

CHEMISTRY AS A TOOL FOR HISTORICAL RESEARCH: IDENTIFYING PATHS OF HISTORICAL MERCURY POLLUTION IN THE HISPANIC NEW WORLD

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Introduction

This article is the first of a series that explore the potential of chemistry as an efficient tool for historical research. Basic chemical principles such as the stoichiometry of chemical reactions provide the historian with a powerful tool to judge the reliability of archival records and interpret better the historiography of events that relate directly to processes of production based on chemical reactions. Chemical mass balances have determined both revenue streams and environmental consequences in the past.

A very appropriate case study to apply this approach is the first industrial scale chemical process to have caused a global economic impact. The application of mercury amalgamation to extract silver from the ores of the Hispanic New World during the Early Modern Era was a complete break in technique and scale from all previous methods used to extract silver around the world. Until the middle of the sixteenth century all refining methods applied in Europe to refine silver ores were lead-based: smelting of argentiferous lead or liquation of silver-bearing copper ores (1). In the Hispanic New World initial smelting with lead would be overshadowed by the industrial scale amalgamation of silver ores. During 250 years over 120,000 metric tons (t) of mercury would be lost to the environment through a combination of physical and chemical pathways. This article will use the chemistry of the reactions that occur during the amalgamation of

silver ores to identify and quantify the different mercury loss vectors that resulted from the amalgamation process as practiced in the Hispanic New World.

The Scale of Anthropogenic Emissions of Mercury in the New World

From 1521 to 1810 Spain produced nearly 69% of the total world output of silver from its mines in New Spain (present day Mexico) and in the Vice-Royalty of Peru (present day Peru and Bolivia). During this period there was no other non-Hispanic major silver production in the New World (2). The global economic impact of these exports of silver to Europe and China during the Early Modern Era has received wide coverage in the historiography of this period (3). The same cannot be said regarding the collateral damage to the health of the indigenous people and to the environment, suffered as a consequence of the scale of the use of mercury in the silver extraction process. To quote Richards: “the true environmental costs of silver have not been fully explored or acknowledged by scholars” (4). In the early 1530s Spain began its large scale processing of silver ore deposits mainly from New Spain and some ten years later from the area around Potosí (present day Bolivia) (5).

Smelting with lead was the refining method used in the early stages, but as of the mid 1550s in New Spain and the early 1570s in Potosí, amalgamation with mercury

was implemented, although it never managed to displace completely the use of smelting techniques. The intensive use of mercury to amalgamate silver ores in the New World led to a total loss of at least 1,253,702 *quintales* (57,670 t) of mercury in New Spain from 1558 to 1810, and of 1,386,950 *quintales* (63,800 t) in Peru from 1571 to 1810. The total losses of mercury to the environment thus amount to at least 121,470 t over a period of just over 250 years, an annual average of at least 486 t (6). This total represents the lower limit of the losses of mercury to the environment, as mercury by-products or elemental mercury, during transport, storage and amalgamation in all the mining regions of the Spanish colonies in the New World and their vicinity, without taking into account contraband or losses of mercury at the mercury mine of Huancavelica in present day Peru. It is a scale of yearly mercury losses only observed in modern times on a much wider geographical scale, though not for a continuous period of over two centuries. Anthropogenic mercury emissions registered for whole continents in the year 2000 were North America 146 t, South America 92 t and Europe and Russia 248 t. On a country level, China was the largest contributor in the year 2000 with 605 t, followed by South Africa with 257 t (7).

The environmental implications of historical mercury loss on the global depositions of mercury were reviewed initially by Nriagu, who estimated total emissions of mercury in the New World related to the production of silver at 126,000 t between 1570 and 1820, and assumed that up to 65 percent of the mercury would have been released directly to the atmosphere, with 10 percent lost during transport and 25 percent during washing or lost in the solid wastes of the process. According to Nriagu, this magnitude of airborne emissions of mercury has contributed to the present high background concentrations of mercury on a global scale (8). Camargo has also worked on the assumption that most of the silver-related mercury emissions in this period were by direct volatilization to the atmosphere at different stages of the amalgamation process. He proposes that 75 percent of his projection of 117,000 t of mercury consumed in the production of silver between 1570 and 1820 would have been lost through volatilization, the rest through losses during transport, losses in water waste and other residues. However, Camargo argues that due to the time elapsed the majority of these airborne emissions will have been sequestered mainly as marine sediments so that very little background trace remains in the atmosphere at present (9). More recently Strode, Jaeglé and Selin also assume that 60 percent of mercury used in historical mining activities was released directly into the atmosphere (10).

The most recent published research on the environmental history of silver extraction in the New World by Hagan et al. and Robins is a collaborative effort between scientists and historians, using computer modelling to establish the environment impact of projected mercury concentration levels around the historical mining sites of Potosí (silver) and Huancavelica (mercury). Hagan et al. base their projections on the assumption that 85% of mercury was lost via air emissions of elemental mercury vaporized directly into the atmosphere (11).

In order to achieve a comprehensive accounting of the different paths by which these amounts of mercury found their way to the environment it is necessary to start by reviewing the basics of the chemistry of amalgamation and combining this information with quantitative data obtained from primary historical sources. Silver ores can contain both native silver and silver compounds such as silver sulfide and silver chlorides. Mercury only forms an amalgam with elemental silver, not with the compounds. What makes amalgamation of silver ores completely different from the apparently analogous amalgamation of gold is the fact that mercury plays a double role in the former. On the one hand it is a chemical reagent that forms native silver and calomel by reducing the fraction of silver chloride present in the amalgamation mix. On the other hand it also acts to form the physical mix with the elemental silver that is called an amalgam, and as such is the fraction of mercury that is potentially recoverable from every cycle of the process. The aim of this exercise is to quantify the partition of mercury between these two roles.

Mercury Loss During Amalgamation of Silver Ores

The richest of the silver ores of the Hispanic New World were called *tacana* or *machacado*, native silver that could be worked directly with a hammer. Then came the *pacos* or *colorados*, the silver ores closest to the surface that contained silver chloride and some native silver, and finally *negrillos*, the deepest ores made up mainly of silver sulfide and silver sulfosalts (12). Wherever possible the ores with native silver were smelted with lead, not amalgamated. One of the earliest detailed accounts, from 1585, describes how the initial amalgamation process consisted in adding salt and mercury to a slurry of finely ground silver ore and water which was then heated in vats for six days. Once the amalgamation master decided the mercury had absorbed all the silver present in the ore (the step that required

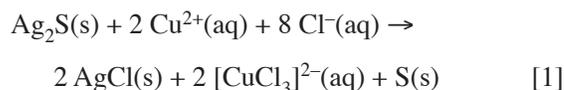
the greatest skill of all) the slurry would be washed so that the lighter material could be entrained by the water and the heavier liquid amalgam stayed in the bottom of the vat. It was then squeezed through a cloth so that the excess liquid mercury was recovered at this stage. The remaining solid amalgam, called a *pella*, was then heated in closed containers to separate the silver metal from the mercury, which was recycled (13).

The first major change in the traditional amalgamation recipe was the addition of ground iron filings around 1587 as reported for Potosí, which was found to reduce the consumption of mercury. By the early 1600s the need to start refining the deeper *negrillos* which were replacing the more superficial *pacos* led to the implementation of an amalgamation recipe that now required a prior roasting of the ore and the addition of roasted copper pyrites (the *magistral*, composed mainly of copper sulfates, though roasted iron pyrites could also be used) to the traditional amalgamation mix of mercury, water and salt. In peak years major mining centres like Potosí could process nearly 700 t of silver ore in each operational day (14).

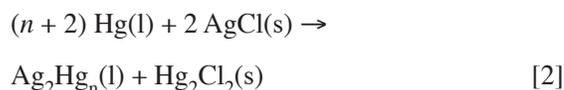
From the earliest reports it is stated that mercury was lost during the amalgamation process, even though the exact cause for the losses was initially unknown. Amalgamation lore held to the notion that one unit of weight of mercury was consumed for every unit of silver extracted. Any additional mercury consumed was due to the physical loss of mercury during operations (15). Sonneschmidt in 1804 recognizes the dual role of mercury and mentions the formation of “sweet mercury” (calomel), as a result of reactions between mercury and the muriatic acid he believed was formed during amalgamation, as well as by the reduction of the silver chloride (16). In his detailed study of Mexican silver mining published in 1843, Saint Clair Duport refers to Sonneschmidt’s work and refers to the formation of a chloride of mercury both from the reduction of silver chloride and from the reaction between mercury and the copper chloride he states is formed from copper sulfate and sodium chloride during the amalgamation of silver ores (17). In his classic work on the metallurgy of silver, Percy in 1880 deals at length with experiments carried out on the conversion of silver sulfide to silver chloride in the presence of cupric chloride, water, sodium chloride and oxygen. He also comments on the reduction of silver chloride to elemental silver in the presence of sodium chloride in solution along with mercury or iron. On the subject of amalgamation he states “a large portion of the mercury used is supposed to be converted into calomel” (18).

Chemical Reactions for the Amalgamation of Silver Ores

Johnson and Whittle’s work is the latest contribution based on actual laboratory experiments, and they postulate an oxidative chloride leaching since they find no major quantities of copper sulfide produced during amalgamation. The silver sulfides (the *negrillos*) are first converted into silver chloride in the presence of chloride (common salt) and Cu(II) ions (from copper *magistral*) (19):



Then mercury reduces the silver chlorides either originally present or produced from the silver sulfides to elemental silver, which in turn is amalgamated by the excess mercury present in the recipe. These two steps are condensed into the following equation (19):



Ag_2Hg_n corresponds to the formula for the liquid amalgam. The elemental sulfur (S) that is produced can combine with mercury to produce cinnabar (Hg_2S), and any excess of *magistral* would have also consumed mercury by producing further calomel (20).

To arrive at a quantitative breakdown of how much mercury was lost through physical or chemical paths the first step is to establish a very simplified mass balance of the amalgamation of a silver ore that contains no native silver and where no physical losses are involved (Figure 1). Since it was common practice to smelt ores rich in

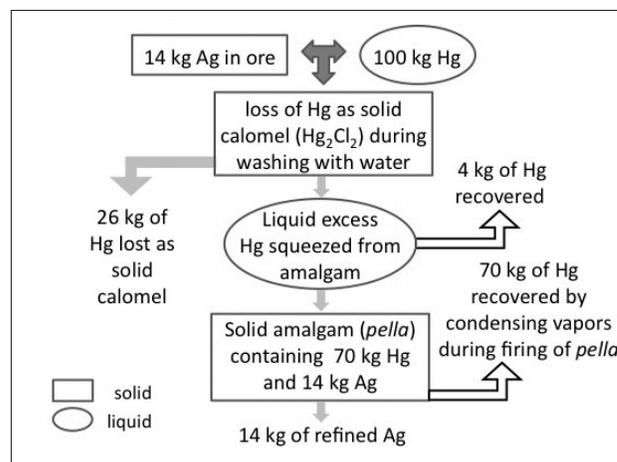


Figure 1. Simplified mass balance of amalgamation process

native silver rather than amalgamate them, this initial premise with respect to the nature of the silver ore is representative of the historical reality.

The total amount of mercury added to the ore during amalgamation was in proportion to the amount of silver estimated to be extracted in the ore. I will use as a starting point a proportion of seven to one in weight (21). Thus if I begin the amalgamation cycle using 100 kg of mercury, that means I am treating a quantity of ore that holds 14 kg (to the nearest kg) of silver in the form of chlorides or sulfides. It is not necessary to know the total quantity of ore treated or the exact proportion of either compound. From equation 2 it follows that every mole of silver extracted is accompanied by one mole of mercury converted into calomel. Therefore, for each kilogram of silver extracted, the amalgamation reaction consumes 1.86 kg of mercury in the form of calomel. It is irrelevant for this exercise whether the silver chloride that is reduced by mercury was present originally in the ore or is the result of the conversion of silver sulfides according to Equation 1. The assumption that matters is that no elemental silver can be produced except by the reduction of silver chloride by mercury.

I further assume that in a single cycle the totality of the 14 kg of silver is extracted, which then implies a total chemical loss of 26 kg of mercury as calomel. (Throughout this exercise I only refer to the weight of mercury lost as calomel, not to a weight of calomel produced.) In the next step of the amalgamation process the liquid amalgam containing the 14 kg of silver is squeezed and hammered very thoroughly so as to recover as much as possible of the excess mercury, leaving a solid amalgam or *pella*. The primary sources from the sixteenth century indicate that the composition of the *pella* was approximately 5 parts mercury to one part silver (22). Because of the way the model has been set up the exact composition of the *pella* does not affect the results. The *pella* now contains 14 kg of silver and 70 kg of mercury, while 4 kg of mercury were recovered by squeezing it.

In this simple model all the 70 kg of mercury will be recovered after the firing of the *pella* since for now I have assumed that there is no physical loss of mercury at any stage. In the final balance, after extracting 14 kg of silver, 74 kg of mercury is recovered in two different batches, one by a simple operation of squeezing a liquid amalgam under a twisted and beaten cloth, and the remainder by the more critical operation of heating the *pellas* and condensing the mercury vapours. In addition 26 kg of mercury are lost as solid calomel carried away in the washings.

In order to be able to correlate the results of this very simple model with historical values of the mercury to silver weight ratio it is necessary to take into account the effect of any native silver in the ore and of the physical losses of mercury. I will designate by f_a the fraction of silver present as silver chloride or silver sulfide in the ore, with values between 0 and 1. This is not equivalent to the amount of silver in an ore, only of the fraction of silver chloride and sulfide of the total silver present, whatever this may be. Thus the weight ratio of mercury lost as calomel to silver refined for ores containing native silver as well as silver chlorides and sulfides can be expressed in the following manner:

$$[\text{Hg/Ag}]_{\text{calomel loss}} = 1.86f_a$$

If the silver content in the ore is made up of pure native silver, f_a is equal to zero and no mercury is lost as calomel. If the silver content is made up only of silver chloride and sulfide, then the weight ratio of mercury lost to silver extracted will be 1.86. I am ignoring further chemical losses in the form of secondary reactions between mercury and excess *magistral* to produce calomel or mercury with sulfur to produce cinnabar, but they could be factored into the equation in an analogous manner.

The most simple way to include the effect of physical losses on the weight ratio is to assume a single physical loss factor (f_b) between zero and unity that encompasses both mercury lost through volatilization and mercury lost through washings and spills. By taking this approach the exact amount of mercury remaining in the *pellas* does not need to be known. Based on the amalgamation recipe of seven parts mercury to one part extracted silver from the ore, the weight ratio of mercury to silver due to physical losses of mercury will then be

$$[\text{Hg/Ag}]_{\text{physical losses}} = (7 - 1.86f_a)f_b$$

The term in parentheses on the right-hand side of the equation corresponds to the weight ratio after eliminating the chemical loss. It would be possible to separate “cold” losses of mercury (spills, washings) from “hot” losses (volatilization) but for the purpose of this exercise I will continue using a single loss factor, f_b .

The total weight ratio taking into account both chemical and physical losses can now be expressed as

$$\text{Hg/Ag} = 1.86f_a + (7 - 1.86f_a)f_b$$

where

Hg/Ag is the weight ratio of mercury lost to silver extracted

f_a is the fraction of silver present in the ore in the forms of chloride or sulfide, between 0 and 1

f_b is the fraction of recoverable mercury (as identified in the oversimplified model above) physically lost during amalgamation, between 0 and 1

The most appropriate cross-check for this simple model is to use the ranges reported in the historiography for the loss of mercury per weight of silver extracted, to see how well the formula can predict these historical values and how sensitive they are to both f_a and f_b .

Calomel and Historical Correspondencia Values

The chemical equations of the previous section tell us that in the absence of native silver in the ore and excluding other side reactions of mercury or physical losses in the amalgamation of silver ores using copper *magistral*, for every mole of silver recovered one mole of mercury would be lost as solid calomel. In this scenario, the theoretical weight ratio of mercury consumed to silver produced using amalgamation would be 1.86. How does

Table 1. Historical values of Hg/Ag weight ratios reported for amalgamation

Mercury*	Silver*	Location	Period	Hg/Ag†	Source**	
1 ql	100 mk	Pachuca, New Spain	16 c	2.1	a, 165	
1 ql	115 mk	Pachuca, New Spain	end 16 c	1.8	a, 184	
1 lb	1 mk	New Spain	1580s	2.0	b, 175	
1 ql	115 mk	New Spain	1590s	1.8	c, 175	
1 ql	150 mk	Potosí, Peru	1588	1.4	d, 82	
1 ql	160 mk	Potosí, Peru	1635	1.3		
13,000 lb	7800 lb	Potosí, Peru	colonial era	1.7	e, 59-60	
1 ql	80 mk	New Spain		2.6	c, 175	
1 ql	140 mk	New Spain		1.5		
1 lb	1 mk	Honduras		2.0	f, 53	
1 ql	100 mk	New World best practice		2.1	g, 556	
1 ql	85 mk	Bolaños, New Spain		2.4		
1 ql	125 mk	Guanajuato, New Spain		1.6		
1 ql	112-126 mk	Zacatecas, New Spain		1.6-1.8		
		Potosí, Peru		1750s	1.5	h, 105
1 ql	120 mk	New Spain		1770s	1.7	i, 75
1 ql	80 mk	San Luis Potosí, Sulpec, others; New Spain	2.6			
1 ql	125 mk	Guanajuato, New Spain	1.6			
1.5 mk	1 mk	Zacatecas, New Spain	1835	1.5	j, 80	
12 oz	8 oz	Guanajuato, New Spain	mid 19 c	1.5	k, 118	
10-24 oz	8 oz	Guanajuato, New Spain		1.2-3	k, 119	
1 lb	1 mk	New Spain	1836	2.0	k, 134	
12 oz	8 oz	Catorce, New Spain	mid 19 c	1.5	k, 143	
15 oz	8 oz	Zacatecas, New Spain		1.9	k, 251	
12-14 oz	8 oz	Fresnillo, New Spain		1.5-1.8	k, 275, 279	
8-13 oz	8 oz	Guadalupe, New Spain		1-1.6	k, 319, 328	

*Units used: 1 mark (mk) = 8 ounces (oz) = 0.224 kg; 1 quintal (ql) = 46 kg.

†Hg/Ag weight ratio calculated from *correspondencia* values.

**Letters refer to ref. 25.

this compare with the historical data for the Hispanic New World?

Tepaske and Brown report a total of 34,184,310 kg of silver produced in Peru from 1571 to 1810, and a total of 1,386,950 *quintales* (63,799,700 kg) of mercury consumed in this period (23). This gives a weight ratio of mercury consumed to silver produced of 1.87. An analogous calculation for New Spain based on their data gives a ratio of 1.19, but since smelting may have produced up to 25% of the total silver, the adjusted ratio would be closer to 1.6 in the period 1560-1810 (24). Both are weight ratios very close to the theoretical value based on calomel of 1.86.

There is another way to test the utility of the model. Shortly after amalgamation was implemented in the Hispanic New World, the authorities applied an estimate of how much mercury was consumed by the production of silver. By controlling the consumption of mercury by each miner they hoped to avoid an underreporting of the silver extracted for the purposes of contraband. This factor was called the *correspondencia* and it is usually expressed as marks of silver per *quintal* of mercury. The theoretical weight ratio of mercury lost to silver extracted of 1.86 is equivalent to a *correspondencia* of just over 110 marks of silver per *quintal* of mercury for an ore with no native silver and with no physical losses of mercury. A selection of historical *correspondencia* values reported in the historiography is summarized in Table 1 (25). It has a greater amount of information on *correspondencia* values in New Spain but neither geographical location nor historical period are seen to play a determining role in defining the values.

The mercury to silver weight ratios have been calculated for each *correspondencia* value, and have all

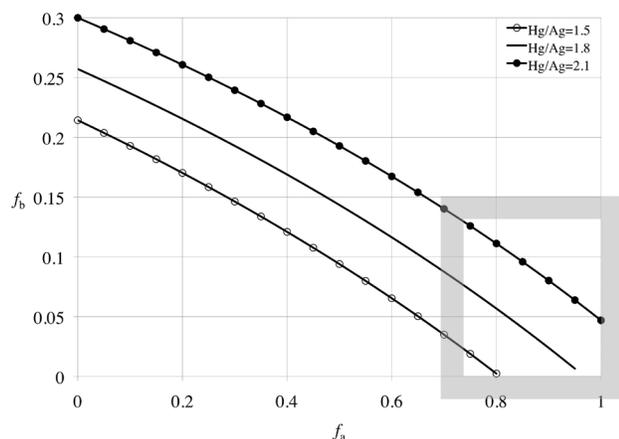


Figure 2. Curves of constant Hg/Ag weight ratio as a function of f_a and f_b .

been given equal weight to arrive at an average value of 1.8 ± 0.3 . The *correspondencia* represented a negotiated figure that balanced the opposing interests of Crown and miners, but it is still an operational indicator of how amalgamation was implemented at each refining region. The proximity of the weight ratio based on the formation of calomel to the average historical values from both New Spain and Peru is a strong indication that the loss of mercury did not simply depend on the skill and experience of each *açoguero* (amalgamation master) but was determined to a great extent by a chemical reaction common to all amalgamation locations and historical periods.

From a purely mathematical standpoint the range of permissible physical losses of mercury is restricted both by the average values of the Hg/Ag ratio (between 1.5 and 2.1) and by the fact that amalgamation is known to have been applied preferentially to silver ores with little or no native silver content (high values of f_a , for the sake of argument > 0.75). Figure 2 illustrates the consequence of these values on the possible range of physical losses of mercury (f_b values). The lower right of Figure 2, framed in a grey box, represents both typical historical Hg/Ag values and the quality of ore one would expect would

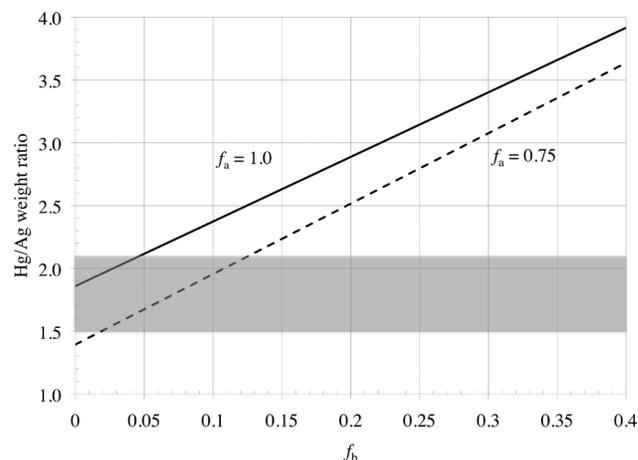


Figure 3. Sensitivity of Hg/Ag weight ratio to f_b . (Grey band represents historically observed weight ratio of 1.5 ± 0.3 .)

have been usually amalgamated rather than smelted during this period. The f_a values near unity represent the deeper *negrillo* ores (high in silver sulfides, very low to nonexistent native silver). In this case the average loss of mercury due to physical causes would have to lie close to the 5 to 10% range to maintain the overall mercury to silver weight ratio in the historical range. If higher physical losses are assumed to apply during the amalgamation of silver ores with low or inexistent

native silver content, the mercury to silver weight ratio would quickly take on values greater than the range reported in Table 1, as can be observed in Figure 3, and such high values are not seen in the historiography. In addition, the model that leads to Figures 2 and 3 already implies minimal chemical losses, so that the inclusion of additional factors that would increase the ratio by consuming more mercury, such as the formation of additional calomel caused by excess *magistral* or the reaction of sulfur with mercury, places a further restriction on the level of physical losses. It is therefore difficult to justify persistent high physical losses of mercury during the amalgamation process of silver ores in the light of the historical range of *correspondencia* values and the nature of the silver ore being amalgamated.

Physical losses of mercury would have been one of the few variables that could be controlled by the *açoguero*, as a means to cut costs and increase profits. There is at least one contemporary voice that indicates that mercury was precisely the one parameter that an *açoguero* should control with skill, and for a very good reason (26):

If mercury is lost [through volatilization during the firing of the *pella*] and the loss cannot be remedied ... this is the greatest loss that can be had, and it can happen to a miner during the refining process; and when it happens, not even the value of the silver [refined] can match the value of the mercury that is lost.

Duport cites mercury losses of just 0.06% during the heating of the *pella* and recycling of mercury in Mexico towards mid nineteenth century (27). Finally, at the risk of further contributing to any confusion between gold and silver amalgamation, it is significant that present day artisanal mining practices using mercury to amalgamate gold in the Amazon basin are estimated to have 5 percent vapour losses using closed containers to vaporize and recover the mercury (28). A low level of physical loss of mercury during the heating of the *pellas* may have been more the norm than the exception.

Two Exceptions: the *Beneficio del Hierro* and the *Beneficio de Cazo*

From 1587 to the early 1600s the silver refiners in Potosí applied a new variation to the traditional amalgamation recipe of mercury, salt and water. The Corzo brothers experimented with adding iron filings to the mix and found that the loss of mercury decreased (29). The reason is that iron can reduce silver chloride in saline solution (30):



When the Corzo brothers added iron filings to the amalgamation mix they found by accident an alternate route to reduce the silver chloride that competes with the conversion of mercury into calomel shown in Equation 2. Under these conditions the expected mercury to silver weight ratio would not be in the range of 1.9, but a much lower value determined by how much silver was amalgamated using the *beneficio del hierro*. The addition of iron filings to the traditional amalgamation recipe did not give good results with *negrillos*, which is now possible to explain since they do not have a high content of silver chloride and the silver sulfide would not be reduced by the iron. By the early 1600s the addition of copper *magistral* was found to be very effective in the amalgamation of *negrillos* and so it would soon displace the *beneficio del hierro* as the amalgamation recipe of choice. The *beneficio del hierro* would only influence the historical data in the short interval from 1590s to the 1600s (14).

The miner-priest Barba proposed in the 1610s a variation in the process using copper vats to amalgamate *pacos* using the traditional recipe of mercury, salt and water, the *Beneficio de Cazo*. Saint Clair Duport confirms Barba's initial claim that no mercury losses occur, but specifies only as long as the added mercury does not cover the whole copper surfaces of the interior of the vessel. This is not a new amalgamation recipe but a change in the batch process, which also uses greater heat to decrease substantially the amalgamation time required. It was never applied on a wide scale and gave its best results only with the richer silver ores. Whether the decrease in mercury consumption is due to the high native silver content of the ores or was the result of the interior copper metal surface of the vat having a chemical role during amalgamation is not clear (31).

Quantifying the Losses of Mercury from the Amalgamation of Silver Ores

In order to arrive at a quantitative breakdown by percentage of losses of mercury as calomel and through volatilization, one can combine the expressions used above for the calomel and physical portions of the Hg/Ag ratio. The percentage of mercury lost to calomel is

$$\% \text{Hg lost to calomel} = \frac{1.86 f_a}{1.86 f_a + (7 - 1.86 f_a) f_b} \times 100\%$$

Similarly, the percentage lost to physical processes is

$$\% \text{Hg physical loss} = \frac{(7 - 1.86f_a)f_b}{1.86f_a + (7 - 1.86f_a)f_b} \times 100\%$$

Bear in mind that these physical losses include losses by volatilization, so they can be interpreted as an upper limit to emissions of mercury to the atmosphere.

Table 2 provides a summary that indicates a loss of mercury as solid calomel that accounts for 66 to 93 percent of total mercury losses, while physical losses would have been in the range of only 7 to 34 percent. The parameters of two of the entries in Table 2 are taken from the left edge of the “frame” in Figure 2; they represent the upper and lower limits of typical Hg/Ag weight ratios and an ore that has a relatively large amount of native silver. The additional point corresponds to an ore containing no native silver and a Hg/Ag weight ratio at the high end of the average historical range.

Table 2. Percentage breakdown of mercury losses to the environment as a result of the refining of silver ores with mercury

f_a	0.75	0.75	1.00
f_b	0.13	0.02	0.05
Hg/Ag	2.1	1.5	2.1
% mercury chemical loss as calomel	66%	93%	88%
% mercury physical loss	34%	7%	12%

Instead of the majority of the mercury emissions (from 60 to 75 percent) taking place as direct volatilization of elemental mercury, up to nine tenths of the mercury pollution would have been in the form of solid calomel washed downstream or buried in landfills from each refining unit (*ingenio* in Peru, *hacienda* in New Spain). Losses during transit or storage plus additional consumption of mercury due to side reactions with *magistral* and sulfur would need to be factored in, but they do not alter the fundamental change in how the historical impact of mercury losses should be analyzed.

Conclusions

Spanish miners in the Hispanic New World were the first in history to apply amalgamation with mercury to silver ores on an industrial scale. From the start they realized that they were losing mercury no matter how skilled they were in distilling the mercury and recovering it by cooling the vapours with water in a special vessel. They had workers recovering the fine silt, or *lamas*, and

heating them to extract whatever silver and mercury may have been entrained in the washings. Even the coarser sediment, the *relaves*, could be sold to those looking to recover the last ounce of mercury and silver from each cycle of amalgamation. In spite of these efforts to maximize the recycling of mercury, within the first thirty years a rule of thumb was established that approximately two weights of mercury would be lost for each weight of silver recovered.

Up to now this weight ratio or *correspondencia* has been commented upon in the historiography as an empirical number with no theoretical justification (32). However the application of the principles of stoichiometry to chemical reactions that are known to occur during amalgamation provides a chemical underpinning to the *correspondencia* that has not been clearly defined before. This theoretical base converts the *correspondencia* from a passive mirror of operational empiricism into an active tool of historical analysis. Using the same simple model that can explain the historical ranges observed for the *correspondencia*, it can also quantitatively break down the vectors of mercury loss into calomel and physical losses. The result is a completely different scenario from that assumed in most studies published to the present. Calomel is the form in which up to 90% of mercury is lost from refining centres using amalgamation, not volatilized mercury (33). The impact of historical mercury loss from silver refining centres therefore needs to be re-examined on the basis that most of this mercury would have been washed away or buried as solid calomel, together with the even larger amount of detritus from the amalgamation operation. The combined risk that calomel and elemental mercury posed to people and the environment during two and a half centuries of continuous silver amalgamation in the Hispanic New World is currently under study. In principle if the amount of mercury consumed or silver refined by amalgamation is available in the official data, it is possible to estimate the quantities of calomel and elemental mercury that would have been issued to the environment. As the next paper will show, the problem lies in determining which, if any, of the historical archival data sets on mercury and silver is reliable enough to arrive at a true value of the extent of mercury losses to the environment.

Acknowledgement

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responsible for any errors in the derivation of the same. The article as a whole has benefited greatly from his observations, as well as those of the anonymous reviewer.

References and Notes

- I. Blanchard, *Mining, Metallurgy and Minting in the Middle Ages. Continuing Afro-American Supremacy 1250-1450*, Vol. 3, Franz Steiner Verlag Stuttgart, 2005, xiv-xv, 973. In the early sixteenth century mercury amalgamation was applied on a very small scale to refine some silver ores of the Venetian controlled Schio mines, according to R. Vergani, "La metallurgie des non-ferreux dans la republique du Venise (XVe-XVIIIe siècles)" in Paul Benoit, Ed., *Mines et metallurgie*, Programme Rhône-Alpes recherches en sciences humaines, Villeurbanne, 1994, 210.
- J. J. Tepaske and K. W. Brown, *A New World of Gold and Silver*, Brill, Leiden, Netherlands, 2010, 140.
- Two viewpoints selected from a very ample historiography on the economic impact of silver from the New World are D. O. Flynn and A. Giraldez, "Cycles of Silver: Global Economic Unity through the Mid-Eighteenth Century," *Journal of World History*, **2002**, *13*, 391-427 and R. Findlay and K. H. O'Rourke, *Power and Plenty. Trade, War and the World Economy in the Second Millennium*, Princeton University Press, Princeton, 2007, 212-226.
- For specific approaches by historians to the collateral damage from mercury see K. W. Brown, "Workers' Health and Colonial Mercury Mining at Huancavelica, Peru," *The Americas*, **2001**, *57*, 467-496 and J. F. Richards, *The Unending Frontier: An Environmental History of the Early Modern World*, University of California Press, Berkeley, 2006, 366-372. An older literary source on the human cost to the New World of the extraction of silver is Eduardo Galeano, *Open Veins of Latin America*, Monthly Review Press, New York, 1973, 30-33 and 42-49; translated by C. Belfrage.
- J. R. Fisher, *The Economic Aspects of Spanish Imperialism in America 1492-1810*, Liverpool University Press, Liverpool, 1997, 94.
- Ref. 2, 139, 211.
- E. G. Pacyna, J. M. Pacyna, F. Steenhuisen and S. Wilson, "Global Anthropogenic Mercury Emission Inventory for 2000," *Atmos. Environ.*, **2006**, *40*, 4048-4063; see 4052, 4056.
- J. Nriagu, "Legacy of Mercury Pollution," *Nature*, **1993**, *363*, 589.
- J. A. Camargo, "Contribution of Spanish-American Silver Mines (1570-1820) to the Present High Mercury Concentrations in the Global Environment: a Review," *Chemosphere*, **2002**, *48*, 51-57.
- S. Strode, L. Jaeglé and N. E. Selin, "Impact of Mercury Emissions from Historic Gold and Silver Mining: Global Modelling," *Atmos. Environ.*, **2009**, *43*, 2012-2017; see 2013.
- N. Hagan, N. Robins, H. Hsu-Kim, S. Halabi, M. Morris, G. Woodall, T. Zhang, A. Bacon, D. B. Richter, J. Vandenberg, "Estimating Historical Atmospheric Mercury Concentrations from Silver Mining and Their Legacies in Present-Day Surface Soil in Potosí, Bolivia." *Atmos. Environ.*, **2011**, *45*, 7619-7626 (see 7621); N. A. Robins, *Mercury, Mining, and Empire: The Human and Ecological Cost of Colonial Silver Mining in the Andes*. Indiana University Press, Bloomington, 2011.
- The terms in Spanish changed from New Spain to Peru, except for the term *negrillos*. A recent summary on the geology of silver deposits that explains how silver chlorides and native silver derived from the original silver sulfides is found in R.H. Sillitoe, "Supergene Silver Enrichment Reassessed," in S. R. Titley, Ed., *Supergene Environments, Processes and Products*, Special Publication 14: Society Economic Geology, Littleton, CO, 2009, 15-32.
- L. Capoché, *Relación General de la Villa Imperial de Potosí*, Biblioteca de Autores Españoles, Tomo 122, Ediciones Atlas, Madrid, 1959, 122-124.
- S. Guerrero, "Chemistry as a Tool for Historical Research: Estimating the Contraband of Silver from Potosí and Oruro, 1576-1650," *Bull. Hist. Chem.*, **2012**, *37*, 72-80.
- St.-C. Duport, *De la production des métaux précieux au Mexique, considérée dans ses rapports avec la Géologie, la Métallurgie et l'Economie Politique*, Firmin Didot Frères, Paris, 1843, 118.
- "mercurio dulce" in F. Sonneschmidt, *Tratado de la amalgamación de Nueva España*, Bossange, Paris, 1825, 107, 127.
- Ref. 15, 124.
- J. Percy, *Metallurgy: the Art of Extracting Metals from their Ores. Silver and Gold – Part I*, John Murray, London, 1880, 73-85, 95, 635.
- D. A. Johnson and K. Whittle, "The Chemistry of the Hispanic American Amalgamation Process," *J. Chem. Soc., Dalton Trans.*, **1999**, *23*, 4239-4243.
- Ref. 19, 4241-4242.
- The amount of mercury required to prepare the amalgam, according to Percy (Ref. 18, 604- 608) ranges from approximately 6 to 8 times the assumed silver content in the ore. I have therefore adopted the intermediate value of 7.
- Ref. 13, 124.
- Ref. 2, 113, 138-139, 211.
- M. O. Mendizábal, *La minería y la metalurgia Mexicanas (1520-1943)*, Centro de Estudios Históricos del Movimiento Obrero, Mexico, 1980, 73.
- The sources for the data in Table 1 are the following:
 - G. Cubillo Moreno, *Los Dominios de la Plata: el precio del auge, el peso del poder. Empresarios y trabajadores en las minas de Pachuca y Zimapán, 1552-1620*, Instituto Nacional de Antropología e Historia/ Consejo Nacional para la Cultura y las Artes, México, 1991;

- b) P. J. Bakewell, *Silver Mining and Society in Colonial Mexico: Zacatecas, 1546-1700*, Cambridge University Press, Cambridge, 1971;
- c) P. J. Bakewell, "Notes on the Mexican Silver Mining Industry in the 1590's." In *Mines of Silver and Gold in the Americas*, P. J. Bakewell, Ed., Variorum, Aldershot, 1996;
- d) P. J. Bakewell, "Registered Silver Production in the Potosi District 1550-1735," *Jahrbuch für Geschichte Lateinamerikas*, **1975**, 12, 67-103;
- e) P. J. Bakewell, *Silver and Entrepreneurship in Seventeenth Century : Potosí : The Life and Times of Antonio López De Quiroga*, Southern Methodist University Press, Dallas, 1995;
- f) L. A. Newson, "Silver Mining in Colonial Honduras," *Revista de Historia de América*, **1984**, 97, 45-76;
- g) D.A. Brading and H. E. Cross, "Colonial Silver Mining: Mexico and Peru," *The Hispanic American Historical Review*, **1972**, 52, 545-79;
- h) G. Arduz Eguía, *Ensayos sobre la Historia de la minería Altoperuana*, Editorial Paraninfo, Madrid, 1985;
- i) Ref. 24;
- j) J. Burkart, "Du filón et des mines de Veta-Grande, près de la ville de Zacatecas, dans l'état du même nom, au Mexique" *Annales des Mines, 3eme serie*, **1835**, 8, 55-87;
- k) Ref. 15.
26. "Si se pierde el azogue y no se puede remediar ... es la mayor pérdida que puede haber y sucede al minero en el dicho beneficio; y cuando sucede, no llega el valor de la plata al azogue que se pierde." Quoted from Gomez de Cervantes (1599) in M. Bargalló, *La minería y la metalurgia en la América española durante la época colonial*, Fondo de Cultura Económica, México, 1955, 245-246.
27. Ref. 15, 117.
28. M. M. Veiga, J. Hinton and C. Lilly, "Mercury in the Amazon: A Comprehensive Review with Special Emphasis on Bioaccumulation and Bioindicators," in *Proceedings of the National Institute for Minamata Disease Forum '99*, Minamata, Japan, Oct 12-13, 1999, 22; available at http://www.unites.uqam.ca/gmf/globalmercuryforum/files/articles/marcello_veiga/veiga_1999.pdf (accessed Oct. 31, 2012).
29. Official reports on the Corzo amalgamation recipe, dated 1588, as quoted in M. Jimenez de la Espada, *Relaciones Geográficas De Indias – Peru*, Vol. II, J. U. Martinez Carrera Ed., Biblioteca de Autores Españoles, Tomo 184, Editorial Atlas, Madrid, 1965, 124-125.
30. Ref. 18, 94.
31. Ref. 15, 151.
32. In 1872 a paper was published that quantified the loss of mercury through calomel as 1.85 times the amount of silver recovered, and conditioned this ratio to the absence of competing reduction routes for silver chloride. Though the author recognized that the physical losses would alter this value, he did not proceed further into the consequences of his analysis. It is a paper that has not figured prominently in the historiography of this subject. M. M. Contreras, "Empleo de los ensayos de pella y de residuos para determinar los adelantos y fin de la amalgamación de la plata en el beneficio de patio," *Historia de la ciencia en Mexico: Estudios y textos*, Elias Trabulse, Ed., CONACYT y Fondo de Cultura Económica, Ciudad de Mexico, 2003, 721-738. The original paper was published in *Anales del Ministerio de Fomento de la Republica Mexicana*, Imprenta de Francisco Diaz de Leon, tomo X, México, D.F., 1872.
33. In mercury mines where no amalgamation takes place this is not the case, and in Huancavelica it remains to be estimated how much mercury was lost to the environment during the firing stage of the cinnabar ore.

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