Saltpetre in medieval gunpowder; Calcium or Potassium Nitrate?

By Geoff Smith

Until recently, it has been accepted that the formulation of gunpowder has always been based on variable mixtures of charcoal, sulphur and potassium nitrate. This has recently been challenged.

It has been asserted that early gunpowder was based on lime saltpetre that is calcium nitrate. This paper examines that claim.

The earliest documentary details of gunpowder manufacture known in western literature are contained in *Das Feuerwerkbuch* written in about 1400. The language is Middle High German and we are indebted to Prof. Gerhard Kramer for a modern translation[i]. The introduction to the translation claims that the text " …refers exclusively to calcium nitrate" and that "… potassium nitrate was introduced into powder making towards the middle of the sixteenth century." It is further stated that… "This surprising inference can now be considered as well established." The translation was reported in proceedings of The International Committee for the History of Technology (ICOTECH) and the editor of the compiled papers commented that this could require revision of our current understanding of early gunpowder[ii]. The idea has been repeated in more recent publications[iii] [ivv] and appears to be taking root in the literature with authors quoting it as established fact.

The proposition that all early gunpowder was based on calcium nitrate represents such a significant shift in our understanding of the history of this important mixture that it should reasonably be expected to withstand rigorous testing before it is universally accepted. In particular, any theory should pass the test of Occam's Razor; that it should be supported by the available evidence and that no simpler explanation is available.

Historical context

First, it must be recognised that the terms saltpetre or nitre were loosely defined at the time and of little help. Chemicals in the 14/15th centuries could have different names in different localities and until about the 17th century, they can only be reliably identified by their associated characteristics of appearance, taste[vi], smell or how they react with other materials.[vii]

Saltpetre was historically either collected from naturally occurring deposits in very limited geographic locations or, more usually, extracted from rotting organic material. Dung, urine and vegetable matter were stacked and allowed to ferment[viii]. Ammonia in the mix was converted to nitrite by *Nitrosomas* and this was converted to nitrate by *Nitrobacter*. Both of these organisms require a

neutral or slightly alkaline environment to operate, whereas the decaying matter is naturally acidic. Lime was added, as in agriculture, to reduce the acidity of the pile to a more suitable level. There was therefore a large amount of calcium present in the mix. However calcium carbonate and sulphate are both essentially insoluble in water and it cannot be assumed that calcium ions were proportionately present in the subsequent leachate. Saltpetre was manufactured by this method until well after WW1 and was well-documented using modern terminology[ix]. The liquor is rich in nitrate and contains variable proportions of sodium, calcium and potassium ions. Conventionally, the potassium salt is enhanced by the addition of excess potassium in the form of potash derived from wood ash. This operation is first described in western literature by Biringuccio in his *Pyrotechnica* dated at about 1538.
Since this post-dates *Das Feuerwerkbuch* (1432) which does not mention the procedure, the translators draw the conclusion that the chemical conversion did not take place and that only calcium nitrate was formed.

This view is open to challenge on a number of fronts.
The 13th Century Arabic text of Hassan al-Rammah gives a detailed description of the purification of saltpetre using wood ash.[x] It should be remembered that trade with the east was well established at that time and a purely Eurocentric view ignores this. Saltpetre was imported from Arabic lands and western alchemists recognised that the art was most highly developed there, hence Al-chemie. *Das Feuerwerkbuch*, Folio 78, states that the salt was imported into Germany and specifically warns of the difficulty of obtaining a good quality product from (or via) Venice[xi].

Crystal chemistry

Even in the absence of additional potassium ions, the relative solubility of the salts present dictates that the first crop of crystals precipitated from a cooling concentrated solution will be potassium nitrate. The unwanted sodium and calcium salts remain in solution to be rejected or, in later developments of the technology, recycled[xii]. The yield would be low compared with the later potassium enhanced process and purity would be limited by a single crystallisation, but the product would nevertheless be largely potassium saltpetre[xiii]. It is worth noting that instructions for purifying saltpetre universally specify fractional crystallisation rather than evaporation to dryness which would not separate the contaminants. In colonial India, saltpetre extraction was the duty of the *nuniah*. He was specifically forbidden from allowing the evaporation to go so far as to crystallise sodium chloride by the excise authorities since this was a different monopoly and subject to different taxation.[xiv]

Textual evidence

The fact that a published text does not mention a procedure is not proof that it was not understood and/or commonly used[xv]. *Das Feuerwerkbuch* records a wide range of formulations and presumably acted as an aide memoir for gunners who could not be expected to recall accurately the proportions of all the mixtures listed[xvi]. However, medieval craftsmen were well known for

guarding the secrets of their trade. It appears very credible that the one crucial secret of successful gunpowder would only have been passed verbally at the end of an apprentice's training. Indeed, it is not uncommon today to register a patent with sufficient detail to protect a process without giving all of the details required for manufacturing success.
It is also worth considering the (unknown) copyist of the manuscript[xvii]. It is quite possible that the record was dictated to a scribe who did not understand (or was not told) the critical step in the saltpetre manufacturing process for the reason given above. Again, the problem is well known in current technology transfer projects. Nevertheless, this omitted statement of procedure appears to be the sole basis of the claim for the use of calcium nitrate. This violates the basic principle of logic that - Absence of evidence is not evidence of absence.

Hygroscopic or deliquescent?

Early gunpowder was notoriously difficult to keep dry. This is usually attributed to the presence of sodium salts which are hygroscopic i.e. absorb atmospheric moisture, unlike potassium nitrate which does not. However, it is not accurate to describe calcium nitrate as hygroscopic (or even very hygroscopic) as reported in the *Das Feuerwerkbuch* and elsewhere. It is properly described as deliquescent. That is, in the presence of atmospheric moisture, it will continue to absorb it until it dissolves. Crystals of calcium nitrate stored in the open eventually transform into a pool of liquid – not a promising material for a battlefield explosive. The sensitivity to moisture of early gunpowder is sufficiently explained by a trace impurity of the calcium salt (and/or magnesium or sodium). It is not suggested that early saltpetre was pure potassium nitrate. Indeed, the literature records continuous effort to improve the purity of the product. Furthermore, storage conditions at that time were unlikely to be airtight and the problem of dampness in powder for naval use is self-evident. The floor of the Grand Magazine of HMS Victory has a layer of charcoal under the floor to absorb moisture from the bilges and the problem was still present as late as 1855 when Dundas gave details of the procedure for drying naval powder.[xviii]
The suggestion[xix] that the introduction of knurling reduced the absorption of water does not withstand examination. Calcium nitrate already contains water of crystallisation chemically bound to the molecule (vide infra). Further, in the absence of any compression of the gunpowder cake, the knurls would have been relatively porous and the effect on the dynamics of moisture absorption would be slight. The outstanding advantages of knurling are to reduce the considerable hazard of fine gunpowder dust, to prevent separation of the constituents during transport and to promote more uniform combustion by providing for the passage of the burning front through the charge[xx].

Chemical evidence

The most conclusive evidence, however, is contained in *Das Feuerwerkbuch* itself. Modern chemical analysis was not available to artisans of the period but that is not to say that they had no effective tools. Many chemical elements will impart a highly characteristic colour to a flame. Sodium produces

characteristic yellow, calcium a brick red and potassium lilac. This was first reported by Chinese alchemists as early as the 5th century[xxi] (possibly 3rd century) and is commonly reported in later western literature. *Das Feuerwerkbuch,* Folio 77 clearly states that a blue flame is characteristic of good saltpetre. This is repeated in Folio 78 …"If the drops (*of purified nitrate*) burn well and brightly and give blue[xxii] flames, the saltpetre is good". The saltpetre is thus clearly and unequivocally identified as being the potassium salt. The editors of the Firework Book recognise this in a footnote (p 11) but the author fails to acknowledge the force of this direct evidence in the commentary.
It is worth noting that the characteristic lilac potassium flame colour is readily masked by even small amounts of sodium or calcium. Not only is the potassium salt identified but also it is evidently substantially pure.

Experimental evidence

The ultimate test of any hypothesis is experiment. Current UK legislation makes experimentation in this field difficult. However, the Danish Medieval Gunpowder Research Group has manufactured calcium gunpowder and report that the mixture "was difficult to ignite".[xxiii] There is sound reason for expecting this result. Calcium nitrate crystallises with four molecules of water of crystallisation. When heated, these are driven off to give the anhydrous salt. The energy required for this reaction has to be satisfied before the oxygen content of the nitrate group can be made available for combustion; hence the reported difficulty of igniting such a mixture.[xxiv]

Conclusion

The theory that early gunpowder was based on calcium nitrate has been examined. It is based, not on positive evidence, but on the absence of a statement from a medieval document that could have had good reason to omit it.
However, the document does contain a statement (repeated twice) that clearly and irrefutably identifies the major constituent of saltpetre as potassium nitrate and this is supported by the known properties of the calcium salt.

Although the translation of *Das Fuerwerkbuch* remains a valuable contribution to the literature of early gunpowder, the associated notes and commentary must be treated with considerable caution.
From the available evidence, the theory that early gunpowder was exclusively based on calcium nitrate is untenable.

[i] Published as the Jubilee Number of the Journal of the Arms and Armour Society Vol XVII No 1 March 2001
[ii] Buchanan, Brenda, J, ed. *Gunpowder – The History of an International Technique*, Bath Univ Press 1996
[iii] Harding D F, *Smallarms of the East India Company 1600 – 1856*, Vol III,Foresight Books 1999, P 33 footnote a.
[iv] Jack Kelly, *Gunpowder, A History of the Explosive that changed the world*, Atlantic Books 2004, pp36, 62-63
[v]Horst O Hardenberg, The Middle Ages oftheInternal-Combustion Engine 1794-1886, SAE 1999
[vi]" … the soil of such caves, cellars, stables, pens and manure-heaps… should be tested for saltpetre. If the salt exists in considerable quantities, it may be detected by the taste…" Joseph LeConte, *Instructions for the manufacture of saltpetre,* Charles P Pelham, State Printer, Columbia (SC) 1862 P 5. Author's note: This document records the then current French, Prussian, Swiss and Swedish methods of production and confirms the need for alkaline conditions (and a robust approach to chemical analysis!)
[vii] For example, the Biblical quotation "…For though thou wash thee with nitre**,** and take thee much soap…" **(***Jeremiah* 2:22) is evidently referring to natron, a native form of potassium carbonate which would have similar properties to sodium carbonate – washing soda – not potassium nitrate which has no such cleaning properties.
[viii] Saltpetre farms are not recorded during the period under discussion but Buchanan has made a credible case that the conditions existed for unplanned local waste deposits to provide the same conditions giving rise to "natural" deposits. *Gunpowder* Ch 4.
[ix] Arthur Marshall, *Explosives Vol 3 part 2*, Churchill 1932 revision of 1917 ed
[x] *Al-furusiyya wa al-manasib al-harbiyya (The Book of Military Horsemanship and Ingenious War Devices*) Partington , J.R. *The History of Greek Fire and Gunpowder,* Heffer, Cambridge 1960 p 201 Note A more recent annotated edition clarifies some of the linguistic issues. Hassan Aleppo, p130
[xi] The geography of Venice makes it an unlikely candidate for primary production but it was a major trade centre for the region. It is suggested that a major source could have been Petra with the ensuing possibility that the material was originally 'Sal Petra'. Objective evidence is being sought but the materials, Camel dung and water, were available in large quantities from the long established caravan routes. Alternatively the name could have been acquired *en passant* as Stilton cheese is named after the coaching stop.
[xii] Ernst Jänecke, *Uber die Bildung von Konversionssalpeter vom Standpunkt der Phasionehre*, Anorg Chem (Zeitisch) 1911pp1-18
[xiii] Modern practice recognises that the pure crystals are still moist with a solution of the contaminants and this is washed off with a small amount of pure water; loosing a small percentage of the pure product which may be recycled.
[xiv] Marshall, *Explosives.*
[xv] For example; Pliney the Elder is generally credited with the first reference to the use of soap in the first century AD but the Ebers Papyrus, a medical document from about 1500 B.C., describes combining animal and vegetable oils with alkaline salts to form a soap-like material used for treating skin diseases, as well as for washing. *Papyros Ebers.* The first complete translation from the Egyptian, by H. Joachim. Berlin, G. Reimer, 1890.
[xvi] The master must also be able to read and write because in no other way can he keep all the required knowledge in his mind… Folio 75
[xvii] The translation of *Fuerwerkbuch* cited is based on Freiburg MS 362 which is believed to be the earliest copy available but it, and other versions, are not the original primary document.
[xviii] Dundas, *A treatise on Naval gunnery 1855*, para. 447, Conway Maritime Press.
[xix] *Fuerwerkbuch* commentary p71
[xx] Modern, highly compressed, gunpowder is still recognised as being in equilibrium with atmospheric moisture. Exposure to 70% RH for 3 hrs (a standard test) results in a moisture content of 2.2% Cacket. J. C. *Monograph on Pyrotechnic Compositions* Fort Halstead 1965 p 115.
[xxi] Thao Hung-Ching, *Ming I Pieh Lu*, Quoted in Needham J et al, *Science and Civilisation in China.* Cambridge University Press Vol 5 Chemistry and chemical technology. part 7 Military Technology; The Gunpowder Epic.
[xxii] The transliteration between blue and violet is not unreasonable considering the multilingual translations between medieval German, Chinese and English but there can be no credible confusion with the brick red flame colouration of calcium salts.
[xxiii] Not formally published.
[xxiv] Kramer notes this reaction (*Gunpowder pp. 51,52*) and states that when the calcium nitrate solution is boiled above 100°C the water of crystallisation is driven off. This is evidently mistaken. The water of crystallisation is only bound to the molecule when crystallisation takes place. In solution there are no crystals and hence no water of crystallisation.