

The chemistry of the Hispanic-American amalgamation process

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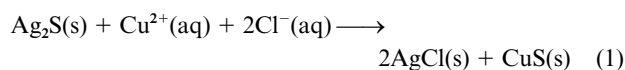
The chemistry of the Hispanic-American amalgamation or patio process for the extraction of silver has been studied through a laboratory model in which a suspension of silver sulfide in concentrated sodium chloride solution reacts with copper(II) chloride before being treated with mercury. Approximately 90% of the silver was extracted and separated as a liquid amalgam. The products of the reaction have been studied by X-ray powder diffraction. The process seems to have incorporated a very early example of oxidative chloride leaching. Copper(II) chloride oxidizes silver sulfide to elemental sulfur, and silver chloride in the form of both a precipitate and solubilized complexes. Copper(I) complexes such as $[\text{CuCl}_3]^{2-}(\text{aq})$ are produced, and then re-oxidized by atmospheric oxygen to copper(II), resulting in the precipitation of insoluble $\text{Cu}_2(\text{OH})_3\text{Cl}$, principally in the form of paratacamite, with smaller amounts of atacamite. Mercury then reduces silver chloride to silver amalgam by forming calomel, and combines with some of the free sulfur to form HgS . In contrast to suggestions made by some previous investigators, no sulfides of copper were detected amongst the products.

From a socio-economic standpoint, the now-obsolete amalgamation process for the extraction of silver was one of the most influential of all chemical operations.^{1,2} This was because it generated nearly all of the Hispanic-American bullion that flooded into Europe from Central and South America during the 16th, 17th and 18th centuries. First, the arrival of this silver coincided with a European inflation that, although small by modern standards, was both unprecedented and socially destabilizing. This experience prompted the formulation of the basic ideas of monetarism which have influenced economic policy in our own time.¹ Secondly, and rather more controversially, there is the claim that the sudden influx of bullion gave rise to profit inflation which stimulated enterprise³ and helped generate a new economic order of the capitalist type. John Maynard Keynes^{4,5} in particular subscribed to this point of view. Thirdly, the eastern movement of the silver from Hispanic-America, through Europe to the Orient, made possible a new and expanded pattern of world trade. In this scheme of things, silver moving out of Western Europe to the east was exchanged for commodities such as timber, grain, flax, furs, hemp, silk, cotton, porcelain, tea, pepper and spices.⁶⁻⁸ The combination of trading logistics and colonialism that this exchange inspired still influences world politics. Finally, the large amounts of mercury that were consumed in making the silver have featured prominently in recent discussions⁹⁻¹¹ of global mercury pollution.

The amalgamation process was introduced into Central and South America soon after 1550, and was made obsolete by the use of cyanide for silver extraction in the early 20th century. During the colonial period the important mining centres included Zacatecas and Guanajuato in Mexico, and Potosi in present-day Bolivia. Mercury came from the notorious cinnabar mines at Huancavelica in Peru, or was shipped across the Atlantic from Almaden in Spain. Although some important variations were later introduced, the essential procedure was that used in Mexico, where silver extraction was carried out on a stone-paved yard called a *patio*, and called the patio process. A modern account of the operation is given by Bakewell,^{12a} and there is a very detailed 19th century description by Percy.^{13a} A mixture of silver ore, salt and water was blended into a mud, and then an ingredient called *magistral*, usually weathered copper pyrites, was added. This was followed by mercury. Thorough mixing over the course of several days was achieved

by continual treading with horses, mules or men. The silver amalgam that was produced was then made more fluid by the addition of extra mercury, and separated by removing less dense material in a current of water. Distillation and recovery of mercury from the amalgam left pure silver which was melted down into ingots.

The chemistry of the process has never properly been established, and standard historical works have noted the inadequacies in chemical understanding.^{12b,14} The most recent reviews^{12b,15-18} agree that the sulfidic ores are converted into silver chloride, or into chloride complexes which arise from the distinct solubility of silver chloride in concentrated chloride solutions. The chloride species can then be reduced by mercury which also forms an amalgam with the silver. There is, however, no agreement over the route by which the silver chloride is formed. Bakewell^{12b,14} quotes equations from Bargallo¹⁷ whose sum, in aqueous media, amounts to eqn. (1). Other



reviewers^{16,18} suggest redox reactions between $\text{Cu}^{2+}(\text{aq})$ and Ag_2S in which the sulfur may be oxidized to the elemental state, and the copper ends up as Cu_2S , $\text{Cu}^{+}(\text{aq})$, CuCl or metallic copper. The direct reduction of silver sulfide by mercury to give an amalgam and HgS has also been proposed.¹⁶ None of these sources gives atmospheric oxygen a role in their reaction schemes. In this respect, the older work of Percy is most interesting. In part 1 of his work on the metallurgy of silver and gold, Percy promised^{13b} an account of his research into the chemistry of the amalgamation process in part 2. Part 2 was never published, but its likely drift can be anticipated from his study of the reaction between silver sulfide, copper(II) chloride and salt in Part 1.^{13c} Essentially, he claimed that copper(II) oxidizes Ag_2S to AgCl and elemental sulfur, while undergoing reduction to CuCl . In a further reaction, atmospheric oxygen then converts both CuCl and Ag_2S into an oxychloride of copper, AgCl and sulfur.

Such inconsistencies justify a new study of the amalgamation process. The pure substances used in a laboratory do not reproduce the indeterminate mixtures of minerals obtained in mining and used on the patio. In this respect, our laboratory studies, like all previous ones, are only a chemical model of the

historical operation. They use Ag_2S in place of the sulfidic ores, and copper(II) chloride in place of *magistral*. This relies on the active ingredient in moist *magistral* being $\text{Cu}^{2+}(\text{aq})$, a belief justified by Percy's observation^{13a} that pure $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was often used in 19th century operations. The other ingredients are pure salt, water and mercury. This choice makes chloride the only anion in the aqueous medium, and strips the process down to the simplest possible combination of reactants. Quantitative accounts of the process^{13a,14} suggest that, in the initial stages of the reaction, silver and mercury were present in the approximate molar ratio of 1 : 3, with a further 30% of mercury being added prior to the final separation of the amalgam. The copper to silver molar ratio seems to have been about 3 : 2 or more. There was also a very large excess of salt. Accurate modelling of the process therefore needs aqueous solutions containing high concentrations of chloride ion. The studies described in this paper were performed in such a medium.

Experimental

The X-ray diffraction (XRD) pattern of our silver sulfide sample (Johnson and Matthey; 99.8% assay) matched the standard pattern of acanthite (14-0072).¹⁹ Other chemicals (*e.g.* $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, BDH 99%) were of Analar grade purity or better. In a typical experiment, 4 mmol of Ag_2S were stirred continuously with a solution of 15 mmol of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 35 cm³ of 4 M NaCl for 4–6 d at 25–35 °C. The solutions were freely exposed to air and no attempt was made to prevent evaporation, but losses were alleviated by occasional small additions of distilled water. When the experiments included amalgamation, 30 mmol of mercury were added after 24 h and, if a full simulation of the extraction process was required, a further 12 mmol of mercury prior to separation of the amalgamated phase by decantation and washing with water. Silver was determined gravimetrically as silver chloride after dissolution of the amalgam in hot nitric acid, followed by sustained heating to ensure oxidation to mercury(II). Sulfate was weighed as barium sulfate, and copper was determined by iodometric titration.

X-Ray powder diffraction data were recorded with a Siemens D5000 diffractometer in reflection mode using Cu-K α radiation. The associated software allowed the patterns to be compared with those in a standard database.¹⁹

Results

The complete extraction process

We first tested the effectiveness of our model system. Acanthite and copper(II) chloride were stirred in water with a large excess of salt for 24 h. Mercury was then added, and stirring continued for 72 h. The addition of further mercury with stirring, and removal of the lighter material by repeated decantation with water, yielded a liquid amalgam which contained some 90% of the silver in the original acanthite. This figure exceeds those claimed in contemporary accounts of the extraction process^{13a} and it shows that our chosen combination of reagents leads to a successful extraction of silver. The soluble phase gave only a very slight acid-insoluble turbidity with barium chloride solution, so sulfate formation is small. The process was next broken up into two stages. This mimics the actual extraction process in that the first addition of mercury was carried out after an interval. It also allows a direct comparison with the work of previous reviewers who broke the reaction up in a similar way.

Stage 1: the reaction between copper(II) chloride and acanthite in concentrated sodium chloride solution

The procedure used above was repeated in the absence of mercury. The X-ray powder diffraction pattern of the lighter fraction of the insoluble phases (Fig. 1) showed the presence of

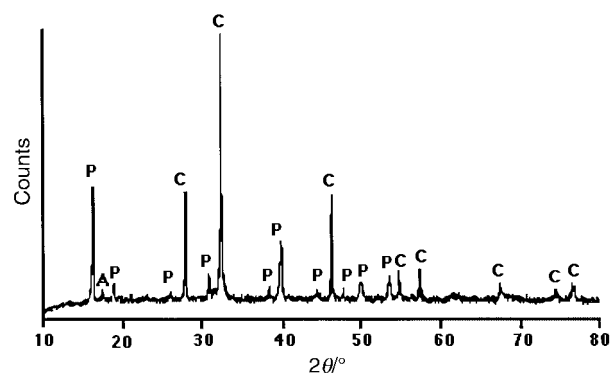


Fig. 1 The X-ray powder diffraction pattern of the lighter fraction of the insoluble material left after the reaction of acanthite and copper(II) chloride in 4 M NaCl in air. A = Atacamite, $\text{Cu}_2(\text{OH})_3\text{Cl}$; C = chlorargyrite, AgCl ; P = paratacamite, $\text{Cu}_2(\text{OH})_3\text{Cl}$.

only AgCl (31-1238)¹⁹ and the basic chloride $\text{Cu}_2(\text{OH})_3\text{Cl}$ in the pale green insoluble material. The pattern for the denser fraction was similar, but the reflections from the copper compound were much less evident. The basic chloride consisted mainly of paratacamite (25-1427),¹⁹ but small amounts of its polymorph, atacamite (25-0269),¹⁹ could also be detected. Atacamite was most easily distinguished from paratacamite by the strong reflection at $d = 5.03 \text{ \AA}$ ($2\theta = 17.6^\circ$). Addition of water to the green filtrate led to the precipitation of further AgCl , showing that considerable silver is present in the form of chloride complexes such as $[\text{AgCl}_3]^{2-}(\text{aq})$. This is consistent with stability constant data²⁰ and solubility studies²¹ which suggest that the solubility of silver chloride at chloride concentrations of 4 M is between 10^{-2} and 10^{-3} M.

Analysis of the filtrate for dissolved sulfate recovered only about 2% of the initial sulfur. However, extraction of the insoluble residue with CS_2 , followed by evaporation of the solvent, deposited 80–85% of total initial sulfur as pale yellow crystals of the element. The elemental sulfur reflections were too weak to be detected in Fig. 1, but they appear (Fig. 2) if paratacamite and substantial amounts of silver chloride are removed by washing with dilute ammonia solution. The XRD pattern then reveals peaks corresponding to those of elemental sulfur (24-0733),¹⁹ the very strong reflection at $d = 3.85 \text{ \AA}$ ($2\theta = 23.3^\circ$) being especially prominent. Apart from sulfur and undissolved silver chloride, the pattern revealed unconsumed acanthite; even after 6 d, therefore, the reaction is incomplete.

The X-ray diffraction patterns of insoluble phases gave no clear evidence of the presence of copper sulfides. Nevertheless, small quantities cannot be ruled out because of the insensitivity of the technique to small amounts (<5%) of crystalline materials and to amorphous phases. Furthermore, it is unfortunate that the strongest reflections of covellite (CuS) coincide with strong reflections in acanthite. Nevertheless, the combination of our observed 85% of recovered sulfur with that present in the unconsumed silver sulfide must account for all or nearly all of the initial sulfur present in Ag_2S . We also found that a copper solution made by combining the initial filtrate with dissolved paratacamite, extracted from the insoluble material by prolonged contact with 2 M HCl, contained 87–90% of the copper in the initial reactants. To draw precise quantitative conclusions is difficult because the long reaction times age the precipitates and make them less willing to dissolve. However, as copper sulfides are insoluble in dilute HCl, these results suggest that nearly all copper in the final products is present as soluble copper(II) or paratacamite, rather than as sulfides. Further support for this conclusion was provided by separate experiments which showed that, in the presence of air, Cu_2S and CuS are oxidized by solutions of copper(II) chloride in 4 M NaCl, the reaction with Cu_2S being very much faster than with CuS . We conclude therefore that if copper sulfides are

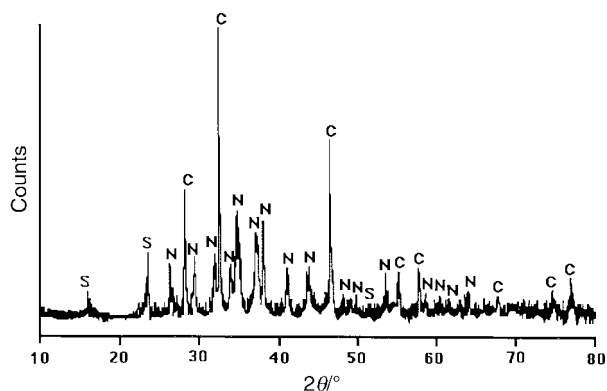
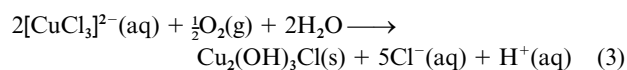
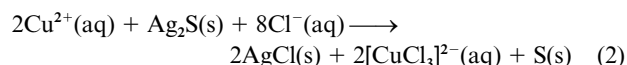


Fig. 2 The X-ray powder diffraction pattern of the insoluble phases left after the washing of the material of Fig. 1 with 3 M ammonia solution. C = Chlorargyrite, AgCl; N = acanthite, Ag₂S; S = elemental sulfur.

present in the final products the amounts are small, and they are likely to be in the form of covellite, CuS, rather than Cu₂S.

The conversion of the sulfide in Ag₂S into sulfur requires an oxidizing agent. When the reaction was performed under oxygen in a sealed container oxygen uptake was apparent through a substantial fall in pressure. If it was carried out under argon in degassed water with a deficiency of copper (molar ratio Ag:Cu = 4:1) no paratacamite formation was visible, and the coloured supernatant solution of copper(II) became colourless after about 24 h. The XRD pattern of the insoluble material revealed only AgCl, but after washing with 3 M ammonia, it resembled Fig. 2, showing additional reflections due to both elemental sulfur and unchanged acanthite. The colourless solution had a pH of about 5, decolourizing bromine water and potassium permanganate solution which, at the cited pH, does not react with chloride.²² It also slowly deposited the basic chloride Cu₂(OH)₃Cl when exposed to air, initially at the surface of the liquid. Again, XRD patterns showed that the precipitated basic chloride consisted mainly of paratacamite, with smaller amounts of atacamite. These reactions of the colourless solution suggest that it contains a chloride complex of copper(I). Copper(I) chloride is very sparingly soluble in water, but dissolves easily in strong solutions of chloride. Thus in 4 M chloride the solubility of CuCl is about 0.74 M and the major species present is [CuCl₃]²⁻(aq), with significant but smaller amounts of [CuCl₂]⁻(aq).^{23,24} The colourless reducing agent that is present in the solution is therefore best written as [CuCl₃]²⁻(aq).

We suggest, therefore, that the chief reactions are ones in which copper(II) is reduced by acanthite to [CuCl₃]²⁻(aq), and that this is then re-oxidized by oxygen, ultimately to paratacamite. Mixed valence chloride complexes of copper(I) and copper(II)^{25,26} may feature as intermediates. The solutions of copper(II) probably contain hydroxychloro-complexes,²⁷ but for simplicity we write them as Cu²⁺(aq). The reactions are then as in eqns. (2) and (3). The second reaction points to a decrease



in pH. This, however, is delayed. With oxygen gas bubbling through the solution to speed the process up, we found that the pH first changes from about 3.6 to nearly 4.0 before gradually falling back to just about its original value. We believe that initially the oxidation of copper(I) yields aqueous copper(II) with an increase in the pH, eqn. (4). At a pH of about 4 precipi-

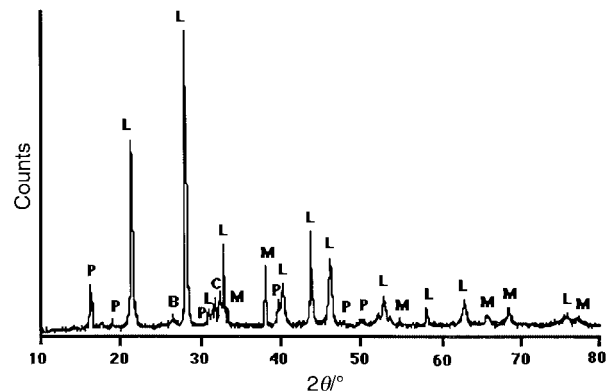
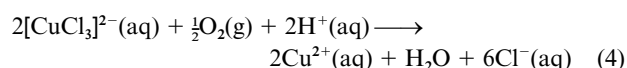


Fig. 3 The X-ray powder diffraction pattern of the lighter fraction of the insoluble material left after the reaction of acanthite, copper(II) chloride and mercury in 4 M NaCl in air. B = Cinnabar, HgS; C = chlorargyrite, AgCl; L = calomel, Hg₂Cl₂; M = moschellandsbergite, Ag₂Hg₃; P = paratacamite, Cu₂(OH)₃Cl.

tation of paratacamite begins, and the pH then falls back before settling down at a value close to 3.6. These observations are consistent with the work of Sharkey and Lewin²⁷ who found that, in chloride solutions containing significant concentrations of aqueous copper(II), copper(I) chloride complexes undergo aerial oxidation to both atacamite and paratacamite, the proportion of the latter being greater when the chloride concentration is high. They also noted that paratacamite precipitation begins at pH values of about 4 or above.

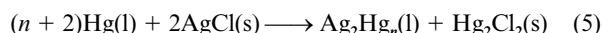
The initial oxidation of [CuCl₃]²⁻(aq) to aqueous copper(II) suggests the possibility of a cycle in which the oxidation of Ag₂S by oxygen is catalysed by copper. In the case of the amalgamation process that possibility is hindered by the formation of insoluble paratacamite. However, if the reaction is performed in hydrochloric acid instead of salt solution, paratacamite formation is prevented, and reaction (4) should prevail. To test this idea, we conducted the reaction in 2 M HCl with a copper(II):silver molar ratio of 1:5, well below the stoichiometric ratio of 1:1. The X-ray powder diffraction patterns suggested that the conversion of Ag₂S into AgCl was as effective as it was in sodium chloride solution when the copper(II) was in excess.

Stage 2: reactions initiated by the addition of mercury

We now turn to Stage 2, the effect of mercury on the products of Stage 1. In our initial test of the extraction process a second batch of mercury was added at a late stage to generate an easily separable liquid amalgam. Here this second batch was omitted. X-Ray powder diffraction patterns of the lighter fraction of the insoluble phases in the final product (Fig. 3) then revealed the presence of paratacamite (25-1427), the amalgam moschellandsbergite, Ag₂Hg₃ (11-0067), and calomel, Hg₂Cl₂ (26-0312).¹⁹ The pattern for the heavier fraction of the precipitate was similar except that paratacamite was less prominent, and Ag₂Hg₃ more so. The three cited compounds accounted for all peaks apart from two weak reflections which corresponded to the strongest lines of cinnabar, HgS (42-1408), and chlorargyrite, AgCl (31-1238),¹⁹ the latter showing that the extractive amalgamation of silver chloride was incomplete.

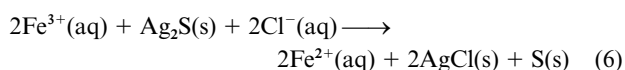
As mercury reacts with free sulfur to form cinnabar, and elemental sulfur is produced in Stage 1, the presence of HgS in the final products of the process is to be expected. Liquid amalgams produced in our model process by adding the second batch of mercury also developed a purple surface dust which gave a powder pattern identical with that of cinnabar.

In the real process the amalgam ends up, not as Ag₂Hg₃, but in a liquid state. We therefore write the general reaction for stage 2 as in eqn. (5).



The reaction between iron(III) chloride and acanthite in concentrated sodium chloride solution

Iron(III) compounds^{13a} or roasted iron pyrites^{12a} were sometimes used either as a supplement or substitute for copper(II) in the amalgamation process. We therefore studied the reaction between iron(III) chloride and acanthite in concentrated chloride solution. Again, like copper(II), iron(III) oxidizes silver sulfide, producing elemental sulfur, and silver chloride or its chloride complexes. With acanthite in excess, the bright yellow solution of iron(III) became colourless, and it then decolourized bromine water and permanganate, turned potassium ferricyanide solution a deep blue, and gave no red colouration with thiocyanate solution. Reduction of iron(III) to iron(II) had therefore taken place. When iron(III) was in excess the XRD pattern of the insoluble material revealed only AgCl, but, as in the copper(II) oxidation, sulfur could be extracted with CS₂. So the initial reaction is as in eqn. (6). As with the copper system,



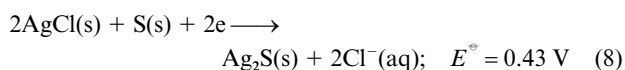
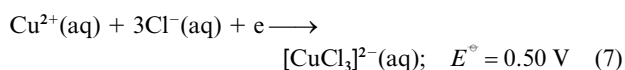
addition of mercury to the products produced an amalgam containing some 90% of the original silver.

In both cases, the higher oxidation state of the transition metal is reduced to the lower in chloride solution. The chief difference is that in the iron system, at normal temperatures, re-oxidation of the reduction product, Fe²⁺(aq), is much slower. Our proposal of eqn. (6) for the initial reaction is consistent with a recent study²⁸ of the leaching of silver sulfide in iron(III) solutions, although this was conducted at temperatures of 40–95 °C in acid solution.

Discussion

Our laboratory model suggests that the essential features of the amalgamation process were first the oxidation of Ag₂S by Cu²⁺(aq) [eqn. (2)], followed by the oxidation of [CuCl₃]²⁻(aq) by atmospheric oxygen, in the first instance to Cu²⁺(aq) [eqn. (4)], but ultimately, after the pH has increased sufficiently, to paratacamite [eqn. (3)]. Overall therefore, there is no change in the oxidation state of copper, and the oxidizing agent is oxygen, with copper(II) exercising a catalytic effect. Since the chloride concentration is high, significant quantities of the silver chloride that is formed will be present as soluble complexes such as [AgCl₃]²⁻(aq). When mercury is added it reduces silver chloride and its complexed forms to silver amalgam phases [e.g. eqn. (5)]. Some will also react with sulfur to form mercury(II) sulfide.

Relevant redox potentials were calculated from thermodynamic data,²⁹ eqns. (7) and (8). At unit activity of chloride



ions the oxidation of silver sulfide by Cu²⁺(aq) is thermodynamically favourable, but the equilibrium constant for the reaction is small. At the higher activities used in practice the difference of 0.07 V will be significantly increased. Moreover, the copper potential will be further raised above the standard value through the constant destruction of [CuCl₃]²⁻(aq) by atmospheric oxygen. The high chloride concentration may also have valuable kinetic effects. It renders potentially insoluble products, such as AgCl and CuCl, at least partially soluble as chloride complexes, and prevents them from inhibiting further surface reactions. The beneficial effects of such solubilization have been noted in the iron(III)/Ag₂S reaction.²⁸

Our reaction scheme explains certain empirical observations

that appear in detailed descriptions^{13a} of the real amalgamation process. Some hours after the addition of *magistral* green solids appeared around air-holes generated in the reacting heaps of material. This would be the paratacamite whose formation we have observed. It was also noticed that the extraction process was more advanced near the surface of the reacting material than in the interior. This marks the contribution made by atmospheric oxygen which, by oxidizing copper(I) chloride complexes, raised the Cu²⁺|CuCl₃²⁻ redox potential. The recognized importance of treading and turning the reacting mass is therefore explained by the need for aeration as well as homogeneity.

It was also known that an overdose of *magistral* wasted mercury.^{13a} We attribute this to some degree of reaction between the two. We have found that copper(II) chloride in chloride solution oxidizes mercury to calomel, and is reduced first to yellow-brown mixed valence complexes,^{25,26} and then to colourless copper(I). This explains why *magistral* was added cautiously, often in a succession of doses, each of which followed an assessment of the state of the reaction. Were it not for the precipitation of paratacamite, the aerial oxidation of these complexes would regenerate higher concentrations of soluble copper(II), and create a catalytic cycle for the atmospheric oxidation of the mercury to calomel. If too much *magistral* was added the prospective loss of mercury could be alleviated by lime or wood-ash. These alkaline substances presumably precipitated dissolved copper(II) as basic chlorides or carbonates. Alternatively, finely divided copper was added. This would reduce the oxidizing copper(II) to copper(I) chloride complexes. The reaction between mercury and dissolved copper(II) also explains why acidic ores obtained from old mine workings led to unacceptable losses of mercury. The remedy was neutralization with lime, presumably because this precipitated much of the copper as basic copper(II) salts.

Hispanic-American amalgamation, it seems, was an early example of hydrometallurgical chloride leaching, a research field of much interest to the metallurgical industry in recent years.³⁰ In such processes, the capacity of copper(II) to catalyse the aerial oxidation of sulfide minerals of lead, nickel, copper and zinc in acid chloride solution is well known.³¹ Apart from a lower pH and the relative solubility of the products, the reactions with these other sulfides resemble those proposed here. Perhaps because of its uncertain chemistry, historical surveys of chloride leaching do not previously seem to have considered the amalgamation process under this heading.

Acknowledgements

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References

- 1 J. Houseman and D. A. Johnson, *Interdiscip. Sci. Rev.*, 1991, **16**, 245.
- 2 J. O. Nriagu, *Sci. Total Environ.*, 1994, **149**, 167.
- 3 D. Hume, *Essays, Moral, Political and Literary*, ed. E. F. Miller, Liberty Classics, Indianapolis, 1985, pp. 281–294.
- 4 J. M. Keynes, *The Collected Writings of John Maynard Keynes, Volume VI: A Treatise on Money, Volume 2*, Macmillan, London, 1971, pp. 135–145.
- 5 J. M. Keynes, *The Collected Writings of John Maynard Keynes, Volume IX: Essays in Persuasion*, Macmillan, London, 1972, pp. 323–325.
- 6 C. M. Cipolla, *Before the Industrial Revolution*, 2nd edn., Methuen, London, 1981, pp. 230–233.
- 7 A. Attman, *The Bullion Flow between Europe and the East, 1000–1750*, Goteborg University Library, Goteborg, 1981.
- 8 A. Attman, *American Bullion in the European World Trade, 1600–1800*, Goteborg University Library, Goteborg, 1986, pp. 11–34.
- 9 J. O. Nriagu, *Nature (London)*, 1993, **363**, 589.
- 10 L. D. Lacerda, *Water, Air Soil Pollut.*, 1997, **97**, 209.
- 11 N. Pirrone, I. Allegrini, G. J. Keeler, J. O. Nriagu, R. Rossmann and J. A. Robbins, *Atmos. Environ.*, 1998, **32**, 929.

- 12 P. J. Bakewell, *Silver Mining and Society in Colonial Mexico; Zacatecas 1546–1700*, Cambridge University Press, 1971, (a) ch. 6; (b) p. 144.
- 13 J. Percy, *Metallurgy; Silver and Gold*, Part I, John Murray, London, 1880, (a) pp. 559–666; (b) p. 656; (c) pp. 73–85.
- 14 P. J. Bakewell, *The Cambridge History of Latin America*, Vol. 2, ed. L. Bethell, Cambridge University Press, 1984, pp. 116 and 117.
- 15 J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green, London, 1928, vol. 3, pp. 303 and 304.
- 16 T. A. Rickard, *Trans. Can. Inst. Min. Metall.*, 1936, 23.
- 17 M. Bargallo, *La Minería y la Metalurgia en la América Española durante la Época Colonial*, Mexico, 1955, p. 194.
- 18 F. Habashi, *Can. Inst. Min. Bull.*, 1982, 75, 133.
- 19 Joint Committee in Powder Diffraction Standards (JCPDS), International Center of Diffraction Data, Swarthmore, PA.
- 20 L. G. Sillen and A. E. Martell, *Stability Constants of Metal Ion Complexes*, Special Publication No. 17, Royal Society of Chemistry, London, 1964.
- 21 A. Pinkus and A. M. Timmermans, *Bull. Soc. Chim. Belg.*, 1937, 46, 46.
- 22 A. G. Sharpe, *Principles of Oxidation and Reduction*, Royal Institute of Chemistry, London, 1962, p. 20.
- 23 R. Vestin, A. Somersalo and B. Mueller, *Acta Chem. Scand.*, 1953, 7, 745.
- 24 B. Liedholm, *Acta Chem. Scand.*, 1969, 23, 3175.
- 25 M. Mori, *Bull. Chem. Soc. Jpn.*, 1960, 33, 985.
- 26 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, 10, 312.
- 27 J. B. Sharkey and S. Z. Lewin, *Am. Mineral.*, 1971, 56, 179.
- 28 J. E. Dutrizac, *Hydrometallurgy*, 1994, 35, 275.
- 29 D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *The NBS Tables of Chemical Thermodynamic Properties*, American Institute of Physics, New York, 1982.
- 30 J. E. Dutrizac, *Hydrometallurgy*, 1992, 29, 1.
- 31 J. A. Grieg, *Separation Processes in Hydrometallurgy*, ed. G. A. Davies, Ellis Horwood Ltd., Chichester, 1987, p. 35.

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