible decline in the vegetation cover, the loss of species-specific habitats over the years, the increase in industrial areas and growth of large urban areas are some of the leading factors resulting in the loss and change of diversity of lichens in India[7]. Another factor with a potential influence in the natural distribution of