Medieval Gunpowder Research Group

Making Saltpetre -Part 2

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Introduction

One of the primary research aims for the Ho Group is to produce all the ingredients, charcoal, saltpetre and sulphur, of blackpowder using methods and processes which are as close as possible to those used in the medieval and early modern period. The intention was that, once each material was made, detailed analysis and further experimentation, including comparison with modern blackpowder, would allow a better understanding of the properties and effectiveness of early gunpowder. Producing usable quantities of charcoal and sulphur has proved relatively easy but making large amounts of saltpetre has, so far, eluded us. In 2013, a series of experiments to extract saltpetre from a prepared pile of raw materials led us to believe that we were on the right lines though the quantities obtained were extremely small - less than 100g. The project for 2014 was to use the experience and knowledge gained from those experiments and attempt to make a greater quantity.

Method

The production and extraction of saltpetre can be broken down into a number of steps:

- The production of nitrate in a saltpetre bed consisting of a large, open pile of the raw materials, earth, animal dung and urine. Bacterial action within the pile converts the nitrogen in the urine and dung into nitrate.
- Extraction with water of the nitrate from the soil and subsequent concentration by evaporation of the water
- Conversion of calcium to potassium nitrate using ashes
- Precipitation to produce the raw material
- Purification of the raw material resulting in 'pure' saltpetre

The production of nitrate

The saltpetre bed was prepared in 2012 and received regular additions of urine over a period of 2 years - see Ho Report Number 11: http://www.middelaldercentret.dk/pdf/Ho_report11.pdf

This was again used for our current experiments and following our experience from 2013, the material was carefully sieved by forcing it through a sieve with a hole size of approximately 0.5cm.

The saltpetre bed

Extraction and concentration

Extraction entails the dissolution of the soluble salts in the material from the saltpetre bed. Following from the work of 2013 this was done in the following manner.

Four wooden tubs were assembled on a large table, each fitted with a tap about 3cm from the bottom, and slightly tilted forward. Each was filled with the following:

- A thick layer of straw - about 10cm deep
- A slatted wooden platform which sat on top of the straw
- Approximately 40kg of the sieved saltpetre earth.

Once assembled, approximately 40 litres of water was added by carefully pouring onto a wicker disc placed on the surface to prevent it forming a deep runnel in the earth. The tubs were then left for approximately 16-18 hours before being drained into a collecting tub - the first wash water. Each tub was subsequently filled with water again and left for approximately 4-6 hours before being drained, the second wash water, and the tub of earth emptied and refilled with saltpetre earth.

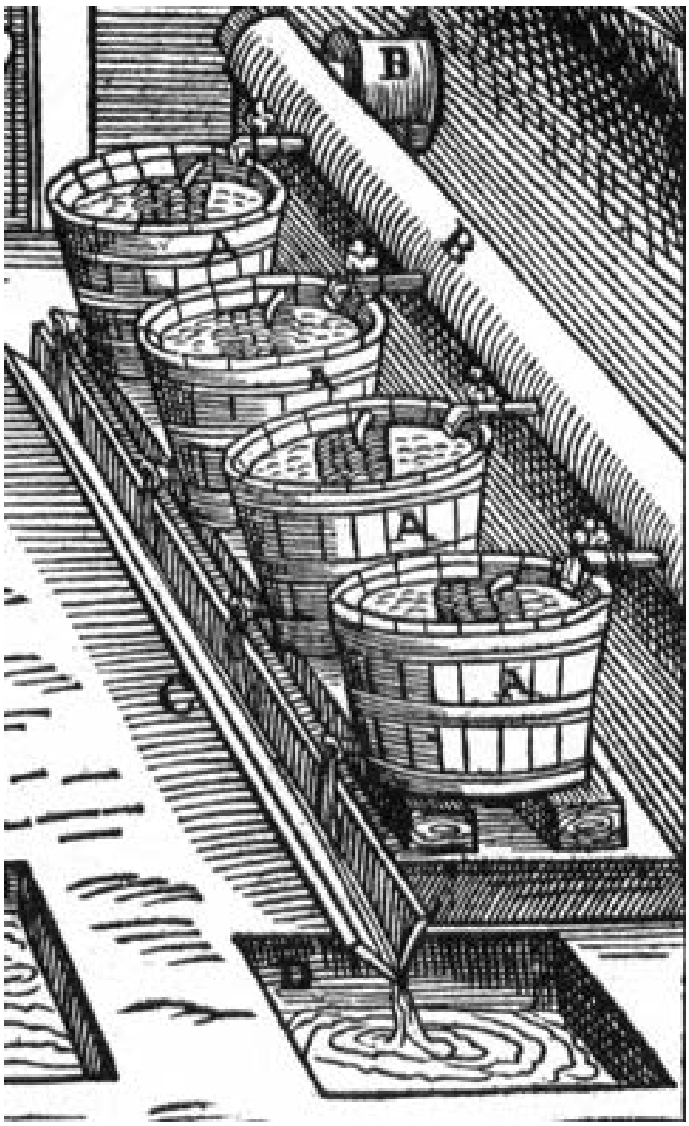


Illustration from Ercker showing the set up of the leaching tubs. Note the permanent water supply system and the small wicker 'rundles' on top of the earth.

Each tub was fitted with a tap

A layer of straw, about 10 cms thick was carefully packed into the bottom of each tub

A slatted wooden platform was then laid on top of the layer of straw

Each tub was then filled with approximately 40 kg of sieved earth

Water was then poured, over a wicker 'rundle' so that there was a layer of liquid aboce the earth

Four tubs were filled in the same way and set up on a table with a drain in front and a collecting tub at one end.

The second wash water was then used as part of the water added to the newly filled tub. The first wash water was boiled down over wood fires to concentrate the nitrate. This procedure was followed over 8 days to extract the nitrate from 24 tubs and approximately 960kg of the saltpetre earth. The leachate totalled some 426 litres.

Essentially, we now had a very dilute solution of nitrate in water and it is necessary to boill down the leachate to concentrate it. We used 4 small cast-iron cauldrons heated by wood fires. The fires were controlled to keep the liquid constantly boiling and small amounts of fresh liquid were added continually using a ladle.

Boiling down the leachate to concentrate the solution. We started with just a single caldron but the quantity of liquid collected meant that we had to increase the number. In order to keep the liquid boiling , only small quantities of liquid were added at a time using a small ladle

We were able to boil down approximately 60-70 litres of the liquid a day to approximately 20 litres. Over the course of 7 days, the leachate from all the tubs was boiled down to approximately 27 litres in total.

Conversion

In order to convert the calcium salt to potassium, we poured the concentrated leachate through a bed of wood ashes.

To do this, one of the wooden tubs was prepared in a similar way to the extraction process. At the bottom we made a bed, 10cms thick, of straw over which was placed a wooden slatted platform. Approximately 25kg of wood ashes was then added. Ten litres of water was poured through the ashes first to wet them thorughly followed by the 27 litres of the concentrated leachate. This was left overnight.

Pouring the concentrated leachate onto the bed of ashes.

In order to attempt to see if the process was working, 2 litres of the liquid from the ash tub was run off into a settling tray and left overnight to see if anything would crystallise out. Nothing appeared but when a few millilitres of this liquid was boiled down even further, tiny needle-like crystals were seen providing us with evidence that saltpetre was present.

After some discussion it was decided to pour additional fresh water through the ash tub to ensure that all the nitrates were washed out. Unfortunately, this resulted in adding water to the distillate which had to be boiled down again to concentrate it.

Precipitation

After additional boiling down, at this stage we had about 34 litres of leachate and this was poured into a large rectangular settling tank to see if anything would crystallise out. After 36 hours, nothing had appeared meaning that eaither the solution was not concentrated enough or there was nothing to crystallise.

To further concentrate the leachate, a gas heater was used to further boil down the liquid to approximately 5 litres in total. This liquid was then left overnight in the settling tank. Large, long thin needle-like crystals formed, approximately 12cm long by 0.5cm wide. Though we had no means

Saltpetre produced in India by a similar process showing their long needle-like crystal structure

of analysis, potassium nitrate is known to precipitate from solution in long needle like crystals.

The crystals of saltpetre.

Detail of the crystals. Their long needle-like appearance is strong evidence that this is saltpetre. The contemporary record describes them as looking like *ickles* - icicles. The brown colour comes from the liquid.

Purification

To purify this material, approximately 350g was removed from the settling tray and dissolved in 1 litre of clean water. This was then boiled down slowly. As it reduced and the solution became more concentrated, crystals of impurities formed in the bottom of the container and were removed with a spatula and a sample retained for future analysis. This confirmed our interpretation of the purification process - the less soluble impurities come out of solution as the their concentration increases with the reduction in water volume. Essentially the process depends on the difference in solubility at different temperatures between saltpetre and the other salts extracted from the saltpetre bed. Most of these latter salts, the unwanted impurities, have roughly the same solubility in cold and hot water. For example common salt, sodium chloride, will dissolve 36g per 100ml of water at 20oC and 39g per 100ml at 100oC. However, the solubility of saltpetre is very dependent on temperature, ranging from 47g/100ml of water at 20°C to 141g/100ml at 100°C - see table and graph below.

This means that, as the water is boiled away and the solution become more concentrated, the impurities will exceed their solubility limit and fall out of solution. The saltpetre, being so much more soluble at high temperatures will remain in solution. Finally, on cooling to room temperature, most of the impurities will remain in solution while the saltpetre, with its much lower solubility at lower temperatures, will precipitate out. It will, of course, contain some impurities but these will be greatly reduced and a second purification will reduce them a little more though it is impossible to remove all impurities by this method.

Drying

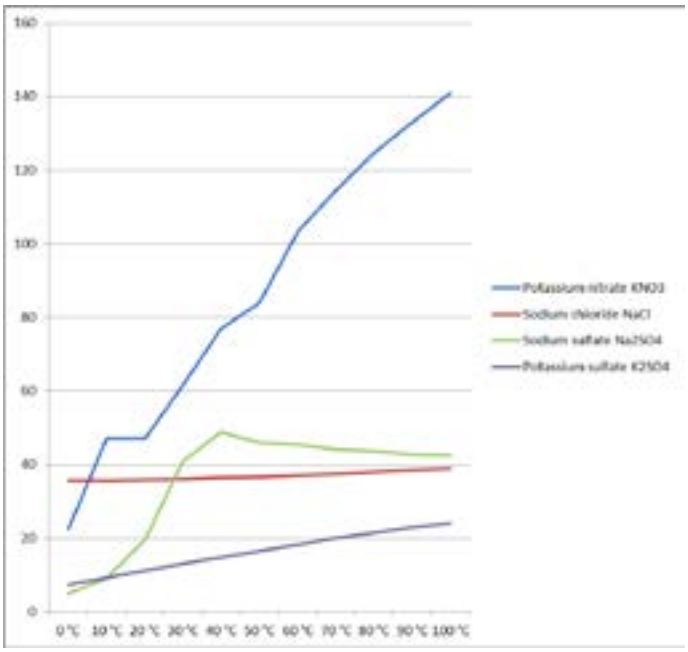
Approximately 200g of wet saltpetre was left overnight to dry out. Interestingly, as the material dried it became whiter and less black. Two small charges. 50g each, of blackpowder were made up with charcoal and sulphur in the ration 75:15:10 and these were loaded into the Loshult gun replica. Using grass as a wad, the first made a small explosion while the second burnt inside the barrel but did not explode.

Conclusions

We were disappointed that we only managed to produce a very small amount of saltpetre though it was clear that the material was largely saltpetre - its purity will have to remain unknown until analysis can be carried out. Future work should, we feel, concentrate on trying to make the saltpetre bed more productive though it is uncertain how this can be achieved. What was important was that we have confirmed the method of making saltpetre and purifying it. Analysis will now be needed to ascertain just how well the various processes worked.

		0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C	100°C
Potassium nitrate	KNO_3	22.4	47	47	61.6	77	84	103.4	114.6	124.6	133	141
Sodium chloride	NaCl	35.6	35.7	35.9	36.1	36.4	36.7	37	37.5	37.9	38.5	39
Sodium sulfate	Na_2SO_4	4.9	9.1	19.5	40.8	48.8	(46)	45.3	(44)	43.7	42.7	42.5
Potassium sulfate	K_2SO_4	7.4	9.3	11.1	13	14.8	(16)	18.2	(20)	21.4	22.9	24.1

Table of solubilities of various salts in g/100ml water



The solubities of the salts shown in graph form.

Medieval Gunpowder Research Group - 2014

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