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Joseph Gauthier, Florian Téreygeol. Small scale reduction of argentiferous galena: first experimental approach to ores assaying techniques. *Historical metallurgy*, 2013, Accidental and Experimental Archaeometallurgy, pp.143-148. hal-01998053

HAL Id: hal-01998053

<https://hal.science/hal-01998053v1>

Submitted on 8 Feb 2019

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Small scale reduction of argentiferous galena: first experimental approach to ores assaying techniques

Joseph Gauthier¹ and Florian Téregeol²

- 1 Centre de Recherche sur les Économies, les Sociétés, les Arts et les Techniques, Campus Fonderie, 16 Rue de la Fonderie, 68093 Mulhouse, France. joseph.gauthier@uha.fr
- 2 LAPA, Bat. 367, CEA-Saclay, 91191 Gif-sur-Yvette, France florian.teregeol@cea.fr

ABSTRACT: Ore assaying techniques are here considered as a part of the silver production chaîne opératoire, in a mining industry context. Our aims are to understand the technique itself but also its role in mine exploitation. The experiments deal with small scale assaying techniques in use from the end of the Middle Ages and well described in 16th-century technical treatises. More than 50 assays have been made with argentiferous galenas. The precise operation studied is the smelting of the ore in a scorifier, in a muffle furnace, which produces a lead and silver regulus (which is then cupelled to obtain the silver content). It allows a reflection on the different steps of the assaying process (sampling, ore preparation, the addition of fluxes, etc) and the way it was considered and practiced in the past. This gives a concrete vision of the technique studied, essential in conjunction with the historical and archaeological approaches.

Introduction

Ore assaying techniques formed the subject of Joseph Gauthier's PhD, at the University of Haute Alsace (Mulhouse) under the direction of Florian Téregeol and Pierre Fluck. The question was studied via history and archaeology, from the 12th to the 18th century in Europe. Our focus was particularly on the transition between large- and small-scale assaying techniques at the end of Middle Ages. The experimental approach complements this study of small-scale techniques that are well described in 16th-century technical treatises (eg Sisco and Smith 1949; Smith and Gnudi 1990; Hoover and Hoover 1950; Sisco and Smith 1951). Experiments were made at Melle (Deux-Sèvres, France), on the CNRS palaeometallurgical experiments platform at the touristic site of the *Mines d'Argent des Rois Francs*, under the Collective Research Programme (PCR) *Palaeometallurgy and Experimentation* directed by Florian Téregeol. They took place during three ten-day campaigns in 2007, 2008 and 2009 (Gauthier 2009). Our aims in these operations were twofold: firstly, to reconstruct the chaîne opératoire of assaying techniques, from sampling to the production of a precious metal button; and secondly, to understand how this know-how appeared and was integrated into the chaîne opératoire of large-scale metal production.

Assaying ores in the 16th century

Historians of metallurgy have perhaps neglected the assaying of ores despite the fact that any profitable mineral exploitation will depend on it — even if it is not an essential step within a large-scale metal production chaîne opératoire. Relevant studies have been published in the last ten years concerning metallurgical activities at Oberstockstall (Martinón-Torres and Rehren 2005; Mongiatti *et al* 2009), but studies of small-scale techniques generally deal with assaying metals rather than ores. Historic sources show that the assaying of ores, which was usually carried out at smelting works, had several functions (Gauthier 2007b; Gauthier and Fluck forthcoming).

Firstly, in a context of prospecting, it showed the quality of the ore, and the quantity of metal which could be expected from such ore — it could indicate whether or not a particular mining operation should be continued. Secondly, to regulate the business between miners and smelting works, it was the means to fix the price of ore. This appears as the main aim of assaying ores in the 16th century. Finally, in the process of industrial production at the smelting work, assaying ores provided important information about their pyrotechnical behaviour and allowed the larger process to be perfected. Thanks to this knowledge, ores were mixed and/or other materials added to the furnace charge. Experiments can help to understand the job of the assayer and their importance in mine exploitation.

We have few sources from the Middle Ages but we know that an important development occurred at the end of the period (Gauthier 2007a); this can be seen in a context of European mining expansion. A new technique was established in the east of the German mining area (Saxony, Bohemia and the Carpathians). This technique used a very small quantity of ore, typically a few grams or a few tens of grams. It took place in a laboratory and used specific equipment, all of which is well documented in technical treatises of the 16th century. There was no real evolution after this time and the technique of small-scale ore assaying has remained in use until the 21st century. Essentially the same technique is still used in Bolivia; although modern equipment is used, the chaîne opératoire has remained largely unchanged. Our study, however, concentrates on this technology as practiced from the 16th century to the 19th century, with the aim to approach as precisely as possible the chaîne opératoire of small-scale assaying of ores in this period.

Experimental parameters

The equipment

Our equipment is based on information from technical treatises from the 16th to the 19th century. The muffle furnace



Figure 1: The muffle furnace used for the experiments.

(Fig 1) was made in clay by François Peyrat (a potter) following depictions and descriptions of 19th-century furnaces. It comprises a round chimney 0.65m high with an internal diameter of 0.2m. The smelting chamber, which is protected by a muffle, is 0.16m long, 0.12m wide and 0.1m high. The muffle provides a chamber with a controlled atmosphere protected from direct contact with charcoal. There is an ash pan at the base, under a grate of clay. The thickness of the walls of the muffle is about 50mm. On the Melle experiments platform, our furnace is within a covered building but this is not entirely enclosed. Therefore, depending on the weather, we sometimes had to use an electric bellows to reach the required temperature of between 1000 and 1100°C (which normally would not be necessary if the furnace was inside an enclosed space). Ores are smelted in industrial clay *scorifiers* with a larger capacity than archaeological ones. We did not have any problem of reaction between ceramic and lead. The ash cupels used are also modern but of a capacity close to that of the archaeological items.

The ores

Our experimental programme focuses on the assay of argentiferous galena; the most important silver ore in the Middle Ages and the 16th century. Furthermore, it is the simplest ore to obtain and the processing is fairly straightforward for the historian or archaeologist, neither of whom is a metallurgist. Experiments on silver ores are in fact much more complex. We used some samples of more or less known ores, of variable quality and quantity. The variability of gangues especially has an influence on the smelting process. The first assays were undertaken to familiarise the experimenters with the furnace and to develop an understanding of galena smelting using Romanian galena which contained no appreciable silver. Subsequently, when good results had been obtained consistently, we collected

ores from archaeological sites (Fig 2). These galenas included some from Melle (associated with quartz gangue), Altenberg, Sainte-Marie-aux-Mines, Alsace (associated with siderite gangue) and the Italian west Alps (Piedmont). The two former sources were abundant, consistent and from known geological contexts but the latter ores were of rather poor and variable quality, their geological context was poorly known and they available in only small quantities. Contrary to some previous experiments, we were in a real situation of discovery, comparable to that of an assayer when prospecting.

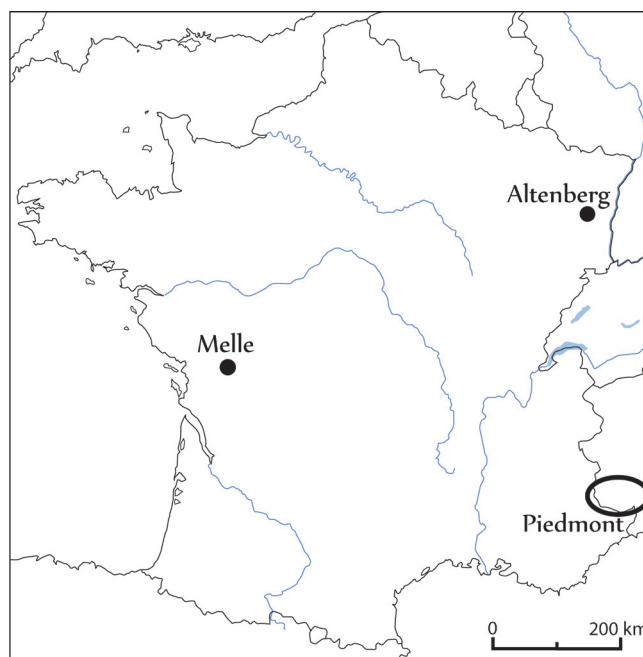


Figure 2: Location of ores used in the experiments.



Figure 3: Crushing galena from the Altenberg.

To compare the results across different experiments, all ores were prepared in the same way (Fig 3): crushing, manual selection and grinding to powder, with a sieve used to keep only the sub-250 μ m fraction. Ores prepared in this way provided satisfactory results during the first session, so we kept the procedure for the following assays. Sieving quartz gangue ores at 250 μ m tended to remove quartz because of the significant difference in hardness between galena (2.5 on the Mohs scale) and quartz (7). This is not the case for limestone (calcite, 3) or barite (3–3.5) gangue ores which are much more difficult to enrich. This reinforces the importance of sampling, of the representativeness of the assayed sample, about which very little technical information is available in historical and archaeological sources. However, the wish to concentrate our study on the metallurgical operations forced us to resist multiplying the number of experimental parameters. So we did not attempt to beneficiate ores by density separation. This choice also allowed us to appreciate effects of fluxes on different qualities of ores.

Assaying metallurgy of galena

Galena is a lead sulphide composed of 86.6wt% lead and 13.4wt% sulphur, with sometimes a small amount of silver. The aim of the metallurgist is principally to obtain this silver, even if the lead had played a significant role in past mining economies. The extraction of silver from galena has multiple steps: the ore may be roasted in order to eliminate sulphur and obtain a lead oxide which can then be reduced by smelting to metallic lead which will contain any of the silver that had been present in the ore. The last stage is to separate the lead and silver by cupellation. In small-scale assaying these three steps are done in two operations: the smelting in a *scorifier*, where roasting and reduction take place. This is possible thanks to the smelting chamber being protected by the muffle, which allows control of the atmosphere. The result is a lead *regulus* which is refined in a bone ash cupel which absorbs lead oxide leaving a silver button on the surface. The quality of the ore is calculated from the initial weight of the ore and the final weight of the silver button. Our main aim is the study of the *scorification* technique, so cupellation will not be examined (Guirado *et al* 2010; Mille and Téreygeol 2011, 97–101). Assaying ores can also involve a preliminary fusion in a triangular crucible, especially for copper ores; as we limited our experiments to galena, this step was unnecessary.

The development of the process

Each assay is a unique event: it is difficult to have the same sequence each time because of the experimental conditions. Nevertheless, we managed to develop a successful process which could be repeated. Good assaying parameters were found for the galenas from Melle and Altenberg, varying duration and temperature of roasting and reduction. In fact, these ores were nearly pure and we had them in large quantities; this allowed the repetition of a particular set of experimental parameters. Assays were made on 40g of ore, although others with less did not show any significant variation. Some of our first experiments with Romanian galena produced a *regulus* of matte, and so we decided to increase the duration of the roasting. Roasting seems to be essentially complete after 30–45 minutes in an oxidizing atmosphere around 850°C. The range of temperature is relatively large but it is obvious that to exceed 900°C would stop the process. We decided to stop the roasting process when the ore stopped producing smoke. The reduction of the ore requires charcoal to be placed inside the muffle which is then closed in order to create a reducing atmosphere. This was generally achieved within 5 or 10 minutes for all assays. The observation of a molten pool which resembled an eye, with lead and slag well separated, is the sign of a successful process. The temperature required depended on the ore. Galena from the Altenberg has a siderite gangue which played the role of a flux and allowed the production of a lead *regulus* with a maximum temperature of 960°C. The Melle galena, associated with silica, needed a higher temperature, sometimes up to 1100°C (Table 1). The molten contents are then poured out into a hole in a metallic sheet, as mentioned in ancient treatises and visible on archaeological items. Lead beneath, and slag on top, are well separated because of the density and mutual insolubility. So it is easy to knock the slag cleanly off the lead and to cupel the *regulus*. For each ore, the process has been repeated several times successfully. To obtain a metallic *regulus* from only one *scorification*, without producing matte, is not a problem. The series of assays with galena from Altenberg shows the reproducibility of the operation (Table 2). With the same sample and nearly the same parameters of time and temperature, we obtained five very similar yields (between 30.4 and 34.8%). Our experiments are also validated by the comparison of silver contents with modern analyses whose results are close to ours.

Italian galenas were much more complex to *scorify*. In fact, the ease with which an ore could be smelted depended mainly on the quality of the gangue as well as the purity of the sample. Ores collected from Piedmont were of poor quality and contained several different gangue minerals. An analysis by portable X-ray fluorescence spectrometer showed the main elements of the gangues and the approximate proportion of lead (Fig 4). The highest concentration of lead is about 33wt%; the lowest (apart from the first sample which we did not assay) is 14.8wt% lead.

The gangue minerals are silica, limestone or barite in varying proportions ranging from 6 to 22.5%. It should be noted that the ore purity can also be estimated by eye: the darker the colour of powdered ore is, the higher the lead content is (Fig 5). This sort of observation is often neglected by modern experimenters, although it is likely to have been essential

Table 1: Maximum temperatures (°C) reached and times (minutes) for assays which produced a metallic regulus.

| Melle | SCO 13/07 | SCO 14/07 | SCO 1/08 | SCO 2/08 | SCO 3/08 | SCO 4/08 | XP1/09 |
|-----------|-----------|-----------|----------|----------|----------|----------|--------|
| Temp | 1050 | 1100 | 1100 | 1000 | 1070 | 960 | 1030 |
| Time | 46 | 49 | 44 | 51 | 53 | 78 | 62 |
| Altenberg | SCO 5/08 | SCO 6/08 | SCO 7/08 | SCO 8/08 | SCO 9/08 | | |
| Temp | 960 | 960 | 960 | 990 | 980 | | |
| Time | 74 | 51 | 51 | 51 | 42 | | |
| Italian | XP4/09 | XP6/09 | XP8/09 | XP9/09 | XP10/09 | XP11/09 | |
| Temp | 1085 | 1030 | 1000 | 1015 | 1060 | 990 | |
| Time | 57 | 35 | 26 | 36 | 31 | 41 | |

Table 2: Results of assays of galena from Altenberg

| | SCO 5/08 | SCO 6/08 | SCO 7/08 | SCO 8/08 | SCO 9/08 |
|-------------|----------|----------|--------------|----------|--------------|
| Sample (g) | 40 | 40 | 40 | 40 | 40 |
| Flux | | | | Slack | Borax 1.27 g |
| Regulus | Pb | Pb | Pb | Pb | Pb |
| Regulus (g) | 12.9 | 12.2 | With slag 29 | 13.9 | 12.1 |
| Yield % | 32.2 | 30.4 | | 34.8 | 30.1 |
| Cupellation | Yes | Yes | No | Yes | Yes |

in the past. Variations of time and temperature were not sufficient to obtain a metallic regulus from these Italian ores. So we studied the issue of fluxes. Indeed, when the quality of the sample makes the scorification impossible, the addition of a flux allows the smelting temperature of the sample to be lowered and the elements of it to be separated and reduced. Three fluxes were tested: borax, charcoal slack and lead. Adding borax to two ores did not produce any satisfactory results (we obtained a more aerated bath which attached to the scorifier); it did not help the operation and actually hindered it. Therefore, we did not continue to experiment with this flux. The charcoal slack had effects that are more difficult to appreciate. The slack was used only to obtain a reducing atmosphere at the end of the operation. We added it to the bath at the end of the roasting period. The charcoal dust stayed on the bath, burning during all the reduction time. It seems probable that it made the reduction easier, although no difference could be noticed with assay without slack. However, it caused a problem at the moment of the pouring which provoked a loss of material. In fact, the molten lead could not be poured in one regulus but formed many little fragments (Fig 6). The most successful flux experimented with Italian ores was lead. Indeed, these samples did not contain enough galena to form a slag with the gangue from which the ore had to be separated. Thus, assays without additional lead produced an agglomerate of more-or-less

smelted powder, with at best a very pasty slag. So the addition of lead compensated for the insufficient lead in the ore and played the role of the lead normally derived from the galena: to lower the smelting temperature of the gangue, to join it to form a sufficiently fluid slag and to constitute a metallic regulus which collects the silver from the ore. Indeed, the adding of lead is often quoted in assaying technical treatises for the assaying of ores. Thus, Schlutter advocated scorifying one part ore with eight parts lead, for an ordinary ore, and with 16 parts lead in the case of an ore that was hard to smelt (Schlutter 1750, 154). The process described the progressive addition of lead whereas Ercker advised the addition of lead with the ore in the scorifier (Sisco and Smith 1951, 38), and Agricola recommended that the ore be placed in a bath of molten lead (Hoover and Hoover 1950, 239). We chose this way due to its ease, even if Ercker cautioned that the powdered ore could fly up and thus lead to a loss of material (Sisco and Smith 1951, 40). In our experiments, the limited quantity of ore available meant that a first assay was made

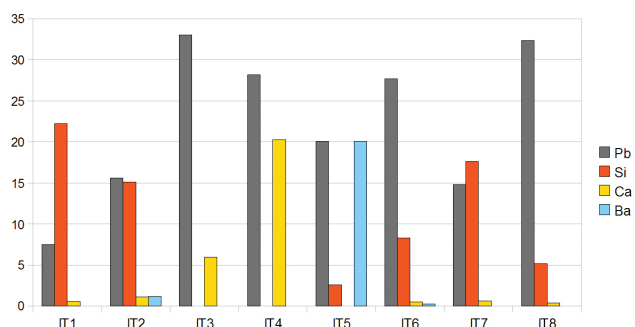


Figure 4: XRF analysis of Italian samples showing proportions (wt%) of lead and gangue elements.

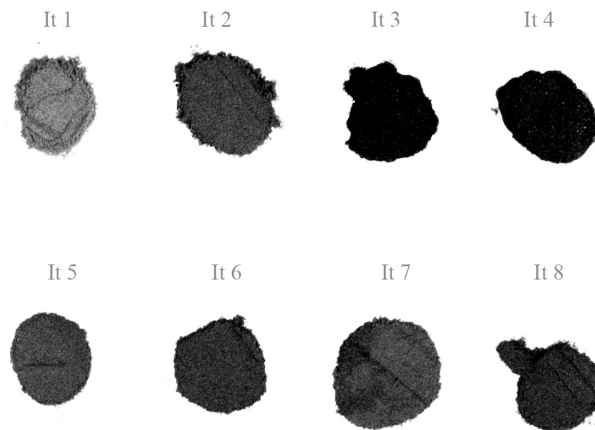


Figure 5: Italian samples in powder form. The visual differences correspond to XRF analyses: the darker samples generally have more lead, cf Fig 4).

without the addition of lead; while a second was made with two parts of lead for one of ore. If necessary, a third assay was carried out with twice the quantity of lead of the second assay. Contrary to our apprehension about the success of roasting, because the ore was no longer in contact with the air, it worked very well. It appeared to be the way to obtain a metallic *regulus*, which concentrated the silver from the ore, with all the Italian ores. The third assay, with four parts of lead for one of sample, allowed the production of a slag fluid enough for all assayed samples (Fig 7). Thus, lead addition is an effective solution that is easy to implement, and allowed the smelting of galena samples of any purity and associated with any sort of gangue minerals. We wonder on one hand if it was systematically applied, and on the other hand, what was the minimum quality of an ore to decide to assay it. Our experiments showed that silver is technically obtainable from very poor ores. This implies that assayers may have assayed a large diversity of materials.

Nevertheless, we have to acknowledge the limits of these experiments. Obviously, it is difficult to control everything in the process because of the weather or other parameters over which we have no control. A frequent problem is that the bath of molten lead and slag was not sufficiently fluid, even with pure samples. This results in a part of the metallic lead being trapped in the slag, and thus a proportional loss of silver at the end. This could be resolved working with fluxes, especially increasing the proportion of added lead. Another limit of our experiments was the production of slag *regulus*. It happened twice among more than 50 assays. We have no explanation for these results which could be due to a mistake in the sampling.

The use of lead as a flux raised two new issues about assaying with a *scorifier*: the first one is that the yield in metal of the sample could no longer be compared with assaying without the addition of lead. This point is very difficult to appreciate because part of the lead formed the slag. The second point concerns the quantity of ore assayed and the quantity of lead



Figure 6: Result of an assay with charcoal slack addition: the regulus is fragmented.



Figure 7: Scorifiers after three assays of one Italian sample: the first without additional lead, the second with two parts of lead, the third with four parts of lead.

added to it. To produce a very fluid slag and still be able to collect all the metallic lead from the ore, we had to increase the lead to eight times the sample, as mentioned by Schlutter (1750, 154). Then the problem is the capacity of the *scorifier*. The more gangue the sample contains, the more voluminous it is, and more lead must be added. Eight lead parts, let alone sixteen parts, could not be smelted in a *scorifier*. Although Biringuccio spoke about an ore charge of an ounce (Smith and Gnudi 1990), assays should have been carried out on less than 10g of ore. Studying archaeological *scorifiers* confirms this idea.

Conclusion

These experiments into assaying techniques of galena with a *scorifier* provide new insights to a topic mainly studied from historical and archaeological sources. They allow a new interpretation of technical treatises and a better comprehension of what their authors wanted to pass on. The role of assaying in the operating system of silver production is also clarified. It gives a better idea of the assayer's work and the way decisions were made about ore assaying. Experimental assaying of ores also offers an interesting analogy between the experimenter's and the assayer's situation. Actually a part of the assayer's job was to discover new ores and to adapt the smelting process to them. The assayer was a specialist who necessarily experimented in order to develop a standardized analytical method, the only way to ensure reproducibility in assays and to offer a good knowledge of the ores to miners and smelters.

From a technical point of view, experiments conducted in Melle have the chance to enjoy a unique platform with facilities which allow a rather coherent approach to past techniques. Nevertheless, it remains difficult to develop a strict experimental protocol, particularly in the case of ores assaying techniques, since choices have to be made during each operation. Thus parameters of time, temperature and atmosphere in the muffle change inevitably in a more or less controlled way. However, our efforts were successful and included several key elements: it is essential that the ore be as rich as possible and fluxes should be added as necessary, especially lead. Thus all ores can be assayed successfully. Many other fluxes mentioned by Biringuccio and Agricola are still to be tried, but would normally be used with silver ores that are difficult to find now. Using such fluxes will necessarily launch a reflection about correspondence between small-

and large-scale operations. Although ancient authors attest that assaying is similar to full scale smelting, it is very likely that significant differences were present. Thus methods, aims and interdependence of small- and large-scale could be compared. Last, capacities of *scorifiers* have to be studied and assays will be carried out on very small charge of ore.

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