

AN OVERVIEW OF THE PRINCIPLES OF COPPER METALLURGY AND THE PRACTICE AT KESWICK 1567-1602

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Abstract: The Tyrolean process for smelting copper sulphide concentrates, with and without the separation of silver is reviewed, together with variations used at Keswick by German immigrants. Process flowsheets and the conclusions from a heat and mass-balance model are presented.

Copper occurs in three main mineral classes, amongst which the following minerals have some economic importance:

Native Copper - rare but widely distributed in sandstones, lavas and conglomerates.

Oxidic Minerals - malachite, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$; azurite, $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$; cuprite Cu_2O .

Sulphide Ores - chalcopyrite or copper pyrites, CuFeS_2 ; chalcocite or copper glance, Cu_2S ; tetrahedrite or fahlore $\{[\text{Cu}_2\text{S}, \text{FeS}, \text{ZnS}, \text{Ag}_2\text{S}, \text{Hg}_2\text{S}]_4, [\text{Sb}_2\text{S}_3, \text{As}_2\text{S}_3]\}$ where the minerals in square brackets can be present in any proportion to give mixed crystals and where specific ratios have names.

Although native copper and the oxidic minerals are less abundant than the sulphides, they hold an important place in ancient metallurgy because of the ease with which they can be reduced to a workable

metal in rudimentary furnaces with single tuyeres, blown by hand or foot bellows and using wood or charcoal as fuel.

SULPHIDE ORES

Sulphide ores are commercially the most important form of copper and are widespread throughout the world and occur in massive veins in the UK. Their metallurgy is relatively difficult even today - partly because of the presence of sulphur but also because of impurities which are present in the copper mineral itself (e.g. tetrahedrite) or as closely associated sulphides. Iron is almost always present and is one of the main features of all copper sulphide metallurgy. Some of the most complex copper sulphide ores are found in Germany and Central Europe with the result that metallurgists working in these areas have been largely responsible for developing most of the techniques of

complex copper extraction up to the mid-19th century. German metallurgists were

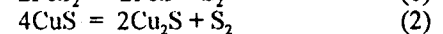
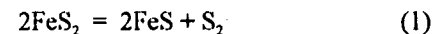
responsible for much of the development of new processes in America in the nineteenth century and were invited to England in the sixteenth century to exploit the sulphide deposits in the Lake District. Early authors such as Ercker¹ and Agricola² demonstrated an understanding of metallurgical principles which is little different from that of today, despite their ignorance of atomic compositions and chemical equivalence.

If one were to put a copper sulphide ore into a crucible or blast furnace and carry out a smelting operation, the product would be much the same as the original material. Some elemental sulphur might be volatilised, the silicate minerals and spars would separate as a slag but the sulphide minerals would simply melt and change in colour from a brassy gold to black. A repeated smelting would produce little further change.

ROASTING

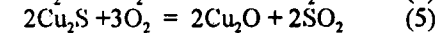
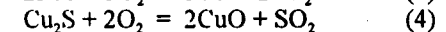
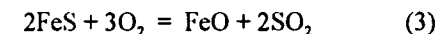
In common with lead metallurgy, a roasting process must be carried out to remove sulphur. However, in the case of copper and iron sulphides, the heat evolved in roasting to oxide is considerably more than that for lead, irrespective of the basis on which this is expressed, (see Table 1) However, because of the higher melting points of the oxides and sulphates which are produced, careful control is less important than with lead.

In the early roasts some evolution of elemental sulphur takes place together with reduction to ferrous and cuprous sulphides:

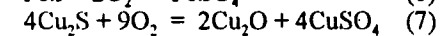
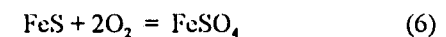


If the heap is made into a large truncated cone and the top covered with fine ore, elemental sulphur can be collected in hemispherical depressions made in the flat top surface. This was proposed by Henry Pope⁵ in 1579 but does not appear to have been taken up.

The roast reactions taking place are:



In addition, partial oxidations also occur:



The eventual products of roasting are now accepted as being dependent on the temperature, oxygen partial pressure and sulphur dioxide partial pressure^{7,8} to which

Mineral	Melting Point °C	Specific Gravity	Heat of Oxidation (cals/mole)	Heat of Oxidation (Cals/gm)	Heat of Oxidation (cals/cm ³)
Galena PbS	1114	7.5	48,740	204	1530
Copper Sulphide CuS	1127	5.6	128,990	811	4542
Chalcocite Cu ₂ S	decomposes	4.7	97,840	1025	4818
Iron Sulphide FeS	1195	4.7	112,140	1274	5988
Pyrite FeS ₂	1171	4.9	170,680	1422	6968
Chalcopyrite CuS.FeS		4.2	299,670	1638	6880

Table 1. Heats of Oxidation of Common Sulphides³

the ore particles are exposed. As a rough generality, CuSO_4 is produced below 700°C and either CuO or Cu_2O above 800°C under normal roasting conditions. Similarly, $\text{Fe}_2(\text{SO}_4)_3$ is produced below 550°C and iron oxides at higher temperatures. The modern thermodynamic approach has been well verified on virtually all types of roaster in use today or in recent years. However, it is now universal practice to grind concentrates or matte to fine powder (commonly 50-300 microns), whereas the classical German processes have traditionally used pieces of matte about the size of a housebrick. Under these circumstances, the outside of the piece is roasted to products predicted by thermodynamic theory, the inner parts are not exposed to oxidising gases and remain substantially unchanged. This eventuality is also predicted by thermodynamics.

However, Schnabel⁴ and others have shown that as combustion progresses, a molten copper sulphide zone migrates to the centre leaving an enriched kernel of copper sulphide and a crust of iron oxide. Ore with 7-10% Cu gave kernels of 35-40% Cu with crusts at 3-4%, of which 2½-3 parts were present as CuSO_4 and ½-1 part was present as CuO . Some impurities such as arsenic and zinc may also transfer to the outer oxide crust. Some smelters have effected an initial separation by breaking off the outer crust by hand but this is tedious and leads to high losses of copper. The accounts of the Keswick smelter in Hechstetter's notebook⁵ indicate that careful, slow roasting of large pieces of matte was normal practice and that some degree of *kernel roasting* must have taken place, although separation of the crust was not reported. Rapid roasting of heaps containing small pieces was reported to give low copper recoveries and smelting difficulties. This explains the views of smelters in Germany who carried out trials on the Keswick ores: 'It is to be observed that your stone roast be very equally and carefully roasted or otherwise you cannot but make waste'. The lowest melting point of pure Cu/Fe mattes is 950°C and melting would put an end to any effective roasting, alternatively, the production of iron and copper sulphates (referred to as *vitriols*) by roasting at too low a temperature (ie below 600°C) would give smelting difficulties or would reduce back to sulphides in the blast furnace. Some German practice involved cooling finished roasts with a slow stream of water to dissolve and remove any sulphates². Gans⁶ proposed this for Keswick in 1582 and to use the sulphates as mordants for the dyeing of cloth but the suggestion does not appear to have been taken up.

Roasting takes place in several stages. The object of the early roasts is to convert iron sulphides (Reaction 3) to the oxide which can then be slagged with lime and silica

from the vein material in the subsequent smelt. Copper is run from the furnace as a matte or 'stone' (Ger. *Kupferstein* or *Stein* of Cu_2S) having a higher density than slag. The two form separate liquid layers which can be separated after tapping. As preferential oxidation of iron is never complete, the roast/smelt processes were carried out repeatedly and iron removed in several stages. Later roastings remove sulphur so that copper oxide remains and final reduction to rough copper can be effected by smelting. Nevertheless, it was always customary to leave a small quantity of sulphur in the final roast (a 'sweet roast' as opposed to a 'dead roast') so that a small quantity of matte was formed in the final smelt to rough copper. This was removed as a thin crust and was known as 'thinstone' (German *Dümmstein*). It contained copper, iron and other impurities and was recycled back to an earlier roast.

Roasting Processes - Agricola² describes the processes of *heap* and *stall* roasting, which were used well into the twentieth century. The term 'heap' is self-explanatory but the construction of the heap requires considerable skill and experience if an effective result is to be achieved. Low grade fuels such as brushwood, heather, coal, bituminous schists etc. have been used. At Keswick, peat appears to have been used exclusively for all but final roasts just before smelting to metal, when wood and peat were used.

Agricola's roasts appeared to use heaps of about 3-4ft high and 6-9ft in diameter. Greenstone (matte) roasts at Keswick contained 5 tonnes of matte and required 870kg of peat for the first fire and 4800kg for the sixth. A roasting fire lasted approximately three days although some lasted for one week; there could be up to eight fires in a single roast. The time taken to produce copper starting from ore was given as 18 weeks 5 days. No reports are given of the effects of rain on the roast or if shelters of any description were erected. Hechstetter gives few significant clues as to how well the process was controlled in terms of heap construction. At Caldbeck, some roasting was carried out at the mines.

Heap Roasting - In the nineteenth century the floor of the heap was made of slag, clay, fines or roasted fines to minimise loss of ore into the ground. This also assisted drainage in wet weather and ensured the lowest tiers of ore were exposed to air. Above the floor was a bed of fuel, preferably with draught channels communicating with flue spaces constructed in the heap. Above this was a layer of ore and usually this was repeated once or twice. During the roast, the volume of material will expand by approximately 20-50%. Peters¹⁰ gives precise details of height and days required for roasting for twelve ore/matte cases having different

sulphur compositions. The height of the bed is critical in determining the draught and therefore the burning rate and heights from 5ft to 8ft have significantly different effects. In general, high heaps give faster burning but also less uniform roasting throughout the pile. Low sulphur ores and mattes could be roasted in a higher heap but this would require more fuel than sulphur-rich ores. The heap size and the fuel content also had to be controlled to prevent melting and to achieve an adequate temperature.

Stall roasting - was carried out in enclosures consisting of three walls forming an open-sided box, approximately 4ft x 4ft x 6ft high, in the 16th century and holding about 5 tonnes of ore. By the 19th century, stalls up to 15ft deep x 11ft wide x 6ft high were used in Sweden and were capable of holding 75 tonnes of ore, 283 cubic feet of firewood and required 4 - 6 weeks to complete the roast. 19th century Styrian stalls could be as large as 380ft x 14 ft x 8ft high and roasting took 6 - 8 months. With stall roasting there is less exposed surface and smaller quantities can be controlled better. A chimney effect can be induced and better penetration of air to the centre can be effected, at least in theory. The stall can be protected against rain and copper losses can be controlled. The main disadvantages with stall roasting are the expense of building the stall, the effects of SO_2 on the health of workers employed to empty it and the indifferent performance over heap roasting particularly with large quantities.

The 1586 inventory of Richard Ledes⁵, refers to the Roasting House at the east end of the Melting House. There are also some references to repairs for the roof of the Roasting House¹⁴, however, both sources also refer to three copper furnaces in this building, one of which was broken and had been cannibalised for spare parts. If we are to take the account literally, then roasting and smelting must have been carried out together in this building and roasting stalls would have been used. Sulphur dioxide would have rendered the working conditions indescribable and some other interpretation must be made.

SMELTING

The shaft furnaces used at Keswick⁵ and those reported by Agricola² were used for a variety of different purposes:

(a) **Ore Smelting** - ore was first melted in the furnace to form a matte of copper/iron sulphides known as 'greenstone'. In some cases elemental sulphur would be eliminated; iron and silica formed a fusible slag but this did not run freely and limestone was added to reduce the viscosity, surface tension and melting point.

**SMELTING OF CONISTON AND
NEWLANDS COPPPER ORES - 1602**

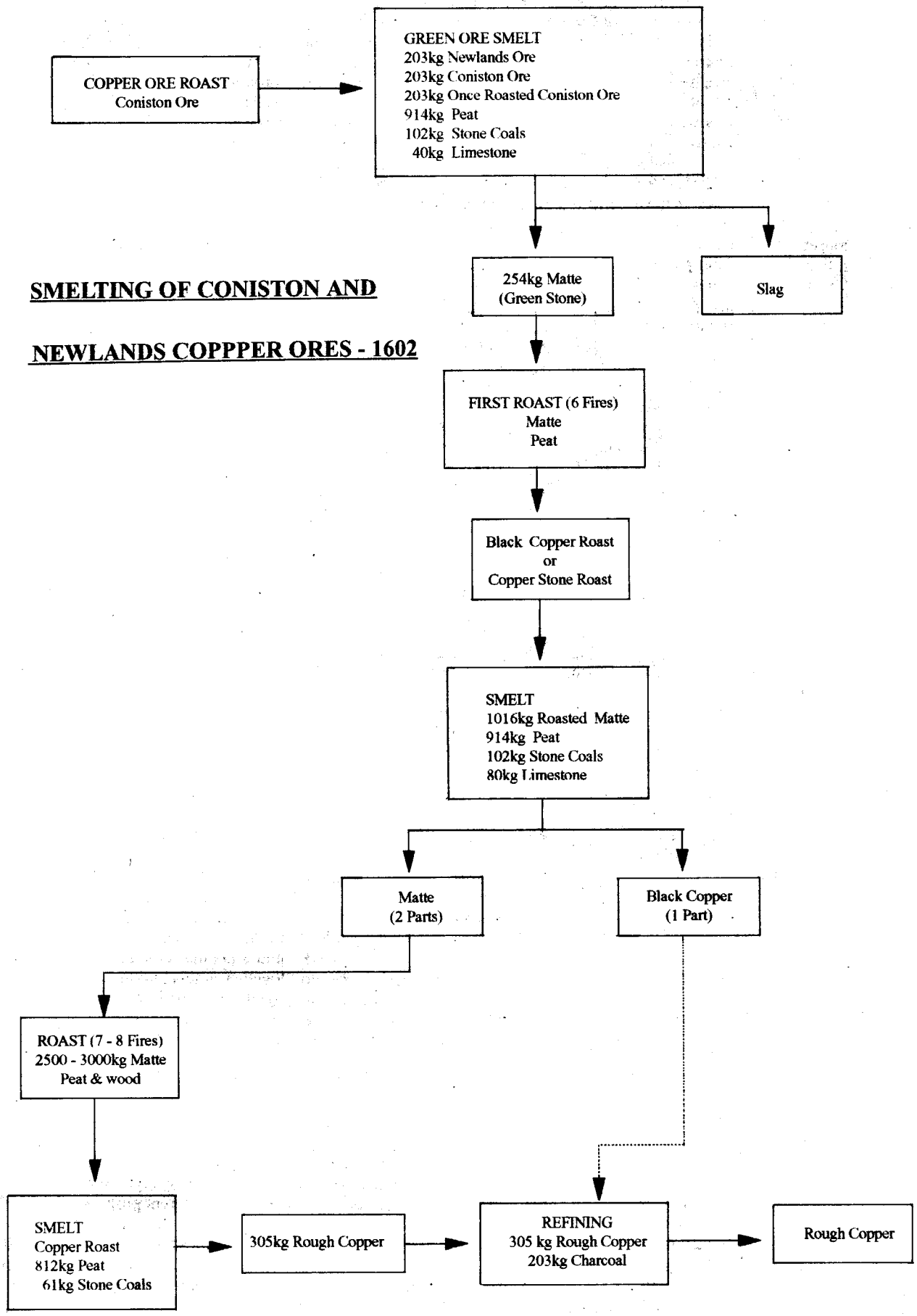


Fig. 1. Flowsheet for copper smelting at Coniston and Newlands.

Matte was tapped into large cakes which could then be roasted in a controlled fashion (see 'kernel roasting'). It appears⁵ that the initial smelt at Keswick (the 'green ore smelt') was designed to produce a good quality green stone which could be easily roasted as well as to provide a separation from gangue materials such as silicates.

(b) *Matte Smelting* - partially roasted ore or matte is smelted, sometimes with limestone and silicate materials. Iron which has been oxidised by roasting is transferred to the slag leaving a matte enriched in copper. The final product of matte smelting is black copper containing about 95% of copper together with iron, sulphur and impurities such as As, Sb etc. Black copper was smelted directly to rough copper in some cases; in others it was subjected to one or more smeltings to remove sulphur and iron (see below).

(c) *Roasting* - repeated smeltings were part of some flowsheets and here the furnace was used to remove sulphur and oxidise iron in a controlled but slow and expensive manner. Oxidation would take place on the top surface of the charge at the stockline, where entrained air is present and also in the immediate tuyere zone.

In some of the ore and matte smelting stages, the addition of limestone and the subsequent formation of slags is noted by Hechstetter⁵, however, this is by no means always the case. Matte smeltings contain few, if any, references to slags; there are no mentions in the accounts of additions of sand or silicate minerals to aid slagging but quartz is a common vein material in the Lake District.

Smelting Furnaces - A site inventory of the Keswick smelter was made by Richard Ledes in 1580 and gives a valuable insight into the furnaces used for smelting and refining. The list of tools is also instructive in understanding how the furnaces were operated and how some of the problems were overcome.

There were eight smelting furnaces at Keswick. These were arranged in two sets of three and blown by bellows driven by 'a great long axle tree of 2 trees with a great wheel going by water. This tree placed between both partitions and serving all 6 furnaces'. At the time of the inventory, the third furnace of each set was inoperable and had been cannibalised to repair the others.

The remaining two furnaces were in another part of the smelter and in the same room as the refining furnace. The smelting furnaces were described as having iron pans (hearth), which supported a lining of charcoal and clay known as *stief*. They had either an iron door or removable 'iron plate in the forepart to take off and on at the dressing of the furnace'. The tools

included:

- 1 stopping iron to stop the pan hole
- 2 hook irons to draw sows out of the ovens
- 1 long pin to make a hole in the furnace pan
- 3 gavellocks staved to dress the oven mouths
- 1 long crow
- a bathing tub for the melter

These implements suggest that the Keswick smelters encountered the same problems as blast furnace operators today but more so.

The descriptions given resemble the shaft furnaces in Agricola² and particularly the Tyrolean furnaces having an internal taphole which discharged directly into the forehearth, rather than above it. The holes look as if they could be prone to blockages and required constant poking to keep open, hence the tools. Today the internal taphole would be referred to as a 'syphon tap'. Slags were removed by lifting off as crusts from the forehearth once they had solidified and were quenched with water. Matte (and lead for silver separations) was run into the adjacent dipping pot once all slags had been tapped. Solidified matte was often broken up and returned to the furnace until metal had ceased flowing. Lead metal was cast into cakes from the dipping pot. Seizing of the furnace bottom with iron accretions (variously known today as 'bears, sows, dogs' etc) was also experienced in the sixteenth century as a special tool was kept for clearing these. However, the short furnaces and lack of reliable slag controls will have exacerbated these problems and the door in front of the furnace could also be used to rake out the residue if the worst happened and the furnace seized up or went out.

REFINING

Copper Refining - Richard Ledes inventory describes⁵: 'the third is called the copper groove for refining of copper. The copper groove is plated with iron at the top, having a broad compassed plate of iron for keeping in the fire at refining of copper and is to be heaved on and off with 2 hooks of iron. Over that groove is a penthouse of iron plates supported on two iron rods'.

Agricola² and Ercker show copper refining furnaces which consisting of one or two open crucibles, lined with a mixture of equal parts of charcoal dust and clay. Red-hot charcoal is placed in the crucibles and copper cakes are laid on top; air is blown over the crucible from three copper tuyeres. Slags are drawn from the surface of the copper as melting proceeds and iron and sulphur are oxidised. Molten copper then passes under the surface of the charcoal and becomes de-oxidised. Samples are taken with an iron through the tuyere aperture and when the copper has a good brassy colour

and sticks to the bar the bellows are stopped, any charcoal or slags are removed, a hazel stick is inserted into the copper and is used to stir it twice. Finally, the surface of the molten copper swept clean. Water is then poured over the metal and the first solidified crust is removed by levering with an iron bar. Separation is assisted by water finding its way under the crust; each crust or cake is quenched immediately in a tub of water. The copper is separated into four cakes in this way.

Liquation - Ledes writes⁵: 'near the three furnaces in the south side of the house stands an oven or open hearth called a sagger qven; being to part the lead of our mines from the copper asunder. Which hearth is now covered with peat: but is floored with 2 thick plates of black copper the same weighing between 6 & 700'.

This type of furnace (Ger. *Saigerofen* draining furnace or liquation furnace), described by Ercker¹, Agricola², and Barba¹¹, consists of two copper plates arranged to form a shallow trough. In the normal mode of operation, disc-shaped liquation cakes (Ger. *Saigerstock*, Lat. *Panes ex aere ac plumbo misti*) of mixed lead-copper are set on their edges along the trough and fuel (peat, charcoal or wood) is mixed in between. Three iron panels are erected around the open hearth and are held rigid by staybars; the fourth, end wall is made of brick or sandstone. As the furnace heats up, lead (Ger. *Saigerwerk*, *saigerblei*, Lat. *Stannum*) is sweated out of the lead-copper mixture and runs down the central channel and into a collection pot for casting lead cakes. Drossing to remove copper from the lead before casting does not appear to have been carried out. The lead cakes were then sent for cupellation. Heating progressed gradually until some of the copper came to the point of melting, when the process was stopped. The spent liquation cakes (Ger. *Kiehnstock*, *Kuhnstück*, Lat. *Panes fathiscentes*) were cooled then broken open and 'stalactites' (Ger. *saigerdörner*, Lat. *spinae*) were broken from the hollow interior and put together with any melted copper 'stalactites' or 'thorns' from the liquation hearth. These are copper/ lead residues with silver and were treated by different routes according to the silver content. The spent copper liquation cakes still contained some lead and silver and were further treated in a large arched, closed furnace fitted with an iron front door which could be raised or lowered (Drying furnace, Ger. *Darrofen*). Lead and more 'thorns' (Ger. *Darrsöhle*, Lat. *Spinae*) were generated in this process and trickled out towards the front of the furnace and 'dried' liquation cakes of copper (Ger. *Darrlinge*, Lat. *Panes torrefacti*) were either re-extracted with more lead or were refined for copper.

Although a liquation hearth has been listed

KESWICK COPPER ORE, SILVER EXTRACTION - 1567

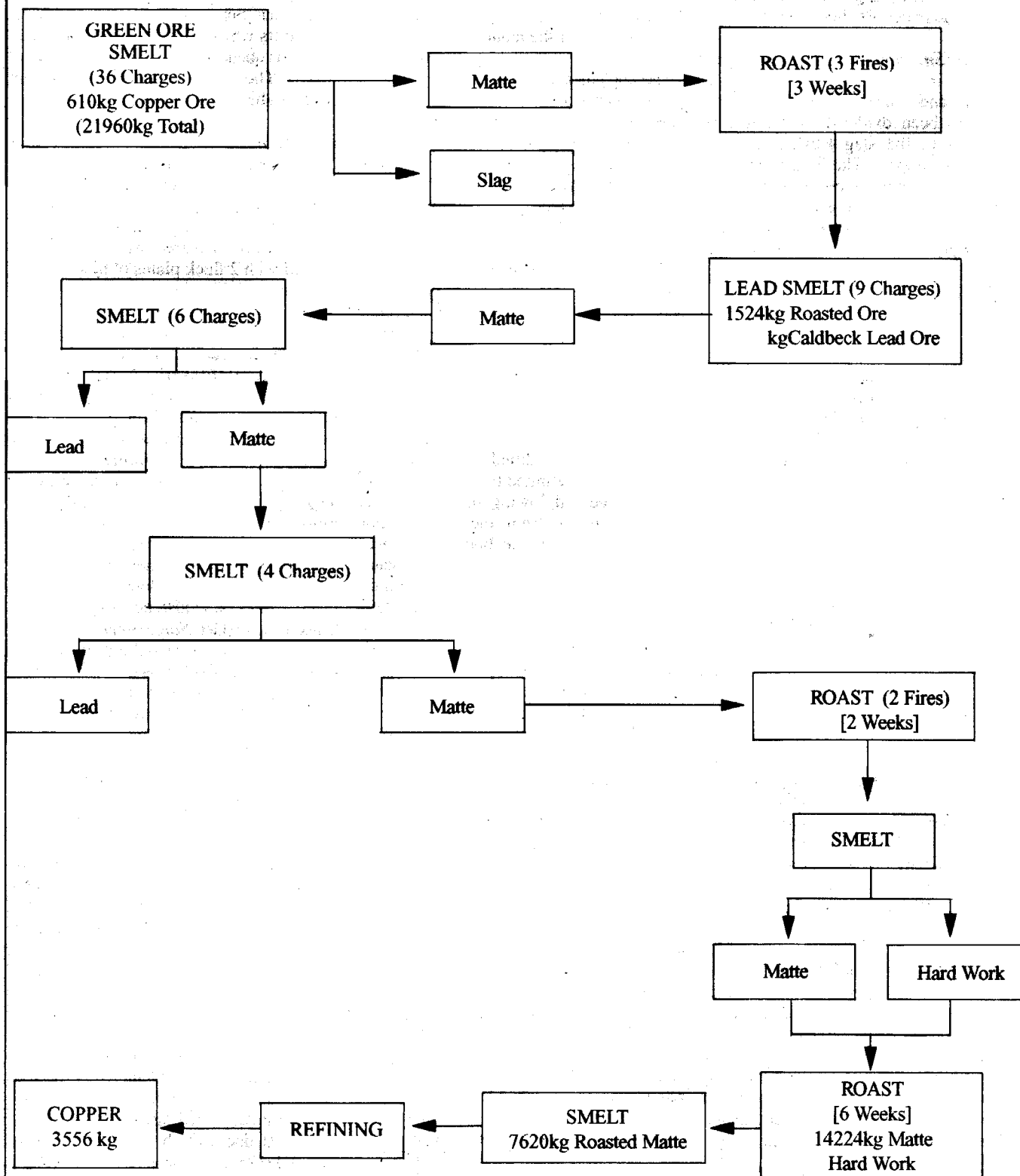


Fig. 2. Flowsheet for silver extraction at Keswick.

Heat Evolution from Cu Ore Roasting

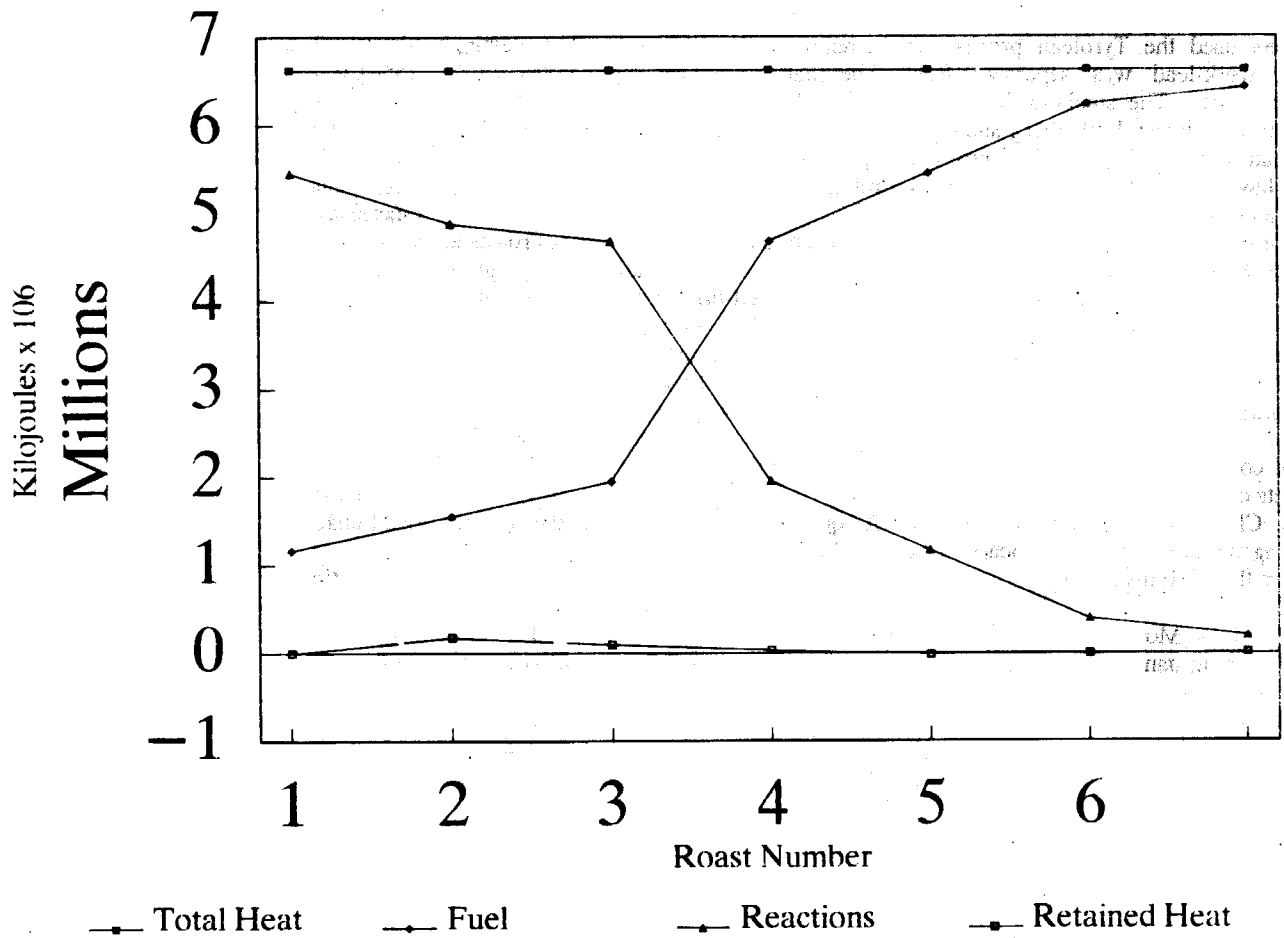


Fig. 3. Heat evolution from copper ore smelting.

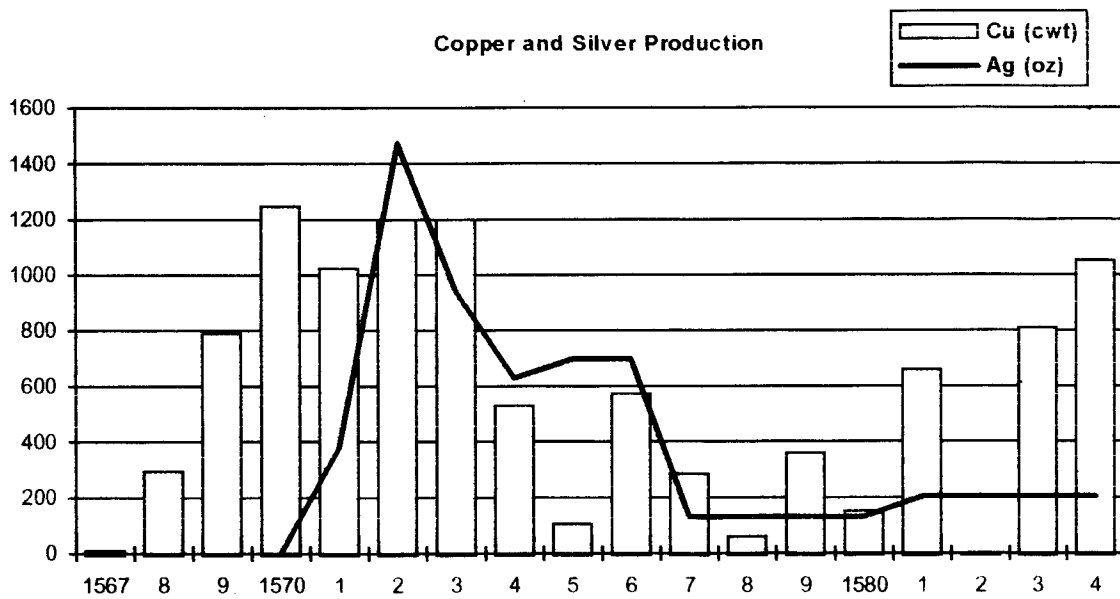


Fig. 4. Production of copper and silver from Keswick smelting mill.

in the 1586 inventory, there were major differences from the classical German method where work-lead was separated from copper metal, in that the Keswick smelters used the Tyrolean process, in which work-lead was separated from copper matte. The smelters themselves came from Schwaz, Rattenberg and other Austrian towns, in or near the Tyrol and would have been familiar with the process. Nevertheless, because of the low silver content of the English ores, the flowsheet used at Keswick shows some significant differences from the Tyrolean method described by Agricola: The liquation cakes obtained from the lead washing of matte would be principally lead and would contain only minor amounts of copper. On liquation they would collapse leaving an ash of copper with some lead and small amounts of iron, rather than porous copper cakes. Clearly there would be no need for a drying furnace and none appears to be listed in the 1586 inventory.

Cupellation - 'More in the said storey is a broad refining pan for silver with a great cover all of iron and a muffle to the same. Which cover is to be let up and down having for that purpose a capstan and great rope'. The corresponding woodcut in Agricola fits this description exactly.

The process of cupellation is described fully in many other texts and there is no reason to suppose that the method carried out at Keswick was substantially different from this.

PROCESS FLOWSHEETS

Two separate smelting flowsheets existed at Keswick:

1. The smelting of copper
2. The separation of silver from copper concentrates, using complex Cu/Pb concentrates, to produce copper, silver and lead.

Copper - The process for smelting copper is summarised in Fig. 1 and varied according to the source of the concentrate. The flowsheet follows the unit processes already described and in most cases started by melting concentrates in a blast furnace using coal and peat as fuels to produce slag and matte. Concentrates from several sources were mixed and limestone was added to assist slag fluidity - silica occurs commonly as a vein material and iron would always be present. It is not clear if slag was separated from matte on cooling by carefully lifting solidified crusts or if it was repeatedly re-run. Matte was accumulated and roasted in six successive roasts, each lasting about 3 days. The decreasing sulphur content was well demonstrated by the fuel requirements for the six roasts which were: 6, 8, 10, 24, 28,

and 32 loads of peat respectively. The roasted matte was then resmelted, to give 2 parts matte and 1 part black copper. Slag is not mentioned but must have been essential to remove iron oxide produced by roasting. The matte was then roasted 7-8 times, although it is fairly clear that this decision rested with the smelter. It was smelted yet again to give rough copper which was then refined with charcoal.

Variations included: the number of roasts at any particular stage and the incorporation of pre-roasted ores in the initial smelt (it was normal to mix one third of once-roasted Coniston ores with equal portions of unroasted Newlands and Coniston ores). The copper flowsheet appears identical in reports from 1567 and in the 1602 commissioners report.

A quantified flowsheet for the copper smelting has been constructed for the smelting of the Newlands/ Coniston ores and consists of mass and heat balance spreadsheets. Given the recorded weights of ores, mattes, fuels and additives at all stages⁶ together with the final yield of rough copper, it has been possible to develop a better understanding of the process. The main inferences from this are:

1. After the first smelt (green ore smelt), the slag fall from 609 kg of ore is approximately 447kg, (matte was recorded as 245kg).
2. Assuming 2%Cu in slag, this would be equivalent to an overall Cu loss of 12%. Although this level of Cu in slag is high by modern standards, which would be typically 0.2-0.5%Cu, the main source of copper in the slag is likely to be entrained matte. The small forehearth would lead to rapid freezing of slag and poor separation of matte.
3. Downstream slags could have been derived by re-running this first slag as the source of silica for the removal of iron oxides produced by roasting. Therefore, there would be no further net losses of copper in slag.
4. The limestone addition of 22kg CaO was equivalent to 5% CaO but otherwise the slag composition cannot be determined.
5. Other copper losses are likely to be mechanical, 'housekeeping' losses such as windblown or rainwashing, together with fuming losses. The latter will be important if furnace fuel ashes were high in chloride.
6. The 245kg of greenstone matte from the first smelt would have contained 25% Cu, 43% Fe, 31% S.
7. Greenstone matte was accumulated and roasted in 6 fires lasting almost 3 days each. It was recorded that 6,8,10,24,28,32 loads of peat were used for each fire. This clearly reflects the reduction in fuel value of the matte as roasting proceeded (Fig. 3). A heat balance, based on this, shows an increase in weight from

4876kg greenstone to 6369kg roasted matte. Hechstetter refers to this and states that it 'swells in the fire so as every 2 barrowfulls put into this roast make 3 out'.

8. The product of the first roast was 25% Cu, 26% Fe 17% S and 32% O.

9. Assuming typical analyses for black copper (95% Cu, 3% Fe 2%S) and *dünstein* mattes (64% Cu, 14% Fe 22%S) from analogous matte smelting in the nineteenth century, the second smelt would yield matte (1416kg) and black copper(740kg) in the appropriate ratio. Hechstetter refers to: 'the copper sto: e roast, if it has been kindly roasted, will, when it comes from the furnace, yield 2 parts of copper stone and 1 part of black copper'.

The remaining matte roasts and smelting to black copper have not been modelled as no additional inferences can be made.

Separation of Silver from Copper - Silver occurred in the complex Cu/Pb ores from Roughtengill near Caldbeck (ca. 25 oz Ag/tonne, although one sample of 50 oz Ag/tonne was reported) and to a lesser extent in some of the Coniston and Newlands ores (10 oz Ag/tonne); the God's Gift lead vein ran 7-8 oz Ag/tonne of lead and Grasmere ore 45 oz Ag/tonne. Tilberthwaite ore was said to contain as much silver as Caldbeck ore but was difficult to smelt gave lower yields of copper and required longer than normal roasting. For the most part, Tilberthwaite ores were unprofitable.

The flowsheet for silver extraction is shown in Fig. 2 and refers to fairly early practice in 1567 but which seems to have been generally adopted and is referred to in 1572 and 1573. The instructions for silver extraction, given by Hechstetter or Agricola are not easy to follow, particularly the more complex flowsheets for high silver ores. The method used at Keswick reflected the low-grade of English ores and was comparatively simple. Nevertheless, this particular method required 18 weeks and 5 days processing time (approximately 5 months). It is possible that Hechstetter may have had to fulfil the optimistic early expectations of the investors by extracting silver at the expense of extending process residence time and exacerbating cash flow problems. The main advantage in applying the silver extraction route appears to have been as a means of treating Caldbeck Pb/Cu ores, which were difficult to process by themselves. When mixed with copper ores, they smelted smoothly and had sufficient lead to remove silver from both. There are numerous mentions⁶ of the purchase of metallic lead, presumably for silver extraction, between February 1567 and the end of 1568. Some expenditure was made at Caldbeck in early 1567 but this was then halted until 1568 when the mines were developed more purposefully.

The metal statistics⁵ (Fig 4) show no significant production of silver until 1571, when the Caldbeck mines had been working for some years.

The process for silver extraction (Fig. 2) started, similarly to the copper smelt, by treating ore in the blast-furnace to produce matte (greenstone) and slag. The matte was then roasted in three fires, which was less than the case for copper smelting and would have resulted in rather more sulphur being retained. Roasted matte was then smelted in 9 charges with lead ore to give matte and slag but as there is no mention of lead metal being produced it is reasonable to suppose that lead reported entirely into the matte phase. The matte was then smelted in six charges to a 'dry stone', implying that some sulphur was oxidised in the short furnace and that lead metal was produced in addition to matte. Matte was then smelted again in four charges, 'to make it dry and to get the lead out of it'. This suggests a second fall of lead and the resultant matte was then roasted in two fires and smelted to black copper or 'hard work' and matte. The matte was accumulated then roasted for six weeks before smelting to copper.

In common with many of the process descriptions there is no mention of the formation of a slag or of additions of slag-forming additives to flux iron oxides or fuel ashes. However, Agricola's description of the Tyrolean process for Cu/Ag ores includes these details. The first furnace charge includes 'stones which melt in the fire' and the description clearly shows that slags from each stage were separated from matte (as matte weights are given) but the slags were then included in the next smelting stage. This practice would allow slag to be added at critical times in the smelt and avoid it melting rapidly at the start, when it would serve little useful purpose.

The metallurgy is very similar to that used until the 20th century at Clausthal and Lautenthal in the upper Harz for smelting complex lead ores having minor quantities of copper by the *iron-reduction process*. Although there were much greater quantities of lead in the initial stages of the process, the later mattes contained very little⁴ and were processed to black copper by repeatedly roasting and smelting.

Many variations of the flowsheet in Fig. 2 have been described⁵, including trials on ores from different mines and the use of lead, litharge and lead ores as the source of lead. In addition to this process, a trial smelt of Newland ores, mainly God's Gift, was carried out in Germany in 1567. This latter involved more smelting and roasting stages before smelting matte with lead and lead ores. As a result more sulphur was eliminated in the earlier stages and black

copper was produced along with lead in some of the later smelts. This necessitated some recycling of silver-rich copper ('fat hard work' Ger. *weiss hartwerck*) to the lead smelt. The variation shown in Fig. 2 was no doubt arrived at after some testwork and would have been less expensive and there would have been little to choose in terms of silver losses, given the low-grades of silver available. The ability to carry out such testwork points to an ability on the part of the Keswick smelters to carry out accurate sampling and assaying at all stages and to be able to make decisions on the whole flowsheet.

No mass balance or heat balance has been carried out on the silver extraction process. The next stage in this work would be to use a free energy minimisation programme such as Solgasmix^{12,13} to calculate matte/metal ratios and to predict silver partition between the several phases.

ACKNOWLEDGEMENTS

I am indebted to David Cranstone for bringing Reference 14 (below) to my attention. It is a verbatim transcript of the Hechstetter notebooks and the Soane MS 2487, reporting the inventory carried out by Richard Ledes in 1586.

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COMMENT

contributed by Peter Hutchison

This is an interesting paper but in some respects contrasts with an English source, Privy Council papers published by George Grant-Francis ("The Smelting of Copper in the Swansea District of South Wales from the Time of Elizabeth to the Present Day" 1881). One letter is dated 1582 from George Nedham to Sir Francis Walsingham. He recounts 'at a Dutch (Deutsch) copper refiner called Iochim Gaunse has few good words for Hoechsetter or the Stembargers, father and son. He offers to make good black copper in two fires and three days from ore that was taking 22 "passings through the fire" in 22 weeks. It would cost 5/- per quintal of copper less than the Stembarger method. He claimed to have identified nine "infections" or "evil Humours" in the ore and his method of removing the worst of them is described. They were Sulphur, Arsenique, Antimony, Vitriall, Calcator (whatever that was), Allom, iron, black stone and spar. His method is described by Biringucchio (*Pirotechnia* 1540) so it was nothing new. The ore was to be crushed to a powder and roasted, presumably at a low temperature with excess air. This would convert some of the sulphides to sulphates, which were washed out and used to make "vitriall or coppriis" (crude iron sulphate). Some of the other "evil humours" were said to be washed out too. The ore could then be smelted to black copper and copperstone in a blast furnace. Two more "fires" and three days gave rough copper.

The ability to roast the ore in "one fire" in about one day suggests that a furnace was used. Biringucchio describes several reverberatory furnaces which "are more for calcining than smelting", and roasting furnaces like limekilns. Perhaps these were the furnaces in the "roasting house".

It is interesting to note that at Neath in 1586 it was possible to smelt 24 cwt of ore in 7 hours "and spend not above 8 or 9 seks of chare coles and thre horslod of sea coles"

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