SIGNIFICANCE OF OXYGEN IN PROCESSING OF BONE CHAR FOR DEFLUORIDATION OF WATER

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SUMMARY: The significance of duration and temperature of bone char processing and the admission of air oxygen during charring is investigated. Different quality criteria are used, i.e. the defluoridation capacity and the specific surface area of the treated bone, along with the pH and alkalinity of the defluoridated water. Processing temperatures between 300 and 800°C and duration between ½ and 5 hours are used. It is found that when admission of oxygen is restricted, i.e. the process is run as of pyrolysis, all measured quality parameters, including defluoridation capacity, are at optimum, independent of charring time and temperature. When bones are exposed to atmospheric oxygen, i.e. the process is run as a calcination, the defluoridation capacity is drastically reduced for temperature above 500°C. Similarly, pH and alkalinity of the defluoridated water are found to increase during the calcination. The specific surface area is highest for pyrolysed bone, and much lower for calcined bone. The results indicate that pyrolysis, when carried out completely, provides the best bone char quality, where the product is all over black and has the highest possible defluoridation capacity. If treated properly pyrolysed bone may even be able to improve the aesthetic water quality rather than deteriorating it.

Keywords: bone char, defluoridation, pyrolysis, calcination, charring procedure, surface area, capacity, optimisation.

INTRODUCTION

Bone char has been used for defluoridation of drinking water in USA in the 1950's and 1960's.[1,2] At that time bone char was commercially widely available, because of its use in the large scale sugar industry. Today the use of bone char in the sugar industry is replaced by synthetic ion exchange resins. As the manufacturing of bone char was previously empirically established for the sugar industry, very few studies have been carried out on its manufacturing for use in drinking water defluoridation. Today there is an increasing interest in using bone char for defluoridation of drinking water in third world countries, and hence the need to investigate how to prepare and to measure a high quality bone char for treatment of fluoride contaminated drinking water.

It has been reported that the defluoridation ability deceases with increasing charring temperatures and duration time even when treated at 550°C for 30 minutes compared with 400°C for 1 hour[3] or 450°C compared to 350°C (time not indicated).[4] Bone char is reported to change its colour from black to grey to white as it is heated from 350°C to 600°C and "black bone char" has therefore been regarded as the good bone char.[4,5] According to this study, these colour changes are only observed when bones are *calcined*, i.e. heated in the presence of atmospheric oxygen. In principle, the end product of such a calcination is pure bone minerals, i.e. compounds related to

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hydroxyapatite. All organic materials are combusted and gassed off. All organic carbon is transferred into carbon dioxide.

The original procedure of charring bones for the sugar industry was different, in the sense that no or limited flow of oxygen was admitted to the process.[6] When the bones thus are *pyrolysed*, the organic material is mainly cracking, and a significant part of the organic carbon is converted to inorganic carbon, graphite. The end product of this treatment will be black. No colour changes at all are observed. The above mentioned criteria of colour changes as a means of characterising the product and the preparation, as described by Phantumvanit et al.[5] and Mwaniki[4] is thus unusable in the case of pyrolysis of bones.

MATERIALS AND METHODS

Preparation of bones: A mixture of all sorts of farm animal bones and teeth has been used as raw bones. The bone materials were delivered from the Danish bone meal and animal feed factory DAKA, where the genuine bones are boiled, washed, dried and crushed down to 2-3 cm particle size.

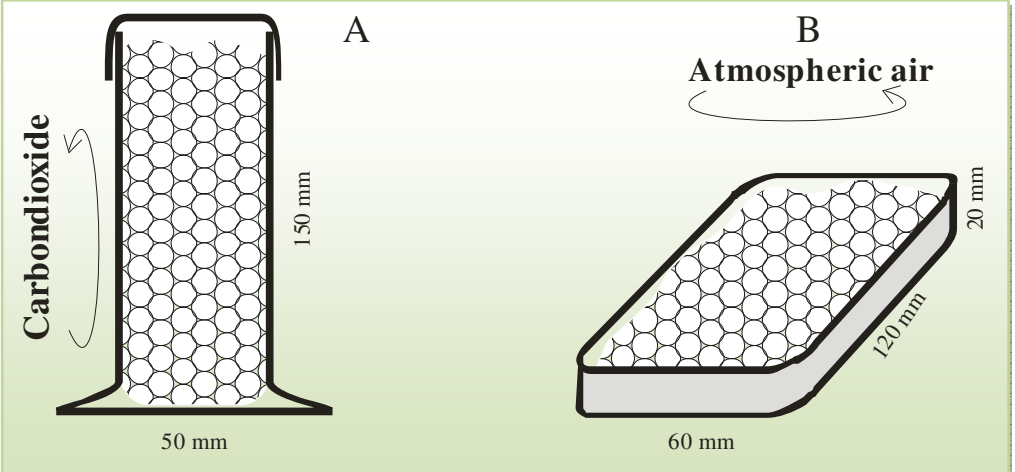

FIGURE 1 Illustration of the containers used for respectively pyrolysis (A) and

The DAKA bones were crushed to a size 4-10 mm in a Morgårdshammars, B-92 plate type crusher. Samples of bone char were placed in two types of containers, type A for pyrolysis and type B for calcination, see figure 1. The bone materials were then charred in a programmable ceramic oven SK 35 S from Scania-Oven A/S. The temperature was gradually raised at a constant rate of ~3C/min from the room temperature and up to the treatment temperature. This temperature was then kept constant for a selected treatment duration. As treatment temperatures for the different batches 400, 500, 550, 600 and 700°C were used. As treatment duration ½, 1, 2, 3 and 5 hours were used. After the said time of treatment samples were taken out for cooling and testing. Pyrolysed samples were cooled down in a CO_2 atmosphere. The bone char was further crushed and sorted out in a test sieve shaker type EFL2 mk3 from Endecotts LTD to grain size diameter between 1 and 2 mm. Samples were weighed before and after charring in order to assess the weigh loss.

Defluoridation capacity testing: Four gram samples of bone char having grain size 1-2 mm were added to 1 litre distilled water containing 20.0 mg/L fluoride in plastic beakers at time zero. The beakers were stirred using a Jar test apparatus Type 7790-402 from Phipps & Birds at a speed of 60 rpm. After stirring in 24 hours, samples of the water were taken for analysis.

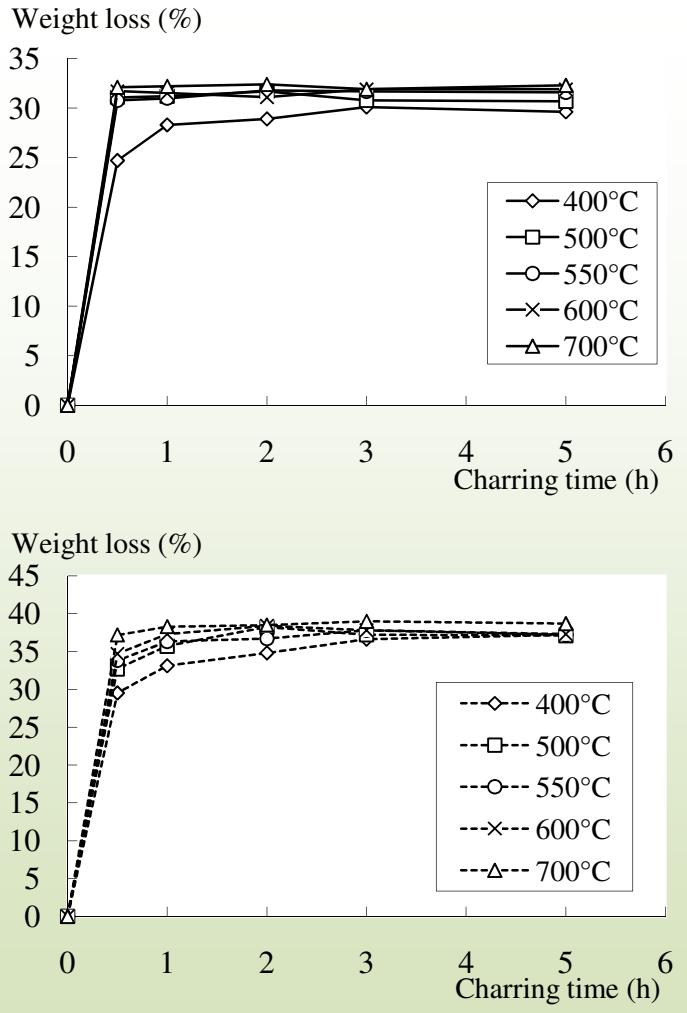

Figure 2. The weight loss in % as a function of heating time and duration. The upper results are obtained through pyrolysis. The lower results are obtained through calcination in atmospheric air.

Analysis: The fluoride concentrations in the water samples were measured using a Radiometer F1052 fluoride electrode and an Ag/AgCl reference electrode with sleeve type diaphragm (Metrohm 6.0726.100) connected to a Metrohm 692 pH-meter. Five ml samples were mixed with 5 ml tisab[7] for measurements and readings, compared to standards of 2 and 20 mg/L F^-, according to Standard Methods[8].

pH was measured in the defluoridation capacity samples using a combined glass electrode (Metrohm 6.0233.100) in connection with a Metrohm 691 pH-meter.[8]

Total alkalinity (TAL) was measured in the defluoridation capacity samples by autotitration of 100 ml solution to pH = 4.5 with standardised 0.1 M H_2SO_4[8], using a titrator set of Metrohm 691 pH-meter, Metrohm 614 Impulsomat and Metrohm 665 Dosimat.

The specific surface (BET-method) was measured in a Micromeritics Flowsorp II 2300.

RESULTS

Figure 2 shows the results of bone char weight loss as a function of 5 different temperatures and 5 different duration times, for pyrolysis as well as calcination. The average weight loss after 5 hours of pyrolysis at 400 to 700°C is 31.2 % standard deviation being 1.05. The average weight loss after 5 hours calcination at 400 - 700 °C is 37.5, the standard deviation being 0.68.

The defluoridation capacity is calculated in the jars from the determination of fluoride concentrations before and after 24 hours of contact time, according to the following equation:

$$DC = \frac{S_0 - S_{24h}}{X_{BC}}$$

Where:

DC_{BC} Defluoridation capacity of bone char (mg/g)
S_0 Beginning concentration in defluoridation capacity measurements (mg/L)
S_{24h} Concentration after 24 hours in defluoridation capacity measurements (mg/L)
X_{BC} Added bone char (g/L)

The defluoridation capacities are shown in figure 3 for all selected temperatures and duration times. When temperatures below 550 °C and duration timed shorter than 2 hour are excluded, the results shows that the utilised bone, on an average, has a defluoridation capacity of 2.27 (± 0.18) mg fluoride per g of bone char when pyrolysed, but only between 0.2 and 1.6 mg/g when calcined.

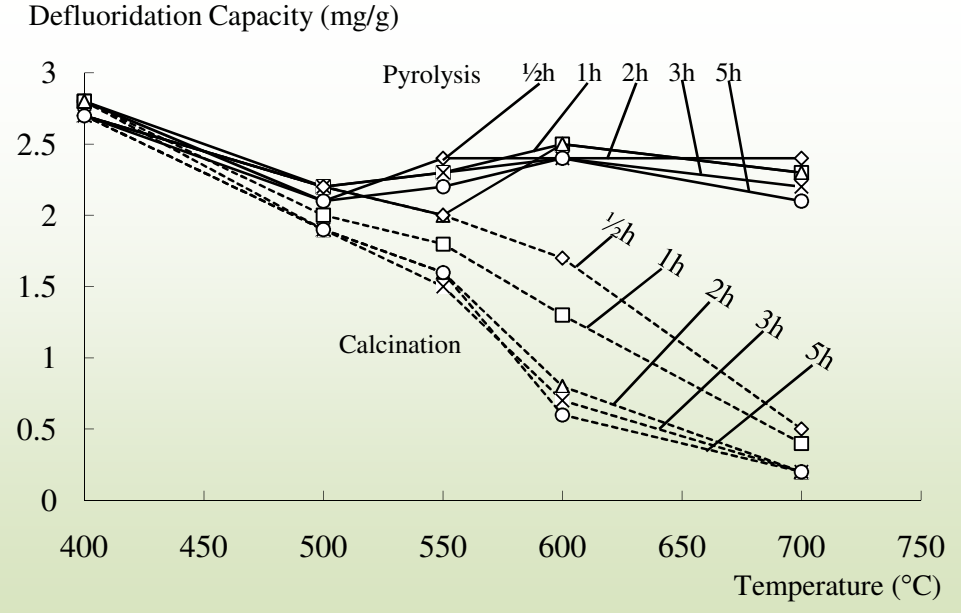

FIGURE 3. The defluoridation capacity of bones pyrolysed and calcined for different temperatures and heating durations.

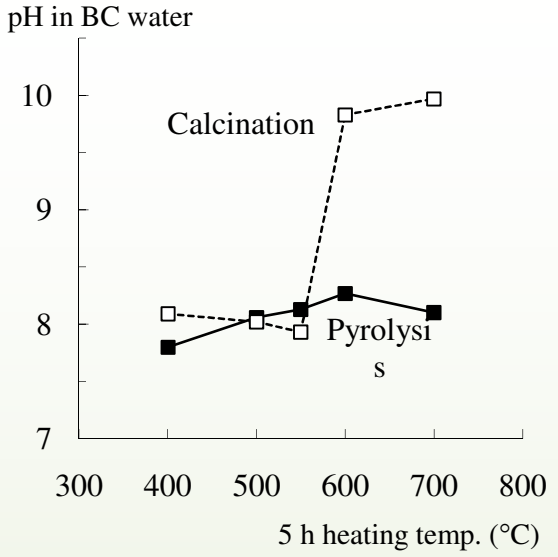

Figure 4. pH in the distilled water contain-ing 20 mg/L fluoride, after treatment for 24 hours with 4 g/L bone char heated for 5 hours at the given temperatures.

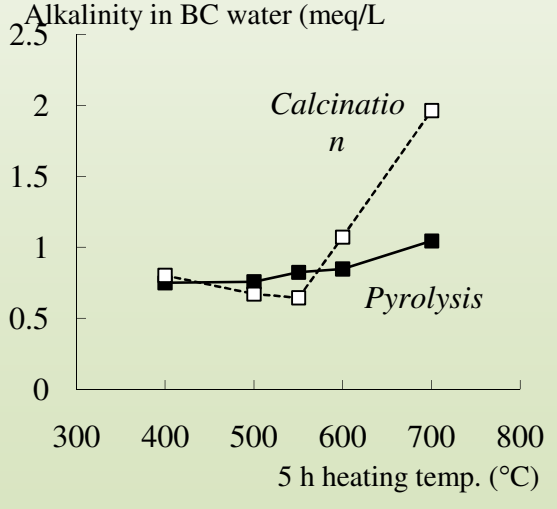

FIGURE 5. The alkalinity in the distilled water containing 20 mg/L fluoride, after treatment for 24 hours with 4 g/L of bone char heated for 5 hours at the given temperatures.

The exclusion of the low temperatures and duration times is made to avoid poor taste, smell and colour in the water treated by the bone char treated under these conditions.

pH in the waters treated with bone char heated for 5 hours are illustrated in figure 4. The pyrolysed bone waters have pH between 7.8 and 8.3, while the calcined bone char waters have pH between 8.1 and 10.0. The alkalinity of these samples, as shown in figure 5 is similarly stable for the pyrolysed bone, between 0.8 and 1.0 me/L, but increasing for the calcined bone, between 0.8 and 2.0 me/L.

Figure 6 shows the measured specific surface area of the heated bones. On an average BET is 131 ± 12 m^2/g for pyrolysed bones, while BET is falling from 94 to 11 m^2/g for the calcined bone. The BET for the not heated bone is measured to less 5 m^2/g .

DISCUSSION

The results of weight loss analysis in this study, figure 2, show that when bone is heated slowly (3°/min) in a well insulated oven, most of the organic materials are lost already ½ an hour after the target end temperature is reached. This is at least valid when the end temperature is more than 400 °C. Through weight loss analysis, it is thus impossible to distinguish between treatment duration of 1-5 hours and temperatures of 500-700 °C.

On the other hand as all pyrolyses are resulting in the same degree of weight loss (about 31 %) and all calcinations are coming up to a higher loss (about 38 %), the weight loss, along with the colour changes may be most useful for characterisation of the admissibility of oxygen during the treatment. Samples which all through are black after being heated for more than a couple of hours at 500-700°C, i.e. properly pyrolysed, would probably contain not less than 10 % pure (activated) carbon. This is of course most important as this graphite carbon may be used in the water treatment depending upon the raw water quality.

The measurements of the specific surface area of the treated and not treated bone, figure 6, indicate that the high surface area is produced during the heating. In case of pyrolysis the surface area will remain at maximum for all temperatures and duration times, contrary to calcination, where the specific surface area decreases with heating temperature.

The defluoridation capacity of the treated bone seem to follow the same pattern as the surface area as illustrated in figure 7. The raw bone has both a low defluoridation capacity and a small surface area, probably because of organic material covering the pores. When this material is removed by heating more surface is made available for adsorption. The defluoridation capacity is preserved all through the pyrolysis and partly destroyed in the calcination process. This is at least valid for temperatures above 550 and less than 800 °C, even when the treatment is as short as ½ an hour, figure 3.

The increase in pH and alkalinity are

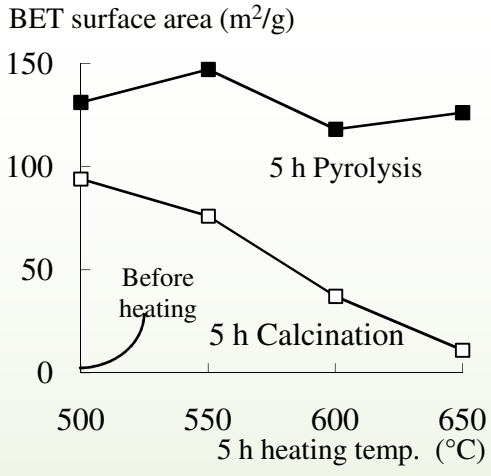

Figure 6. The specific surface area of bone before and after heating for 5 hours at the indicated temperatures, without and with the admission of atmospheric oxygen.

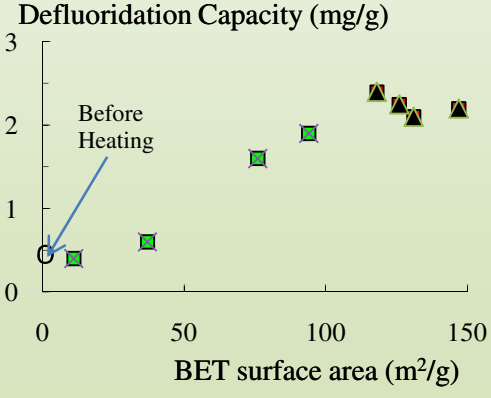

FIGURE 7. Defluoridation capacity as a function of BET surface area of raw bone and 5 h heat treated bone.

probably due to destruction of some of the apatite, where mainly CaO is produced. As this compound is only slightly soluble in the water, the production of CaO may be expressed through the increased pH and alkalinity. This is in agreement with the fact that the decreases in the defluoridation capacities during calcination, up to about 90 % of full capacity as per pyrolysis, are stoichiometrically more significant than the observed corresponding increases in alkalinities. It must be noted that even pyrolysed bone does add alkalinity to the water. This alkalinity increase is however only slightly above the equivalent reduction of fluoride, indication that the pyrolysed bone, in the contrary to calcined bone, does not contain any significant alkalinity.

It may be argued that if the defluoridation capacity is preserved during the short time and low temperatures, this is because the oxygen admitted is only consumed by the organic materials. Thus the apatite structure may not be exposed to entire calcination condition as long as oxygen is consumed by the organic materials.

The heating of bone for water defluoridation should therefore be carried out as a pyrolysis, i.e. where the admission of air oxygen is restricted, in order to:

Preserve the apatite structure uncalcined and hence the defluoridation capacity of the bone at maximum.

Allow for maximum specific surface area of the treated bone, including its contents of pure carbon, which may be used as a general sorption agent in the water treatment.

Minimise the potential of introducing alkalinity and too high pH in the treated water due to destruction of apatite compounds in the calcination process.

As apatite is believed to be durable even in atmospheric air at 400 to 700°C, this study does not give a direct answer to the mechanisms behind the defluoridation capacity deterioration during calcination. One explanation could however be that much higher temperatures are obtained at a micro (molecular) level, as a consequence of burning the organic materials in the bone during the process of calcination.

It has to be added that this study does not recommend certain temperatures and duration times. The experiences gained in the laboratory and in the field show that laboratory experiences can not be directly extrapolated to field conditions. Further more the volume and the design of the container may play an important role in selection of these parameters. Field testing indicate however that the necessary preheating periods are longer, and hence more energy consuming, in the pyrolysis process.

CONCLUSION

The following major conclusions can be drawn from the presented results.

- The best quality bone char is obtained through heating where the air oxygen is prevented or restricted (pyrolysis).

- The bone defluoridation capacity and its contents of black carbon are durable under several hours' exposure to temperatures up to 700. This is valid for the pyrolysis, but not for the calcination.
- The weight loss is an ambiguous indicator in the control of the bone char preparation; maximum weight loss is only obtained in case of calcination, where the bone char quality may be deteriorated.
- Colours of bone char can be used as indicators of defluoridation ability only if the bone char has been calcined. All pyrolysed bone char is black.
- The pyrolysis process, which ensures the maximum defluoridation capacity, would as well result in better defluoridated water quality, with respect to pH, alkalinity and may give rise to a higher potential for removal of colour, taste and turbidity in the raw water.

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