Vol. XLV, No. 2, 2020

Man and Environment

Indian Society for Prehistoric and Quaternary Studies

A.K. Kanungo *et al.*, *Man and Environment* XLV(2): 87-94 [2020].

Understanding Ancient Zinc Technology: An Experimental Study

Alok Kumar Kanungo, K. Raviteja, Oishi Roy and Jeewan Singh Kharakwal[1]

Archaeological Sciences Centre, IIT Gandhinagar, Palaj, Gandhinagar 382355
Email: alok.kanungo@iitgn.ac.in

1. Sahitya Sansthan, JRN Rajasthan Vidyapeeth, Udaipur 313001

Abstract

The ancient zinc furnace at Zawar was excavated in December 1983, and since then, there have been a number of publications on the same. With these, the antiquity of zinc mining in the Zawarmala has been traced back to 5th century BCE, and the production of metallic zinc to 9th century CE. It has been further postulated that the method of zinc extraction has been a downward distillation process. The furnace, the retorts and the pyro technology that has been recorded is one of its kinds and thus a local innovation. Based on the findings, archaeometallurgical investigations were carried out and, on the basis of derived data, the furnace which was probably used for zinc smelting was conjecturally recreated. Bringing the raw material from the original source and following the published literature, the authors carried out an experimental zinc extraction at Indian Institute of Technology, Gandhinagar. Following which, they analysed both the retorts and zincs from Zawarmala, and what they obtained in their experimental study under XRD. The present paper is an outcome of this experimental study.

Introduction

Zinc (Zn) is a non-ferrous base metal, which is generally found in bluish-white, yellow, brown or in black colour. Its chief and important minerals are sphalerite or zinc blende, smithsonite, calamine, zincite, willemite and franklinite. As zinc is a relatively volatile metal, it boils at 907 °C under controlled atmospheric conditions. However, the beginning of the reduction process of zinc oxide to zinc by carbon starts at 950 °C. Therefore, successful extraction of zinc in a retort made of suitable refractory material would be achieved at a temperature of 1150-1200 °C. For pure zinc production; therefore, distillation technology was developed, in which, India has been one of the pioneers. Zinc is used for galvanising iron and steel, brass making, alloying, manufacture of white pigment in chemicals and medicines. But in ancient times, it was mainly used for brass making. In fact, brass has a much longer history than zinc. Brass can be produced either by smelting copper ores containing zinc or copper and zinc ore in reduced condition or by mixing copper and zinc metals.

As far as India is concerned the firm evidence of zinc smelting is known only from Rajasthan.

Zawar: The Oldest Production Centre of Zinc

Zawar (24° 21′ N; 73° 41′ E), situated in the Aravalli Hills about 38 km south of Udaipur, Rajasthan, is the only known ancient zinc smelting site in India. The entire valley of Tiri at Zawar is marked by immense heaps of slag and retorts, which indicate a long tradition of zinc smelting. The perennial Tiri River and the associated geological deposits are the Precambrian rocks traversed by veins of spalerite and galena. Tod (1829), Crookshank (1947), Carsus (1960), Mookherjee (1964), Morgan (1976), Strackzeck and Srikantan (1967) and Werner (1970) reported the evidences of deep mine working and extensive heaps of debris at the site which were probable markers of ancient mining and smelting practice. The excavated site at Zawar when located was a massive debri heap of fragmented zinc distillation retorts, some used and a few unused, along with furnace fragments and ash (Fig. 1). The location of the site is important because of its close proximity to argentiferous zinc – lead ore which are embedded in the dolomite formation. The area under question is now controlled by the Hindustan Zinc Limited (HZL). Besides Zawar, the evidence of early zinc mining and smelting has also been found 2 km south east of village

Fig. 1: Spent retorts and furnace remains at Zawar

Received : 11-07-2020
Revised : 19-08-2020
Accepted : 01-09-2020

Kaya (6 km north of Zawar, and about 15 km south of Udaipur town) in the form of small retort heap and ancient mine workings in the adjacent hills.

Previous Work

The exploratory work at Zawarmala by archaeometallurgist P.T. Craddock, geologist L.K. Gurjar, and archaeochemist K.T.M. Hegde led to a path breaking paper published in 1983 on zinc production in Medieval India. This was followed by the pioneering archaeometallurgical investigation by a team formed from the Maharaja Sayajirao University of Baroda, British Museum and HZL under the joint leadership of K.T.M. Hegde, P.T. Craddock and H.V. Paliwal in the same year. The work yielded evidence of ancient mining and smelting of zinc along with *in situ* furnaces and retorts used for zinc smelting from the dam fill at Zawar (Craddock *et al.* 1983, 1985, 1989; Willies *et al.* 1984; Freestone *et al.* 1985; Paliwal *et al.* 1986; Craddock 1986, 1998; Hegde 1989, 1991; Gurjar *et al.* 2001). Kharakwal and Gurjar (2006) situated the Zawar zinc in Indian archaeology perspective and Kharakwal (2011) situated the same in the world perspective. All these works hypothesised the extraction method of zinc to be through the downward distillation process.

Evidences found from the excavations at Zawar revealed featureless mine walls and presence of charcoal ash. Evidences of fire setting used to widen the rock joints were also noticed. Along with these, evidence of mining tools like iron chisels, pestle shaped hammers and pear shaped pots which were used for transporting water into the mines were recovered. Ancient wooden ladders, scaffolds and launders used for draining water from a higher to a lower level were also noticed.

Craddock *et al.* (1985) have pointed out that zinc ore was being mined from the 5th century BCE (PRL 932 430 $\pm$ 100 BCE; BM 2381 380 $\pm$ 50 BCE) at Zawar. Radiocarbon dates suggest the deposits here were exploited for lead and silver for at least two thousand years; and the metallic or pure zinc was produced here by the distillation process from around the 9th century CE. The earliest evidence of zinc smelting on an industrial scale is the carbon date of 840 $\pm$ 110 CE recovered for one of the heaps of white ash removed from zinc smelting furnace (Gurjar *et al.* 2001: 633). It appears that the main expansion of the industrial phase of zinc production began at Zawar sometime from the 11th or 12th century. Several radiocarbon dates bracketed between the 12th and 18th century also confirm to this activity.

The method of extraction of zinc is regarded to be a path breaking technological advancement as zinc boils at 907 °C and the smelting temperature required is higher than what is generated to reduce the oxide in the presence of carbon. Therefore, the metal is liberated as gas and a distillation process is required rather than smelting. The theories were developed based on the findings of the zinc distillation furnace at Zawar.

Various scientific studies were done revolving petrographic analysis of retorts and samples from the furnace walls which revealed that local material was utilised. An Energy Dispersive Analysis of X-rays (EDAX) was also done so as to derive a quantitative chemical compositional data of the retorts.

Firing temperature was also recorded based on the degree of vitrification and it was recorded at 1200-1250 °C. The analysis was done using the heat conduction equation where the relation between temperature gradients which developed on the furnace wall and the time span of the smelting process was calculated (Tite *et al.* 1985).

Conjectural Reconstruction of the Furnace

At Zawarmala, an array of seven distillation furnaces, roughly squarish on plan (67 x 69 cm at base), were discovered. Each furnace had two chambers, upper and lower one, separated by 5.50 cm thick perforated plate of clay (four combined to form a single square). Each clay plate had 9 large holes (3.50 cm diameter) to accommodate the snouts of the retort's condenser, and 26 smaller holes (plus 9 shared with neighbouring plate) for the passage of

Fig. 2: Excavated zinc extraction furnace at Zawar (Photography by L.K. Gurjar)

the air into the furnace and for the ash to drop through. It is presumed by the excavators that the furnaces may have looked like truncated pyramids and their height may have been about 60 cm. Retorts are found principally in two sizes the smaller ones are approximately 20 cm long by 8 cm in diameter, and the larger ones are about 35 cm long by 12 cm diameter. The smaller retorts are hypothesised to be earlier in date. These brinjal-shaped earthen retorts, filled with charge, were placed on the perforated plate in an inverted position in the upper chamber (Fig. 2). As many as 36 retorts were placed in each furnace for smelting and they were heated for three to five hours. The retorts were made in two parts and luted together after filling the charge. To prepare the charge the ore was subjected to crushing and grinding and mixed with some organic material and cow dung rolled into tiny balls and left for drying. These balls were then placed in retorts after drying. A wooden stick was placed in the narrow snout, which would prevent the boiled charge from escaping before the condensation started in the lower chamber. After heating, the zinc vapour was collected and condensed in the lower chamber in small earthen pots.

This process has been accepted without any further research and development or trying the process as experiments.

Experimental Study

On the basis of conjectural recreation of the process, an experimental study to extract zinc was attempted under the auspices of Archaeological Sciences Centre of Indian Institute of Technology, Gandhinagar. Geologist, Dr. Arvind Singh (Field Training Centre, Geological Survey of India, Zawar) was invited to participate in the experiment. Before venturing into the experimental process, it was important that the temperature within the furnace be maintained at 1150-1200 °C, and this condition had to be kept constant for the next six hours. The above proposition was made by I.C. Freestone of the British Museum after observing the degree of fusion of clay and other minerals under the Scanning Electron Microscope (Freestone *et al.* 1985). The temperature inside the retort was allowed to go up to around 1100 °C for the reaction to be $ZnO + CO = Zn + CO_2$ and around the condenser the temperature needed to be maintained below 913 °C and above 432 °C to prevent solidification. It should be borne in mind that highly reducing conditions are required otherwise the zinc vapour emitted would re-oxidize. Controlling of the temperature was extremely important. Otherwise, there was a possibility that the clay retorts would fuse and the thin walls would collapse.

Ore Dressing

The authors started the experimental procedures by first undertaking the ore dressing. This process aimed at separating the metallic compound from the undesirable gangue and non-metallic inclusions in the ore. Firstly, the large chunks of ore were collected from HZL. Secondly, the most common method of hand-picking the ore was performed. This was done by breaking the ore using hammers and manual separation of non-metallic inclusions from the matrix. By doing this, sphalerite [(Zn, Fe) S] components were separated which was easy to identify based on the colour. They were pinkish, pale brownish or yellowish in colour. This process of ore-dressing is reflected in the debris heap on the surface. Thirdly, it is necessary to roast sphalerite before it can be smelted because during the reduction reaction sphalerite does not decompose. Roasting sphalerite to zinc oxide is represented in this equation: $2ZnS + 3O_2 = 2ZnO + 2SO_2$. Roasting was done on wood and charcoal fire until the odour of sulphur (S) disappeared. This kind of roasting process is well reflected in the archaeological context by ash mounds composed of stratified layers of ash, charcoal and fragments of calcined dolomite situated at the periphery of the ancient smelting site of Zawar. Such burnt deposits would have required a much higher temperature for a considerably longer period of time. Fourthly, after roasting the sphalerite chunks were crushed using a mortar pestle. The crushed ore was mixed with fresh cow dung and then shaped into balls (Fig. 3). Finally this ball shaped chunk, which is basically the charge, was dried under a shade. After drying, the charge was finally ready for the smelting process.

Furnace Building and Lighting

For the experimental study, a 93 cm high and two chambered (height of the lower chamber is 40 cm and of upper chamber is 47 cm) squarish planed furnace (34 x 34 cms at inner side) was made using one 5 cm thick furnace plate (40.50 x 40.50 cms) to hold nine retorts (made using the local clay of Zawar), 100 furnace bricks and 25 kg of clay (Fig. 4). Five (instead of nine) U-shaped retorts (23 cm long by 8.25 cm in diameter, 16 cm long condenser, of which lid is 2 and snout is of 14 cm), made using the local

Fig. 3: The making of the charges

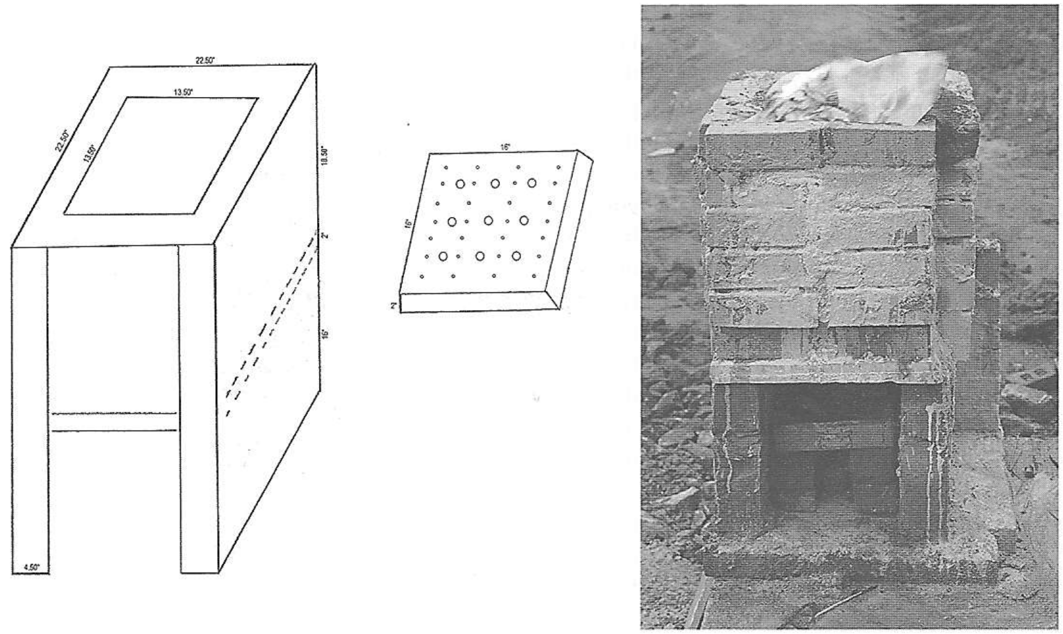

Fig. 4: The experimental furnace and its schematic plan

Fig. 5: The luted retort

Fig. 7: Placement of the thermocouple in the snout along with the condensing flasks in the water

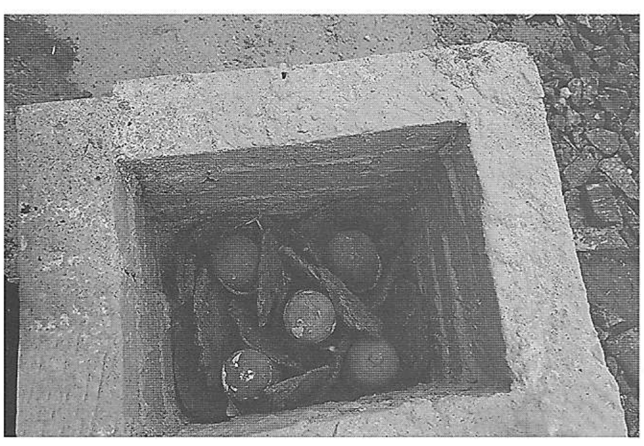

Fig. 6: Retorts are placed in the furnace

Fig. 8: The lighted up furnace and the experiment team

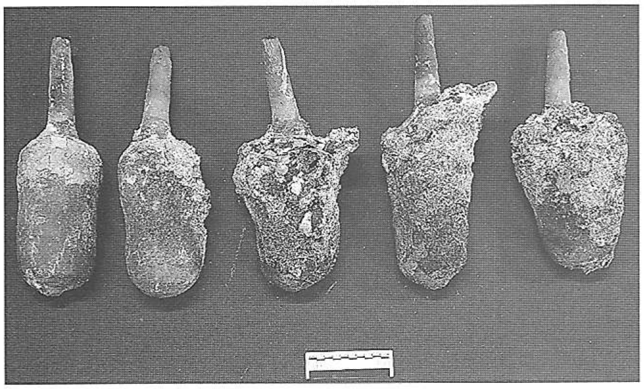

Fig. 9: Experimental spent retorts

clay of Zawar (Fig. 5), 2/3rd of which were filled with dried zinc ore balls and the long snouted condenser were luted to the open end with clay (Fig. 6).

These brinjal-shaped retorts were placed downward in the designated holes after neem stems were fixed to each snout (Fig. 7). By utilizing 25 kg of charcoal and 35 cow-dung cakes, the upper chamber of the furnace was fired for six hours. The temperature was flamed to 1000 °C which fluctuated till 1100 °C rarely touching 1150 °C. However, the temperature could not be maintained for next six hours. The temperature in the snouts which protruded into the lower chamber was always < 500 °C. Measurement of the temperature was done using two thermocouples, one fixed inside the upper chamber of the furnace and outside the retort, and the other one at the snout of the retort in the lower chamber. In the lower chamber of the furnace, five round bottomed flasks were floated in a water filled tray, the snout of each retorts being inserted in one flask to collect the zinc (if any). This was done so as to recreate the probable distillation process (Figs. 8-9).

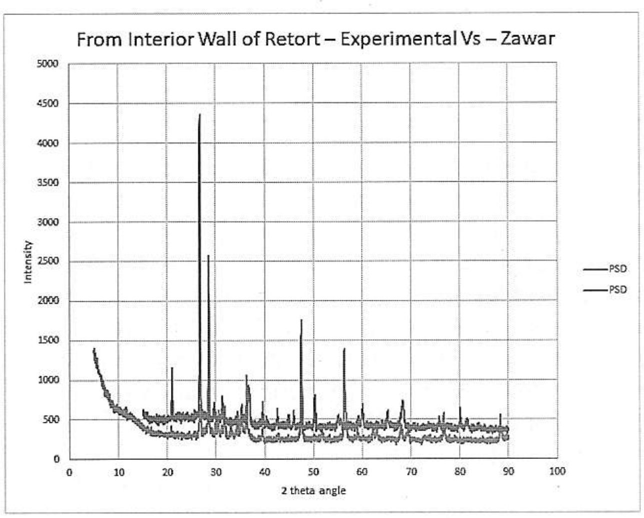

Fig. 10: Presence of zinc oxides on the luting

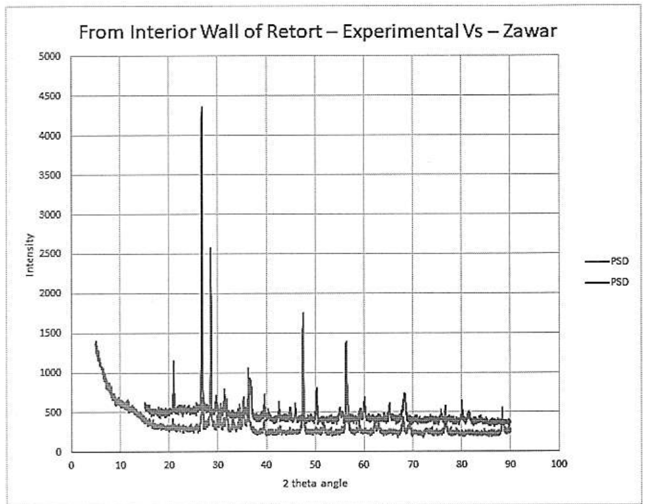

Fig. 11: XRD analysis of the zinc sample (Experimental Vs Zawar)

Results

After the furnace was cooled down for a day, the researchers found out that in only three retorts the mineral balls had got melted (Fig. 10). This was probably due to uneven distribution of firing temperature. Neither was there any trace of zinc in the flasks nor in the retorts' bottom part or in the snout. However, there was a good amount of white and black powdery formation near the joints of the retorts. The zinc vapour gas escaped from the luted area and then settled on the surrounding. During the cooling process, it got stuck to the outside walls of the retort (Fig. 11).

Analysis of the Spent Charge from the Retorts of the Archaeological Context

The chemical analysis of the spent charge found from the archaeological context at Zawar by Hegde (1991) throws light on the smelting process and the chemical reactions that took place inside the furnace (Table 1). Firstly, the low level of sulphur suggests that sphalerite ore was used and completely roasted before using it as charge inside the retorts. Smelting process was perfected by the Zawar smelters as suggested by the low level of lead oxide. This clearly shows that the process of beneficiating the zinc ore was practised, and before the smelting process zinc and lead sulphides were manually separated. It is interesting to note that we had a considerable high proportion of sodium oxide, and it had been postulated by Hegde that a small quantity of common salt was deliberately added to the charge as due to the heat in the furnace sodium chloride would disintegrate into soda and chloride. The soda formation would aid in the sintering process and open up the pores which would eventually aid in the easy flow of zinc vapour. If we accept the purposeful inclusion of common salt then the literary reference in *Rasaratnasamuchchaya* (a 14th century text dealing with technologies) is deemed accurate (Hegde 1991: 71).

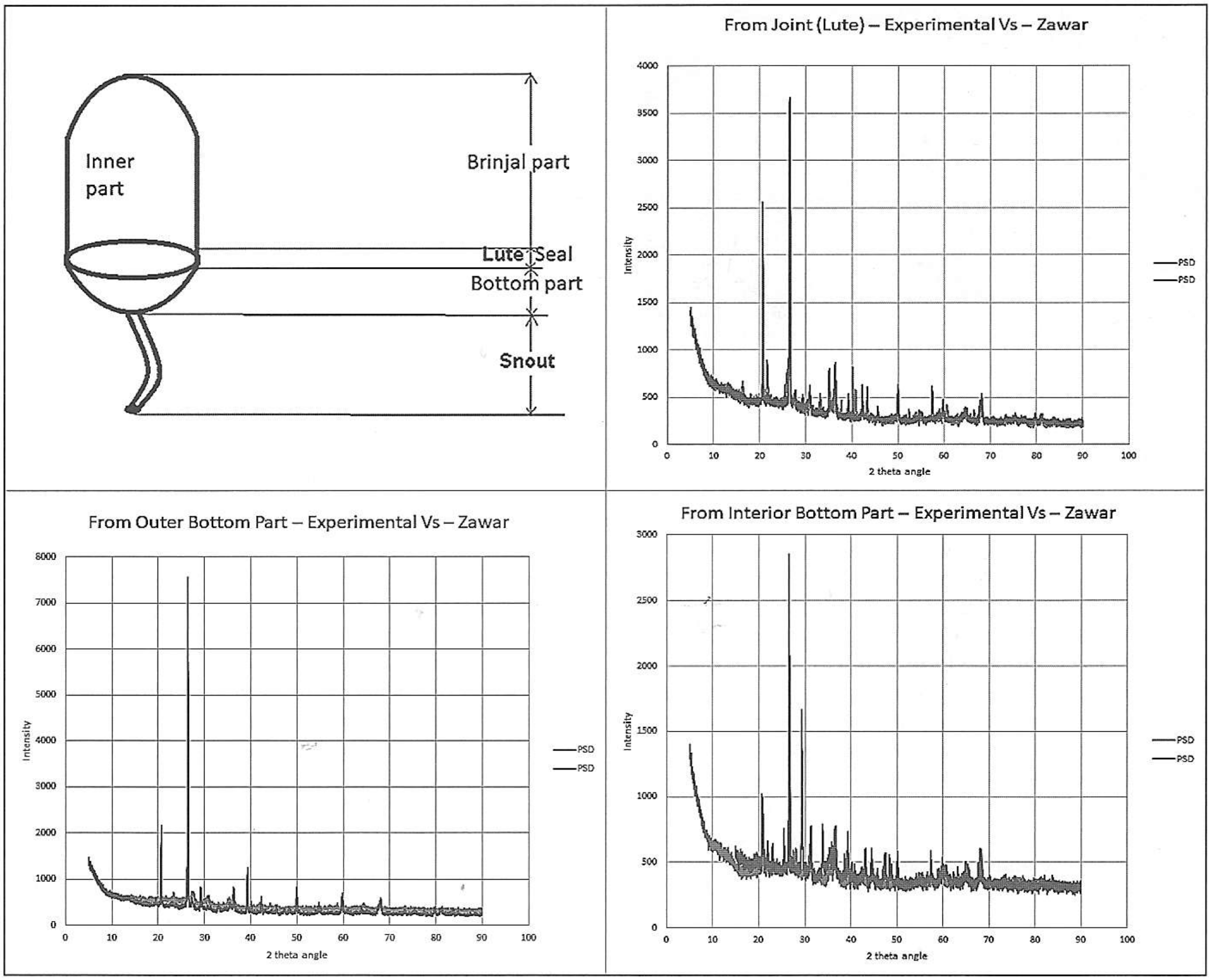

Fig. 12: XRD analysis of zinc oxides from luting, inner and outer parts of the snouted bottom (Experimental vs Zawar)

Table 1: Analysis of spent charge from Zinc smelting retorts (%) (Hegde 1991: 69)

Element	%
SiO_2	42.48
TiO_2	0.17
Al_2O_3	5.42
Fe_2O_3	8.12
MnO_2	1.64
MgO	11.16
CaO	24.54
Na_2O	1.28
K_2O	0.31
P_2O_5	0.27
Cl	0.53
S	0.23
PbO	1.72
ZnO	2.28

XRD Analysis of the Extracted Zinc and Zinc Oxide

Samples were taken for analysis from different sections of an experimental retort. The researchers found that the interior walls of retort were covered with the white material (which is supposed to be zinc). Same chemical residues have been found from all the three retorts, in which the charge got boiled. Similar powdery material was also collected from a retort collected at Zawar by the first author during the 2015 explorations. Both the samples were analysed using XRD.

Although the peaks found are similar in both Zawar and experimental sample, the samples from the retorts found in the Zawar showed phases which were formed during the heat treatment process (Fig. 12).The peaks between the 2 theta angle 30 and 40 shows the compounds of zinc (Zn and ZnO). It can be comfortably said the zinc vapours that were formed during the smelting process due to unavailability of space got stuck on the interior surface of the retorts. Similar evidence has been found from the archaeological context of Zawar from which the spent charges were analysed by Hegde (1991) as mentioned earlier. The analysis of all the three contexts (archaeological, exploration and experimental) shows similar elemental composition.

Samples collected from the luting, inner and outer parts of the snouted bottom were in the form of white and black oxide layer (which is supposed to be zinc oxide). Samples were collected from identical portions of the retort collected at Zawar and our experimental retorts were analysed under XRD.

Continuation and Future Experiments

The chemistry behind the process of smelting and condensing the zinc was already postulated in 1980s and in the early part of 1990s by the referred scholars. However, it was for the first time that the entire furnace along with retorts and distillation system was experimentally recreated and the entire process was carried out. The distillation process as postulated by the earlier works could not be achieved as zinc did not get condensed in the flasks kept in the lower chamber. It is important to develop a fool proof condensation system to be able to recreate the ancient zinc smelting furnace found from Zawar.

To overcome the problem of re-oxidisation of zinc vapour, zinc oxide has to be smelted with a high amount of charcoal powder or another suitable carbonaceous matter so that carbon monoxide is generated and through the distillation process formed using retorts placed in a furnace where the temperature can be raised and maintained at 1200+ °C, so that the temperature inside the retorts gets to the required 1150 °C. The retorts are connected to the condenser vessels placed outside the chamber where the temperature is below 500 °C.

For any future experiments, the following caution needs to be undertaken:

1. Roasting the ore at a higher temperature;
2. Making the furnace spacious enough for equivalent heat to be generated inside the chamber;
3. Retaining the heat at above 907 °C in the retorts for longer duration of time;
4. Adding a sodium compound to the charge, in the form of common salt, so as to aid in the sintering process;
5. Application of a gypsum coating to the retorts;
6. Ensuring proper sealing of the joints;
7. Create reducing conditions required to obtain pure zinc; and
8. Provide a mechanism to condense the zinc vapour to the flask.

Acknowledgements

We are thankful to Hindustan Zinc Limited (HZL) for providing the zinc ore for the experiments, and Dr. Arvind Singh for facilitating the acquisition of the same. We are grateful to Sahitya Sansthan's research staff: Dr. Kulshekar Vyas, Dr. K.P. Singh, Narayan Paliwal, Hitesh Bunker and Shoyab Kureshi for getting the charge prepared, and asssiting with the experimental process. This work would not have seen the light of the day without the XRD lab support of IIT Gandhinagar and Department of Scientific and Industrial Research grant for Common Research and Technology Development Hub (F. No. DSIR/CRTDH/NM/IIT-Gn/2016), and the permission to recreate the furnace by our Institute.

References

Bhatnagar, S.N. and L.K. Gurjar 1989. Zinc - A Heritage, *Hind Zinc Tech* 1(1): 5-8.

Carsus, H.D. 1960. Historical Background, in *Zinc* (C.H. Mathewson Ed.), pp. 1-8. New York: American Chemical Society.

Craddock, P. T. 1995. *Early Mining and Metal Production.* Edinburgh: Edinburgh University Press.

Craddock, P.T. 1986. A History of Distillation of Metals, *Bulletin of the Metals and Museum* 10: 3-25.

Craddock, P.T. 1998. Zinc in Classical Antiquity, in *2000 Years of Zinc and Brass* (P.T. Craddock Ed.), pp. 1-7. London: British Museum.

Craddock, P.T., L.K. Gurjar and K.T.M. Hegde 1983. Zinc Production in Medieval India, *World Archaeology* 15: 211-221.

Craddock, P.T., I.C. Freestone, K.T.M. Hegde, L.K. Gurjar and V.H. Sonawane 1985. Early Zinc Production in India, *Mining Magazine* January: 45-51.

Craddock, P.T., I.C. Freestone, L.K. Gurjar, A. Middleton and L. Willies 1989. The Production of Lead, Silver and Zinc in Early India, in *Old World Archaeometallurgy* (A. Hauptmann, E. Pernicka and G. Wagner Eds.), pp. 51-69. Bochum: Selbstverlag des DeutschenBergbau-Museums.

Crookshank, H. 1947. Zawar Silver-Lead-Zinc mines, *Indian Minerals* 1: 22-27.

Freestone, I.C., P.T. Craddock, K.T.M. Hegde, M.J. Hughes and H.V. Paliwal 1985. Zinc Production at Zawar, Rajasthan, in *Furnaces and Smelting Technology in Antiquity* (P.T. Craddock and M.J. Hughes Eds.), pp. 229-241. London: British Museum.

Gurjar, L.K., P.T. Craddock, L. Willies and H.V. Paliwal 2001. Zinc, in *History of Technology in India* Vol. III (K.V. Mittal Ed.), pp. 621-638. Delhi: Indian National Science Academy.

Hegde, K.T.M. 1989. Zinc and Brass Production in Ancient India, *Interdisciplinary Science Reviews* 14(1): 86-96.

Hegde, K.T.M. 1991. *An Introduction to Ancient Indian Metallurgy*. Bangalore: Geological Society of India.

Kharakwal, J.S. 2011. *Indian Zinc Technology in a Global Perspective*. New Delhi: Pentagon Press and Infinity Foundation Series.

Kharakwal, J.S. and L.K. Gurjar 2006. Zinc and Brass in Archaeological Perspective, *Ancient Asia* 1: 139-159.

Mookherjee, A. 1964. The Geology of the Zawar Lead-Zinc Mine, Rajasthan, India, *Economic Geology* 59(4): 656-677.

Morgan, S.W.K. 1976. *Zinc and its Alloys and Compounds*. New York: Ellis Horwood Ltd.

Paliwal, H.V., L.K. Gurjar and P.T. Craddock 1986. Zinc and Brass in Ancient India, *Bulletin of Canadian Institute of Metals* 885: 75-79.

Strackzeck J.A. and B. Srikantan 1967. Geology of Zawar Lead-Zinc Area, Rajasthan, India, *Memoirs of the Geological Survey of India* 92: 47-83.

Tite, M.S., I.C. Freestone, N.D. Meeks and P.T. Craddock 1985. The Examination of Refractory Ceramics from Metal-Production and Metalworking Sites, in *The Archaeologist and the Laboratory* (P. Phillips Ed.), pp. 50-55. London: Council of British Archaeology, Research Report 58.

Tod, J. 1829. *Annals and Antiquities of Rajasthan, of the Central and Western Rajpoot States of India*. Vol. I. London: Smith, Elder, and Co.

Werner, O. 1970.Uber das Vorkommen von Zinc, *Erzmetall* 23: 259-269.

Willies, L., P.T. Craddock, L.K. Gurjar and K.T.M. Hegde 1984. Ancient Lead and Zinc Mining in Rajasthan, India, *World Archaeology* 16(2): 222-233.