From laboratory to field experiments: shared experience in brass cementation

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ABSTRACT: The aim of the paper is to present the experimental approach followed by the authors in order to investigate ancient metallurgical processes. Multi-scale experiments based on model systems where complexity is gradually increased are both necessary and complementary. They are a way of optimizing the scanning of working conditions inferred for ancient metallurgical processes. The example of the on-going experimental investigation of the brass cementation process serves as an illustration.

Introduction

The C2RMF is involved in the reconstruction of several ancient metallurgical processes, including protohistoric copper smelting (Bourgarit *et al* 2005, Burger *et al* 2010a and 2010b), fusion welding in antique large bronzes (Azéma *et al* forthcoming), and brass production (Bourgarit and Bauchau 2010). An integrated approach is systematically carried out for each topic, including the thorough investigation of related material evidence and experimental simulation more or less directly related to the process. The latter approach proves to be particularly relevant, given both the technological complexity of brass making and the chemical/physical complexity of the material evidence. In order to optimize the efficiency and benefits of the experiments we have developed multiple-scale simulation, from the modelling of the theoretical mechanisms underlying the processes to the field reconstruction of the *chaine operatoire*. The present paper discusses this approach. Examples are taken from the ongoing experiments carried out by the authors who are attempting to reconstruct ancient brass cementation processes.

Reasons for experimental simulation

Prior to the mastering of metallic zinc production in Europe in the mid 18th century (Day 1998), brass making used to be based on the so-called cementation process. The understanding of this process is quite complex for two reasons.

First, the process is actually the combination of two interacting chemical systems (Fig 1). Gaseous zinc is produced by the carbothermic reduction of zinc ore at around 1000°C (±100°C), within a more or less closed vessel. The gaseous zinc thus produced diffuses into the copper, the latter being either in the liquid state or in both solid and liquid states depending on the temperature and the duration of the process. The theoretical simulation of such a combination is not straightforward unless a few approximations are made, which anyway need to be tested experimentally.

Second, documentation is quite scarce. Related archaeological evidence is restricted so far to vessels (Bayley 1998, Picon *et al* 1995, Rehren 1999), which mainly enable the scale of the reacting system and some features of its configuration, like the presence or absence of a lid,

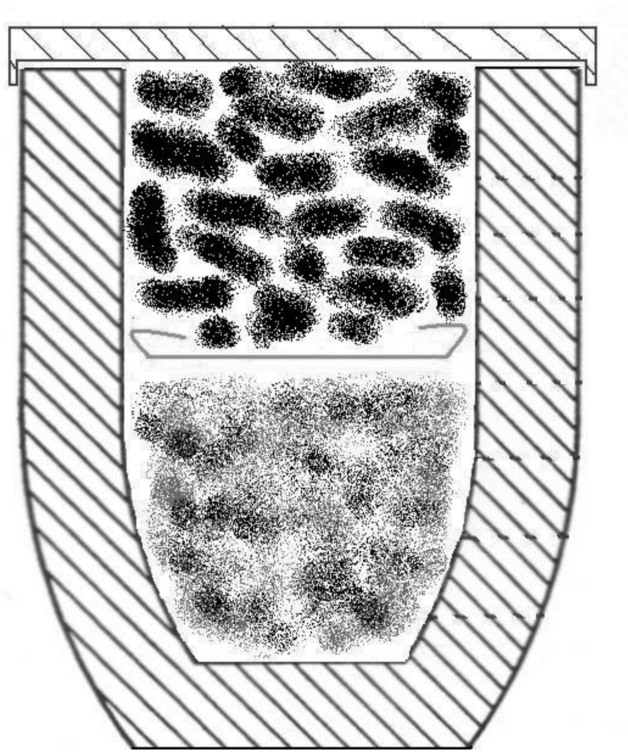

Figure 1: Diagram of a crucible and its charge used for laboratory simulation of brass cementation. In the lower part the mixture of zinc ore and charcoal (the cement) leads to the formation of gaseous zinc, which either diffuses into the copper foil (on top of the cement) or escapes from the crucible. The layer of coarse charcoal in the upper part of the crucible prevents the oxidation of the copper.

to be inferred. Known written sources consist mainly of technical treatises (see Craddock and Eckstein 2003, Martinon-Torres and Rehren 2002, Welter 2003), which provide some useful information but lack quantified data on variables like temperature, duration, composition of the charge and efficiency.

Few ancient brass objects dated before the Industrial Revolution analysed so far have more than 30wt% Zn, so this zinc content has become a dating criterion for these artefacts (Werner 1970). Quite a number of archaeometallurgical experiments have dealt with brass cementation (Doridot *et al* 2006, Maréchal 1938, Newbury *et al* 2005, Rolandi and Scaciatti 1956, Ullwer 2008, Welter 2003, Welter and Revet 1997), questioning this compositional limit and/or documenting the working conditions of the processes. Yet none of these attempts

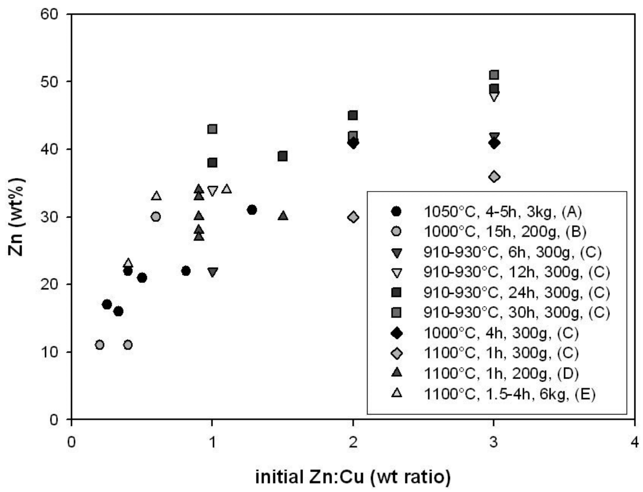

Figure 2: The zinc content of brass produced by previous cementation experiments is plotted against the initial Zn:Cu ratio. The letters in brackets refer to the following: A = Rolandi and Scaciatti 1956, B = Newbury et al 2005, C = Ullwer 2008, D = Ullwer 2001, E = Welter and Revet 1997.

have reconstructed a complete historically-documented process. Three main reasons are responsible for this. First, each team focused on particular working conditions (Fig 2) whereas scanning of the main possible working conditions was needed in order to understand the basics of the process (the influence of temperature, duration, etc). Second, repeatability has not been tested, except in one case (Ullwer 2008), which has prevented any serious quantification of the influence of the parameter tested. Third, none of the experiments were aiming at fully reflecting a particular historically-related technological environment. Instead, 'modern' working conditions such as electric furnaces were systematically used within a 'modern' laboratory setting.

The need for laboratory experiments

A preliminary understanding of the basics of the process consists of characterizing at least six parameters, summarized in Table 1. The potential range of these parameters is mostly indicated by ancient texts. Hence, the descriptions 'red copper' or 'full liquid copper' may be translated into a 900–1100°C temperature range. Thermodynamics and particularly the Boudouard equilibrium graphs also help in showing that reduction of zinc is not very efficient below 900°C. Scanning by steps

Table 1: The parameters for brass cementation and their range of variation. The bottom row shows the minimum number of values which need to be tested for each parameter.

Parameter	Temperature	Time	Zn:Cu	Ore	Reactor configuration	Charge quantity	Total
Laboratory conditions	900–1100°C	1–24h	1–3	pure ZnO or natural ore	lid or no lid	small or large	
No of options	5	5	3	2	2	2	600

of 50°C seems reasonable, which makes five different temperatures to be tested.

Similarly, in technical treatises the process is either said to be short or to last overnight: durations from half an hour to one day or more need to be tested. The initial zinc to copper ratio is rarely indicated although it may have a crucial role (Fig 2) so at least three different ratios may be worth testing. The configuration and dimensions of the reacting system are the only parameter so far documented by archaeology. At least two configurations deserve comparison, namely a crucible with and without a lid. Moreover, while there is evidence of a large variation in the size of the crucible (see for example Rehren and Martinon-Torres 2008), the size-effect on reaction kinetics cannot be overlooked; at least two different sizes need to be tested. Finally, the purity of the ore might also be a fundamental parameter for a basic characterisation of the process. As a minimum a pure laboratory zinc oxide should be compared with a natural ore, which makes two further conditions.

Table 1 shows that 600 different combinations of working conditions need to be considered. Of course not all combinations need to be tested; for example, the high-temperature process is not supposed to last more than a few hours. Moreover, for a given objective a so-called experimental design may help to minimize the number of trials. The scanning of some 70 combinations led to a first overview of the process (Bourgarit and Bauchau 2010). Yet, this still makes quite a large number of experiments, especially when repeatability also needs to be tested. These cannot be easily handled through experiments in the field, which have their own difficulties. Although the comparison is not straightforward, one cannot help recalling one of the most comprehensive archaeometallurgical experimental programmes ever carried out, by Peter Crew and his team on iron smelting: over 25 years some 130 experiments were carried out (*eg* Crew 1991). The laboratory offers much more flexibility and also much more controlled conditions, notably because a small laboratory furnace is much easier to instrument than a large open-air clay-built furnace. This is especially crucial if one wants to measure and control the gaseous atmosphere prevailing within the reacting system (Burger *et al* 2010b).

The 150 experiments reported by Bourgarit and Bauchau (2010) were carried out in less than three months. The year after, the number of tests was almost doubled. It is beyond the scope of this paper to describe thoroughly either the experimental set-up

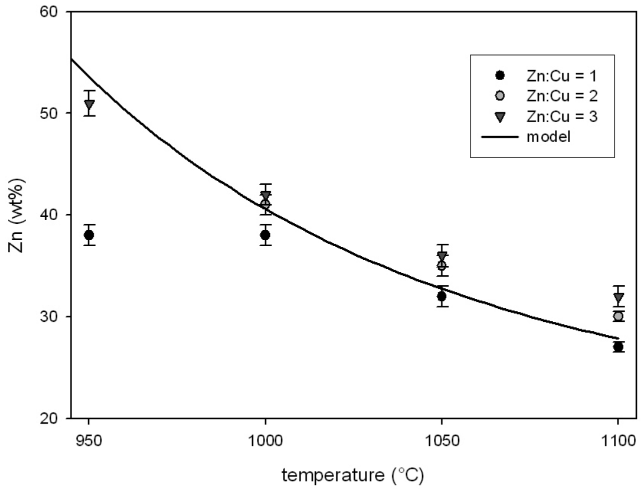

Figure 3: Change with temperature of the maximum zinc content of the brass produced experimentally for different initial Zn:Cu ratios. All experiments have been performed at least twice, the error bars report the variations observed. The theoretical curve (solid line) is based on our proposed thermodynamic model (after Bourgarit and Bauchau 2010, fig 5).

or the results obtained, yet a rapid overview may help readers understand the approach. Laboratory experiments were performed in the newly built indoor experimental platform of the C2RMF, using an electric chamber furnace (Fig 8a). Thermal analysis was performed as well in order to investigate the kinetics of zinc oxide reduction. Various working conditions, including temperature, isothermal treatment duration, initial zinc to copper ratio, purity of the ore, presence or absence of a lid, initial configuration of copper and quantity of the charge have been tested in a quite comprehensive manner; the size of the crucible has remained unchanged.

The influences of all parameters on the maximum zinc content of the final products, on the optimal duration of the treatment, and on the zinc recovery rates have thus been determined. Some of these results are presented (Figs 3—5), for more details see Bourgarit and Bauchau (2010). The maximum zinc uptake can reach 50wt% and more under particular conditions. The optimal duration may last from 20 hours at 950°C to less than one hour at 1100°C. The recovery rates are largely dependant on the initial zinc to copper ratio, varying from 60% to less than 30%. The lid is crucial at low temperatures but useless at 1100°C. Thus, quite a lot of interesting data has been produced so far, which may already help to address some of the issues raised by archaeologists and historians.

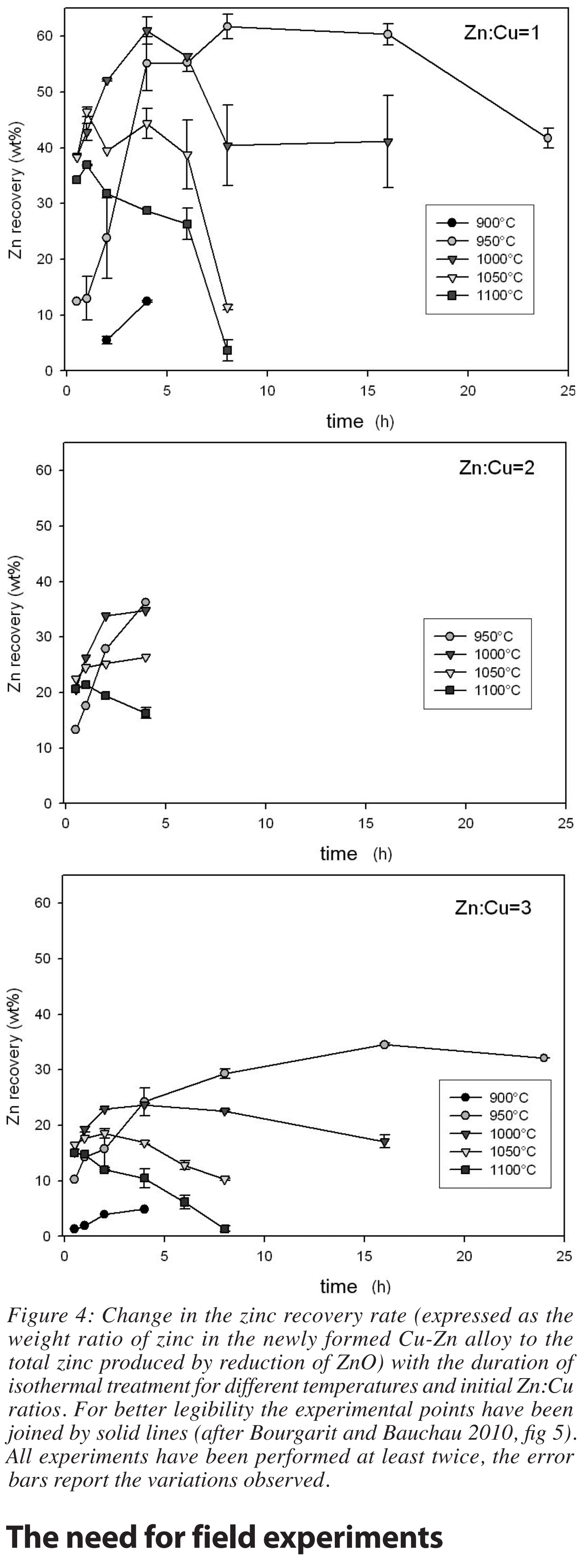

Figure 4: Change in the zinc recovery rate (expressed as the weight ratio of zinc in the newly formed Cu-Zn alloy to the total zinc produced by reduction of ZnO) with the duration of isothermal treatment for different temperatures and initial Zn:Cu ratios. For better legibility the experimental points have been joined by solid lines (after Bourgarit and Bauchau 2010, fig 5). All experiments have been performed at least twice, the error bars report the variations observed.

The need for field experiments

The laboratory trials were almost totally disconnected from any historically-documented technological environ-

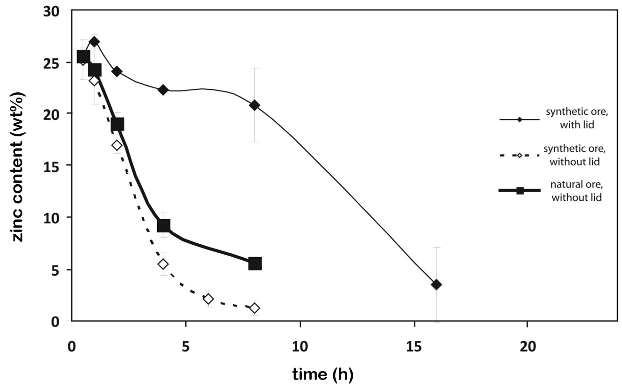

Figure 5: Change with the time of the zinc uptake at 1100°C in newly formed brass for different crucible configurations and types of zinc input. All experiments have been performed at least twice, the error bars report the variations observed.

ment: an electric furnace was used, relatively small crucibles (less than 0.1l) and charges were tested, only high-purity materials (copper, zinc oxide, charcoal) and inert refractories were used. This was a deliberate choice in order to avoid, as far as possible, any uncontrolled variability and to guarantee as much reproducibility as possible. It meant that the reconstruction of ancient processes was beyond the scope of such an approach. In the case of brass cementation, the very nature and size of the reaction vessels are at the centre of the technology and may indeed greatly influence the working conditions and the outcome of the process. In this case a handful of parameters may vary in a more or less controlled manner and influence the results. These include the nature and size of the furnace (which both affect temperature variability), the nature of the crucible, and the influence these parameters have on the final product, like the quantity of zinc, the purity of the final alloy etc. Moreover, the potentially large size-effect induced by the crucible dimensions must be mentioned: in our field experiments the internal crucible volume was from two to ten times larger than those used in the laboratory.

In addition, most information about the way brass was produced, things such as human and material costs and the human skills required, is missing from the potential lessons to be learned from laboratory experiments. Field experiments may help to address some of these issues. If the variety of working conditions to be tested is sufficiently small, the experiments are well-adapted to the field set-up. In our research program, this has been achieved in two ways.

Our field experiments focused on one particular technological environment. The process we attempted to reconstruct was closely related to recent excavations

Figure 6: One of the furnace bases found at Bouvignes, Porte Chevalier (structure # F6, 15th century AD). Internal diameter c.1m (Jean Plumier - ©Service Public de Wallonie - D Pat).

of 13th- to15th-century workshops at Dinant and Bouvignes, in the Meuse Valley (Thomas *et al* 2010; Fig 6). The model approximately fits the descriptions by Theophilus, in particular using natural-draft furnaces (fig 8b) in order to achieve high temperatures (Dodwell 1961; Thomas 2009). The copper is hence in the liquid state from the very beginning of the process. This means that only one temperature is tested, instead of the five temperatures investigated in the laboratory.

We also took advantage of the results obtained in the laboratory regarding the process duration, the initial zinc to copper ratio, and the crucible configuration. Hence, we were able to restrict the range of process times to be tested based on the optimal process duration as determined in the laboratory. Moreover, in view of the recovery rates measured in laboratory, the only acceptable zinc to copper ratio was 1:1 so there was no need to study the two other values. In addition, the lid had been shown to have little effect at high temperature, so *a priori* it is pointless to try the two configurations in the field.All this means that the working conditions to be tested have dropped to only eight (Table 2). This makes some 16 experiments to carry out in one campaign, which is quite feasible within the framework of a one-week experimental programme per year.

The first field campaign was carried out in July 2010 at the experimental platform at Barsy, Belgium (Thomas and Plumier 2010; Fig 7 and Fig 8b). It is beyond the scope of this paper to present the results obtained so far, but they stress two points that illustrate the complementary nature of laboratory and field experiments.

First, it is noteworthy that the zinc uptake measured in the field is more or less that predicted by both thermodynamics and the laboratory experiments (Fig 9). Practically, this means that laboratory experiments may be used to predict the performance of larger-scale process. Conversely, the laboratory may confirm the validity of some of the field results.

Secondly, the agreement between field and laboratory results is, as expected, not good for all parameters. A clear size-effect has been demonstrated within the large crucibles. In both small and large furnaces, the measured temperatures (outside the crucible) varied between 1200-1400°C. In the small furnace (crucible volume 0.2l), the maximum zinc uptake was reached between half an hour and one hour, as in the laboratory. After one hour in the large furnace (crucible volume 2.0l) the copper sheets had not yet melted (Fig 10a); two hours were needed to produce liquid brass containing some 25wt% Zn (Fig 10b). The characterization of this size-effect has dramatically refined our understanding of two of the main working parameters, the temperature required and the process duration.

As far as the organisation of the medieval Mosan workshops is concerned, many more field campaigns need to be carried out before robust data can be delivered. For instance, the very large ratio of fuel consumption to brass produced observed in 2010 was mostly due to the inadequacies of the crucible and furnace sizes. Similarly, the long times required to prepare the charges should be drastically lowered with growing skill and experience. Moreover, the study of the impact of the process on the refractories, both furnaces and crucibles, will be carried out, in order to enhance our understanding of the only archaeological evidence related to the process recovered so far.

Table 2: The working conditions used in the field experiments, showing how the laboratory results allowed the number of permutations tested to be drastically reduced when compared with Table 1.

Parameter	Temperature	Time	Zn:Cu	Ore	Reactor configuration	Charge quantity	Total
Field conditions	1100°C	around the maximum	1	pure ZnO or natural ore	no lid	small or large furnace	
No of options	1	2	1	2	1	2	8

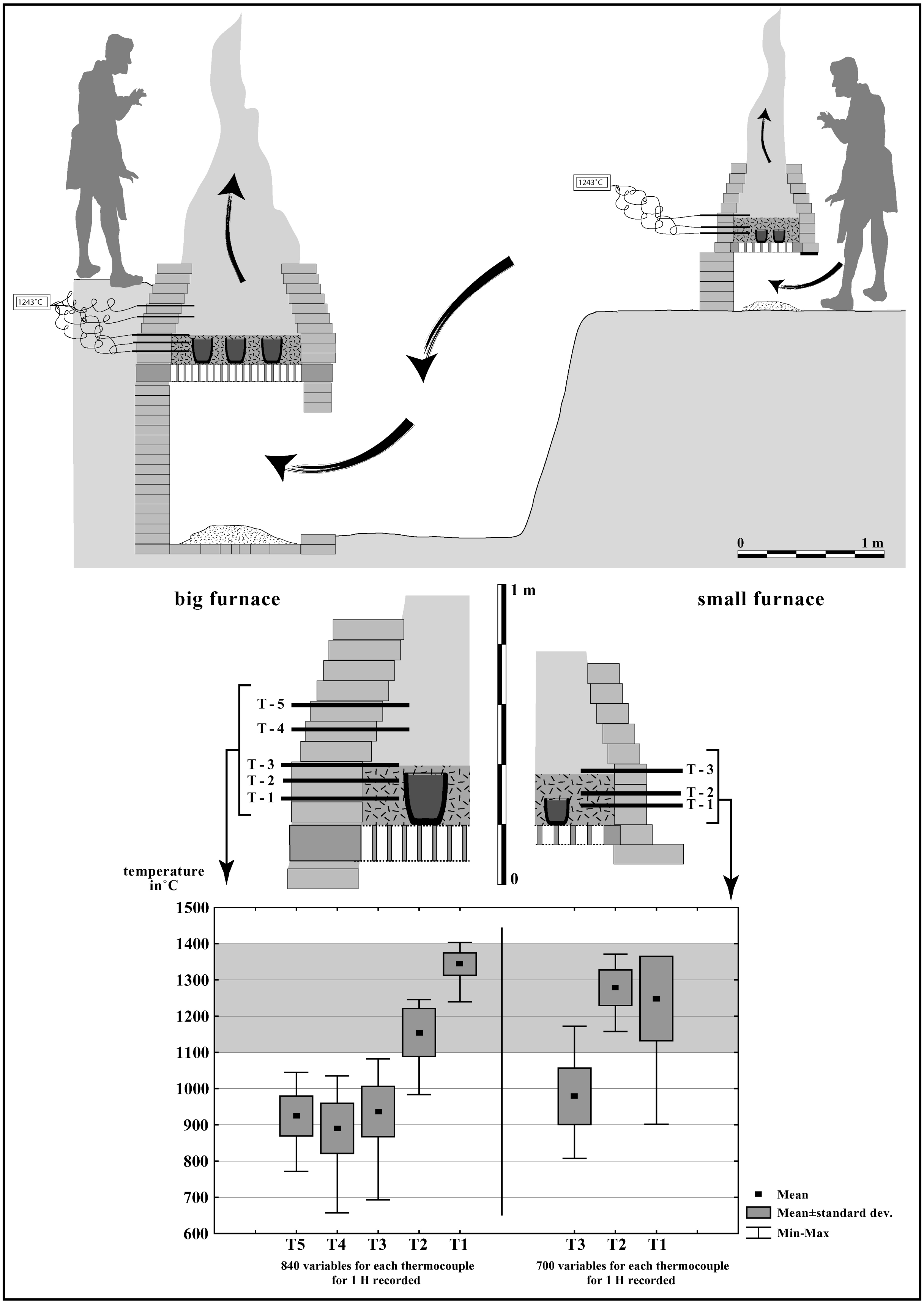

Figure 7: The two wind-powered furnaces constructed at Barsy in July 2010, with details showing the size of the crucibles. The graphs show the temperature measured at different heights within the furnace, along the inner wall. The centre of the box is the mean temperature measured during one hour, the box the standard deviation and the whiskers the extreme values.

Figure 8: above) The furnace used for the laboratory experiments at C2RMF, and below) the large furnace during field experiments at Barsy, Belgium.

Conclusions

Because of the complexity of most ancient metallurgical processes, and given the frequent scarcity of related documentation, experimental simulation can help to both clarify and quantify the details of a given process. Experimental simulation therefore appears an important tool for archaeometallurgical investigation. Depending on the topic to be addressed, the whole or only part of the process may be reconstructed, sticking more or less tightly to a given archaeological or historical framework. Such a view is not new in archaeometallurgy, having been promoted by Tylecote and his co-workers in the 1980s. Indeed, the use of experimental reconstructions is now widespread within the archaeometallurgical community, as seen at the conference organised by the Historical Metallurgy Society in 2010 (Dungworth and Doonan forthcoming). Other benefits of experimentation such as education (of students, and self-education) have not been mentioned here, though they are part of the added-value sought by the authors.

By sharing their experience the authors would like to stress one aspect which still seems largely neglected: the fact that laboratory experiments should be considered prior to field experiments. For example, small-scale laboratory experiments may be necessary for a rigorous understanding of the basis of the process, especially since the indoor reactors are much easier to instrument than large-scale field furnaces. Moreover, such experiments prove to be very efficient in terms of saving time and money, and as a predictive tool for larger-scale reconstructions. However, the field remains the only route for those who wish to reconstruct all aspects of a given process, including the *chaine operatoire*. Brass cementation was chosen here to illustrate this multi-scale approach since it represents quite a simple and successful example, but a similar approach has also proved useful for more complex metallurgies such as those dealing with copper-sulphide smelting.

Neither the limitations nor the drawbacks of the experimental route have been discussed. They seem to grow in number as the degree of fidelity aimed for in the reconstruction increases. Our experience in the field is as yet too small for us to produce a comprehensive list, though Dungworth (forthcoming) has recently reviewed the subject. It seems to us that the operator's skills are one of the potentially most limiting parameters. That is perhaps the reason why the brass cementation programme described above has gathered together in the field people with an impressive variety of backgrounds, including archaeologists, historians, archaeometallurgists, founders, curators, restorers, industrial metallurgists and furnace designers. Did the experiment succeed? As far as the reconstruction of the medieval process(es) in the Meuse Valley is concerned, it is still too early to say, although the surpris-

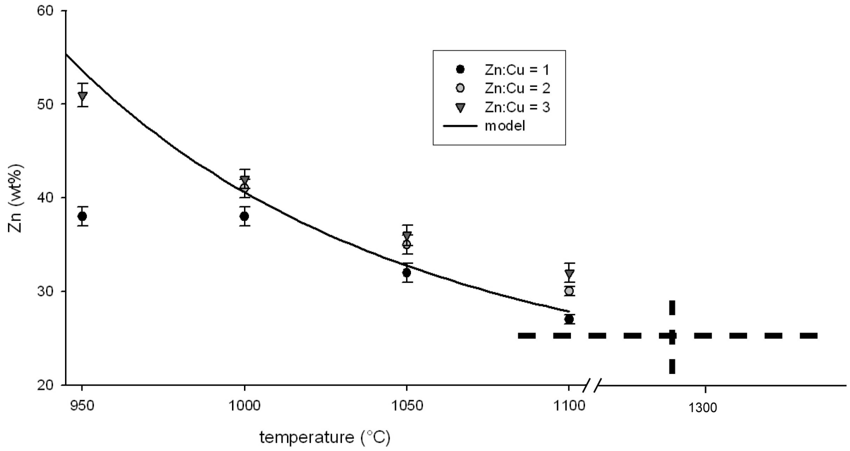

Figure 9: The maximum zinc content in the copper-alloy produced experimentally by the authors (data from Fig 3). The results obtained during field experiments at 1200—1400°C are shown as the large dashed cross, representing the variation in both effective tmperature and zinc content.

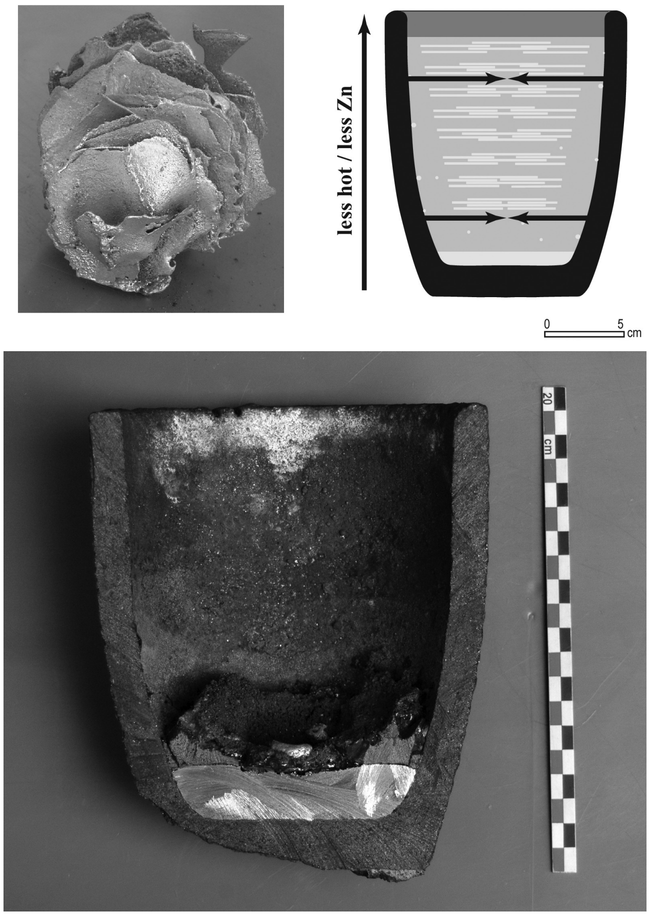

Figure 10: Typical products obtained in the large crucibles. above) After 1 hour at 1300 ±100 °C the copper sheets had not fully melted; they could be removed from the crucible only partly fused. The vertical and horizontal arrows on the diagram indicate the temperature gradient; below) Brass containing 25wt% Zn has melted and coalesced at the base; a slag layer floats on top of the liquid metal.

ingly good repeatability achieved deserves mention. However, as regards communication and sharing of knowledge, there is no doubt that the melting pot has been very successful.

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