Medieval Gunpowder Research Group

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The Saltpetre Extraction Experiments

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Introduction

Evaluating the effectiveness and value of early cannon is not at all easy. Contemporary texts are not extensive nor are they easy to interpret and the problem is further exacerbated by the use of comparisons with which we are unfamiliar - what does 'very far' or 'much further' mean in the context of range or 'more powerful' or 'twice as strong' in that of the gunpowder itself. Just what were the ranges of early cannon and how fast was the shot going when it left the barrel are questions we are completely unable to answer with any accuracy. In an attempt to overcome these limitations, experimental work has been attempted to obtain some numerical data and as a means to more closely understand the sources. Over the past 5 years several successful replicas of early guns have been made and experiments with these have shown the effectiveness of these early weapons. However most of these trials have used modern gunpowder and, as useful as these experiments have been, they cannot be considered to have answered all the questions about just how effective these early gunpowder weapons really were. What is needed is a closer approximation to the gunpowder used in the past.

This problem was partly addressed by experiments in 2002 and 2003 when different gunpowder recipes were tried.[1] These showed that simple mixtures of gunpowder made quite effective propellants in a small piece of artillery in which the powder was tightly confined. However, although these experiments were carried out using gunpowder made with charcoal and sulphur produced as closely as possible to medieval methods, modern, pure saltpetre – potassium nitrate – was utilised. The question is how would this compare to medieval saltpetre and how would those differences affect the performance of the gunpowder and the artillery using it?

There are at least two factors that might affect the saltpetre. The first is what and how much impurities it might contain and the second is whether the saltpetre was potassium or calcium nitrate. Saltpetre was produced by extracting it from animal wastes in which it was formed by the action of bacteria. The extraction process was quite simple, washing the saltpetre and other salts out with water followed by precipitation from a saturated solution. However, though this process would concentrate the nitrates it could not completely separate them from other salts. Just what these would be, the amount present and their effect on the gunpowder made from it are all questions which we cannot answer.

The second important factor is its chemical composition. Extracting saltpetre from waste materials by a simple washing and precipitation method will result in calcium nitrate. To convert it to the potassium salt needs the addition of a potassium source, wood ashes, during the manufacturing process. Though this process is only directly referred to for the first time in the 16th century there is evidence from the 15th century that ashes were used in making saltpetre. This has led some writers to conclude that in the early phase of the use of gunpowder, calcium nitrate was used and that the numerous recipes for restoring decayed powder could be explained by the fact that it a particularly deliquescent salt which rapidly becomes damp when left in the open air. However experiments have shown that gunpowder made using just calcium saltpetre will not explode – in fact does not even ignite – so that the conversion process must have been known from the very beginnings of the use of gunpowder. However this has led to the proposition that saltpetre may have been very variable in quality - 'good' saltpetre makers converted almost all the calcium to the potassium salt (and kept the amount of other impurities to an absolute minimum) whereas others did not manage either the conversion process nor the purification process well enough and the resultant powder was liable to become damp over time and really was not a very good powder at all. However this must remain, for the moment, somewhat conjectural. In order for us to more fully understand early gunpowder,

what is required is some way to evaluate the saltpetre that may have been made in the period before 1500 and to this end experiments to extract it from a bed of animal waste were attempted as a first step.

The 'nitre bed'

The bed from which we hoped to extract nitrates was assembled in 2001. It consisted of a pit, approximately 1 metre deep by approximately 3 metres square, in which layers of chicken shit approximately 30 cms thick were alternated with thin layers, about 5 cms thick, of lime. Once full the top was covered with a layer of straw and a chicken house was built over the top of the pit in which chickens were kept. Periodically pig urine was added to the pit and it was aerated by forcing an iron bar repeatedly into it.

Figure 1. The nitre bed with the chicken house built over it

In August 2004 part of the contents of the pit were dug out and an attempt was made to extract nitrates from it. On digging down into the bed a strong ammonia-like smell was very noticeable. The upper layers appeared to consist of large clods of manure while further down there was a grey, crumbly 'earth'.

Figure 2. Left - digging out the nitre bed showing the layers of chicken shit and lime. Right – a close up of the material from the nitre bed

The extraction process

There are no detailed descriptions of the extraction of saltpetre from a 'nitre bed' before the 16th century. For our experiments the actual process used was a mixture of what was used then and some educated guesswork. In addition the process was conducted in the public area of the Medieval Centre in Nykobing in Denmark so that it was carried out, as far as possible, using medieval type utensils and equipment and wearing medieval dress!

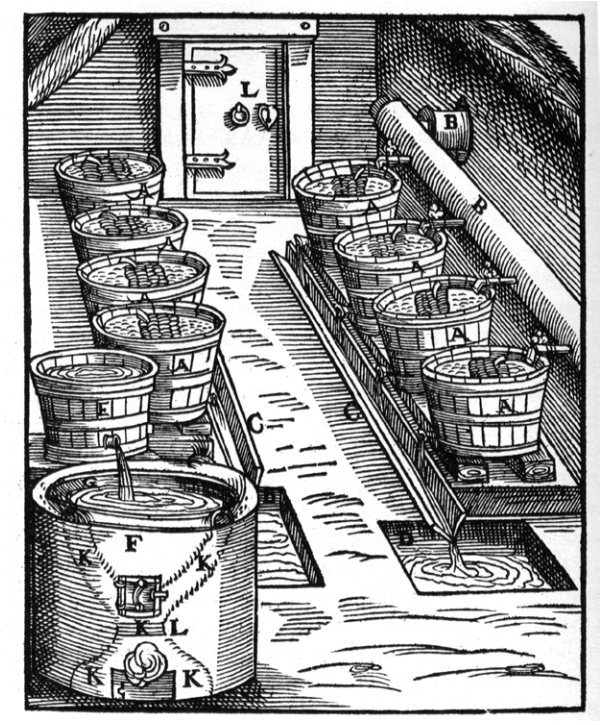

Figure 3. Saltpetre extraction – from Lazarus Ercker, Treatise on ores and assaying, 1580

Figure 4. The contents of a barrel containing the chicken manure draining into a second container

The process was carried out as follows. Wooden barrels were used in which a small hole, approximately 1 cm in diameter was made in the bottom and fitted with a wooden plug. These were then filled as follows: first a layer of twigs was laid down in the bottom of the barrel. These were then covered with a layer of straw about 7-8cms thick. A layer of ashes was then spread over the straw – approximately a kilogram of ashes from a wood fire. The container was then filled to within about 7cms of the top with the material from the nitre bed and finally water added to near the top of the container. This was then left for a period of between an hour and overnight – about 18 hours. The wooden plug was then removed and the water allowed to drain into a second container. Where the flow of liquid was very slow the contents of the container were agitated with a stick to speed up the process.

The liquid obtained, which ranged from a light to a quite dark brown, was then poured through a piece of fabric to remove any coarse solid material into an iron cauldron. After the first filling of water had drained through the container, it was refilled with fresh water which was also allowed to drain through and this was then used as the liquid to add to a second barrel which had been filled with fresh twigs, straw, ashes and chicken shit as before. In this way it was hoped to maximise the extraction of nitrate from the manure.

Figure 5. The complete set up for the extraction showing the two barrels and collecting containers

Figure 6. Boiling down the leachate and removing the scum that formed with a ladle

The same procedure was then repeated until ten loads of the chicken manure had been extracted in total. The leachates from all the extractions were then boiled down to about approximately 10 litres in total. As it boiled a thick scum continually rose to the surface and this was removed using an iron ladle. The whole process took approximately 5 days to complete.

Analysis

At each stage in the process samples of the leachates were taken and analysed for the concentration of nitrate that they contained.

Sample number	Extraction number	Concentration ppm	Notes
1	L01A	480	Single
2	L01B	-	Sample empty
3	L02A	550	Double
4	L02B	1300	Second water
5	L03A	1000	Double
6	L04A	1200	Single
7	L04B	700	Second water
8	L05A	700	Double
9	L05B	1200	Second water
10	L06A	1300	Double
11	L06B	420	Second water (After shaking 440 ppm)
12	L07A	5000	Double - Left overnight
13	L08A	1200	Single - Left overnight
14	L08B	460	Second water
15	L09A	1200	Double
16	L10A	1200	Double
17	L10B	1500	Second water
18	L11A	-	-
19	L11A	-	-
20	L12A	1900	-

Note: Single means that it was the result of a single pass through with fresh water, second water is the second extraction of a barrel and double means that the water used was partly the second water with some added fresh water.

Further filtration

The final boiled down leachate, approximately 5 litres in total, was a very dark brown liquid. To try to obtain a clear solution this was filtered through coffee filters several times but these did not remove the colour and the resultant liquid was still a dark brown and somewhat oily. As a trial a small amount, approximately 150 ml of this filtered material was then boiled down until crystals could be seen forming. On cooling, dark brown coloured crystals were found in the bottom of the container. The problem was how to produce clean white nitrate crystals. Pouring off the resultant brown slightly viscous brown liquid and re-dissolving the precipitate in clean water and boiling that down did not really produce much of a change though the crystals changed from dark to a lighter shade of brown.

A review of the literature on saltpetre brought out the following 17th century text:

> But the workmen seldom make use of any further indication, than by finding the liquor hang like oyl on the sides of the brazen-scummer, when 'tis dipped into it, which is a sign it is fit to be passed through the ashes, which is done in this manner.
>
> You must prepare two tubs fitted after the manner of the first, where you put the

> earth, saving that at the bottom of these tubs, you must lay reeds or straw about a foot high, over them place loose boards, pretty near one another, over them, a little more straw (which is to keep the ashes from the top, and to give the liquor room to drain the better from them:) Then fill up your tubs with any sort of wood-ashes to half a foot of the top; then pour on the foresaid liquor, as it comes scalding hot out of the copper, and the ashes contained in the first tub; then after a while draw it off at the to; and so continue putting on and drawing off, first at one tub of ashes, then at the other, till your liquor grow clear, and lose the thick turbid colour it had when it went on.[2]

The implication is that the boiled down liquor in the 17th century, was also somewhat 'turbid' similar perhaps to what we had produced and that they used ashes and straw to filter it and of course to transform the calcium salt to potassium nitrate. To see whether we could produce a clearer solution a similar setup was attempted. Straw and ashes were put into a small plastic bucket as described above and the hot liquor poured through it. The resultant liquid was not really any different in appearance and was still very dark brown.

In order to ascertain just what we had made about one litre of the solution was boiled down till crystals could be seen forming and left to cool. Once cold and a precipitate formed excess liquid was poured off and the brown crystals re-dissolved in clean water and the process repeated before leaving the resultant precipitate to dry. This was then sent for analysis.

Results

Analysis of the precipitate proved it to be potassium sulphate with very little nitrate present. Intriguingly it shows that the conversion process – substituting potassium for calcium – worked very well. However the conversion of the waste material to nitrate had just not occurred. The reasons for this probably include:

- Insufficient aeration of the bed. The subsequent lack of oxygen slowing down and preventing the breakdown of the ammonium ions by bacteria to nitrates. This was exacerbated by the fact that the bed was sunk into a pit and not built up as a pile on the ground
- Insufficient addition of urine. Although urine was added it is clear, especially from the work of Williams (1975) that it is very necessary for higher yields.
- The use of bird faeces may have been detrimental as they tend to be highly acidic and there is some evidence that the bacteria involved in the breaking down processes are not tolerant of acidic conditions. The addition of lime to the original bed helped in this respect but it may be that insufficient was added.

The way forward

The experience gained from carrying out the extraction and precipitation has been invaluable in understanding the processes involved. The way forward is to build a nitre bed upon the ground made up of waste material from cows, pigs or horses and not from chickens. Urine must be added at regular intervals and the pile turned periodically to aerate it. Checking on the nitrate content of the bed should also be carried out at regular intervals – carrying out small-scale extractions coupled with analysis – to ensure that the bed is producing nitrate.

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Figure 7 The Group members who carried out the extraction of saltpetre

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Notes

1 The reports of these trials can be found at www.middelaldercentret.dk/gunpowder2002.pdf and www.middelaldercentret.dk/gunpowder2003.pdf.
2 Taken from the 'History of the making of salt-peter' by Mr Henshaw in Sprat 1667.

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