More efficient alkalisation with ground limestone in groundwater treatment

J. Sallanko, J. Hietala, R. Lindström, A. Kytövaara and T. Väisänen

ABSTRACT

Most Finnish groundwater must be alkalised before use as municipal drinking water because it is corrosive. The corrosiveness is due to low pH and softness of water. Groundwater also often contains aggressive carbon dioxide (CO_2), so there is more free CO_2 than is required to keep calcium and hydrogen carbonate in solution. The most popular alkalisation method in the past was addition of sodium hydroxide, but use of limestone (calcium carbonate) for alkalisation is becoming increasingly popular, the main reasons being that the overdosing risk is avoided and that water hardness is increased by limestone. The most common method of alkalisation using limestone is through limestone filters, but these are quite large and the empty bed contact time needed often ranges from about 40 minutes to more than 2 h. The investment cost and size of plant required can be substantially reduced by using mechanically ground limestone instead of limestone filters. Incorporation of mechanical grinders into two commercial-scale water treatment plants in Finland greatly reduced the space and treatment time requirements, but some problems were observed by consumers because the harder water increased limescale formation.

Key words | alkalisation, calcium carbonate, grinding, groundwater treatment, limestone, water treatment

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INTRODUCTION

In Finland, approximately 60% of the municipal water supply originates from groundwater or artificial groundwater. Surface water is used only in a few larger towns and cities, so water treatment plants using groundwater are more numerous and often smaller than plants treating surface water. Typical Finnish groundwater-forming areas have restricted dimensions, with limited or no interaction with neighbouring groundwater-forming areas. Finnish groundwater is often quite corrosive because it is acidic and soft. Furthermore, it often contains aggressive carbon dioxide (CO_2), so there is more free CO_2 than is required to keep calcium and hydrogen carbonate in solution. A study on water quality in 1,000 Finnish wells found that the median pH in dug wells was 6.4 and in drilled wells 7.2, while the median degree of hardness in dug wells was 2.2 °dH and in drilled wells 3.4 °dH (Lahermo *et al.* 2002). Corrosiveness is the most common reason for groundwater treatment. However, problems caused by excess amounts of iron (Fe) and manganese (Mn) are also regrettably common in Finland (Table 1). The guideline values on water quality for inhibition of corrosion in Finland (VVY 2002) are:

pH > 7.5
Alkalinity > 0.6 mmol L^{-1}
Calcium > 10 mg L^{-1}
CI (Corrosion Index) >1.5

$$CI = \frac{\text{alkalinity } [\text{mmol}^{-1}]}{\frac{\text{chloride } [\text{mg L}^{-1}]}{35} + \frac{\text{sulphate } [\text{mg L}^{-1}]}{48}}$$

The most common method of alkalisation in Finland in the past was addition of sodium hydroxide (NaOH). In liquid form, NaOH is easy to apply, but there are some drawbacks associated with its use. For example, in small plants where

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Table 1 | Mean values of quality parameters for Finnish groundwater from different types of aquifer and statutory limits for tap water (adapted from Hatva (2002))

Parameter	Units	Anticlinal aquifers	Synclinal Bothnia aquifers	Covered aquifers	Statutory limit for tap water
pH		6.5	6.2	6.9	6.5–9.5
O_2	mg L^{-1}	7.7	2.0	0.04	
Alkalinity	mmol L^{-1}	0.57	0.59	1.90	
CO_2	mg L^{-1}	23.2	42	21.7	
Fe	mg L^{-1}	0.01	5.0	1.5	0.20
Mn	mg L^{-1}	0.05	0.29	0.43	0.05
$KMnO_4$	mg L^{-1}	3.1	9.3	3.4	19.75
Hardness	°dH	1.9	2.4	7.3	
Conductivity	mS m^{-1}	10.9	14.7	43.2	250
NH_3-N	mg L^{-1}	1.6	0.4	2.0	
Cl	mg L^{-1}	9.2	8.4	34.0	250
SO_4	mg L^{-1}	7.8	29.9	45.7	250

there is a limited degree of automation and only a few employees, overdosing with NaOH is not uncommon. In addition, NaOH raises the pH but not the degree of hardness of groundwater. In contrast, when limestone (calcium carbonate; $CaCO_3$) filters are used for alkalisation, it is possible to raise the pH while also raising the hardness of the water (Gier & Schagen 1983; VVY 2002; Gude *et al.* 2011). Furthermore, there is no possibility of overdosing because the equilibrium pH when $CaCO_3$ is used is rarely over 8.5.

Limestone filters also have the capacity to remove some of the Fe and Mn present in groundwater (Sallanko *et al.* 2003; Gude *et al.* 2011). When a limestone filter is used for Fe and Mn removal, it may be included as a wet alkalising filter before a slow sand filter in some cases. In such cases, effective backwashing must be included in order to avoid chemical saturation or passivation of surfaces in the limestone (Sallanko *et al.* 2002).

The normal way of using $CaCO_3$ in groundwater treatment in Finland and other countries is in limestone filters and the main factor limiting their use is the long contact time. The empty bed contact time (EBCT) needed with a limestone filter ranges from about 40 minutes to 2 h or more, depending on the alkalinity and CO_2 content of the raw water and the particle size of the limestone. In conventional water treatment plants, the most commonly used particle size classes of limestone are 2–4 and 4–8 mm.

The long EBCT times needed for limestone filtration result in major investment costs and large buildings. This paper introduces a novel solution to decrease the investment costs of limestone alkalisation. It is based on the principle that reducing the particle size of the limestone material reduces the EBCT required. Particle size can be reduced in a very effective way by mechanical grinding.

BASIC REACTIONS IN LIMESTONE ALKALISATION

$CaCO_3$ is a slightly soluble material that dissolves slowly in clean water, as shown in Equation (1) (Stumm & Morgan 1996):

$$CaCO_3 + H^+ \Rightarrow Ca^{2+} + HCO_3^- \tag{1}$$

Some limestone contains small amounts of magnesium (Mg) and even a low content (~5%) of magnesium carbonate in limestone makes its dissolution in water substantially slower (Sverdrup 1985).

$CaCO_3$ reacts with CO_2 in the groundwater according to Equation (2) (Stumm & Morgan 1996). In this case, the amount of aggressive CO_2 decreases, the pH of the water rises and the hardness of the water increases.

$$CaCO_3 + CO_2 + H_2O \Rightarrow Ca^{2+} + 2HCO_3^- \tag{2}$$

In this reaction with CO_2 the theoretical consumption of $CaCO_3$ is 2.3 mg mg^{-1} CO_2, while in practice it is more often 2.5 mg $CaCO_3$ mg^{-1} CO_2. Using a limestone filter for alkalisation raises the hardness of the water by 0.128 °dH mg^{-1} CO_2 and the maximum pH which can reached by this system is normally 8.3 (VVY 2002). When using limestone filtration for groundwater treatment, the shortest alkalisation time needed is when the alkalinity of the water is under 0.3 mmol L^{-1} and the CO_2 content is under 5 mg L^{-1} (VVY 2002).

PRINCIPLE OF USING A LIMESTONE GRINDER

Use of a limestone grinder for mechanical mixing/grinding of the limestone produces fast-reacting, small limestone particles and thus reduces the reaction time needed (Hietala 2000). This process is illustrated in Figure 1. The water flow in the process unit is divided into two parts. One part flows through the slowly rotating mechanical grinder full of limestone and other part goes directly to the water tank, where it is mixed with other flows and where any limestone particles that have escaped from the grinder can react with untreated water. After the water tank, a filter (e.g. 1.2 μm) can be used for capturing insoluble fine particles. However, the filter is optional because nearly all insoluble particles can settle in the water tank if it is large enough. This type of layout saves space in the water treatment plant.

PILOT TESTS

In pilot tests, we tested many different kinds of grinder. The best type proved to be an auger grinder with a slow rotation speed (Figure 2). In the tests, the limestone used was of particle size 2–3 mm and the water was groundwater from Haukipudas water treatment plant, situated 30 km north of the city of Oulu. The lag time in the grinder was 45 seconds. The lag time needed for alkalisation reactions in the water after incorporation of this grinder into the treatment process was only 5 minutes (Table 2).

Pilot tests were also carried out on raw groundwater with added CO_2. When the CO_2 content of the raw water was 104 mg L^{-1}, with a 20 minute lag time after grinding, the pH in the water was still only 6.7 and the CO_2 content 66 mg L^{-1}. The raw water alkalinity was 0.61 mmol L^{-1} and hardness 0.56 mmol L^{-1} and after this 20 minute lag time alkalinity was 3.8 mmol L^{-1} and hardness 2.05 mmol L^{-1}. This means that very high CO_2 concentrations in raw water must be lowered, for example by aeration, when limestone is used for alkalisation.

The very short lag time needed after grinding the limestone was due to the small particle size of the limestone dust produced. In tests, the particle size range of the fine material was 5–50 μm and its specific surface area was 2.5–2.8 m^2 cm^{-2}, which is very large compared with that

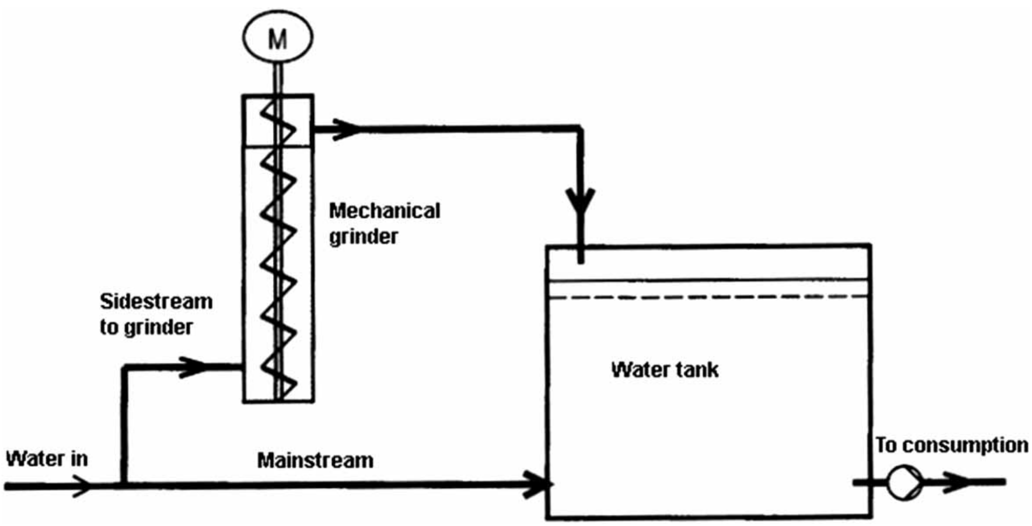

Figure 1 | Schematic diagram of the process involved in including a mechanical grinder in limestone alkalisation of groundwater before consumption. M = motor for auger.

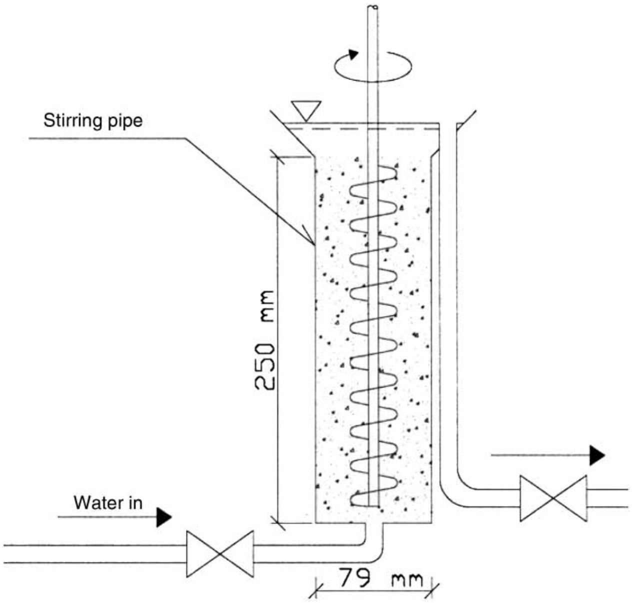

Figure 2 | Best version of limestone grinder used in pilot tests. Mixing auger diameter 32 mm and speed 180 rpm.

Table 2 | Alkalisation results obtained after incorporation of an auger grinder into the treatment process, using raw Onkamo groundwater from Haukipudas water treatment plant

Lag time, minutes	pH	CO_2, mg L^{-1}	Alkalinity, mmol L^{-1}	Hardness, mmol L^{-1}
0 (raw water)	6.6	12	0.44	0.22
2	7.7	1	1.2	0.60
5	8.1	1	1.3	0.65
7.5	8.2	1	1.3	0.65
10	8.1	1	1.3	0.61
20	8.3	1	1.4	0.66

of the commonly used crushed (4–8 mm) limestone (approx. 0.0006 $m^2\ cm^{-3}$). Owing to this approximately 4,500-fold greater specific surface area, it is possible to get rapid chemical reactions (Hietala 2000).

CASE EXPERIENCES

Based on the results of these pilot tests, grinders were incorporated into two commercial-scale water treatment plants in Finland: Haukipudas and Kangasala. The Haukipudas plant, which treats Onkamo groundwater, was built in 1994 and includes a dry-contact filter followed by filters made from rock wool cartridges, which have a surface load similar to that of a slow sand filter. The filter comprises rock wool candles, 1 m tall pipe-shaped insulation columns (diameter 200 mm) in the standing position. There are 28 of these per tank and the flow is from outer to inner. For disinfection, an ultra-violet (UV) system is used. Treated water production is approximately 1,900 $m^3\ day^{-1}$. In 2001, two limestone grinders (diameter 0.40 m, h = 2.4 m, auger diameter 0.25 m, motor 0.75 kW and auger upward lift 14 rpm) were installed (Figure 3). Alkalisation was added as the last process just before UV disinfection. After the grinders, there is a contact tank with approximately 5 minute retention time and no additional fine material filter is used in the outflow. There is also a 25 m^3 storage silo for 4–8 mm crushed limestone, from which an auger conveyor transports material to the grinder approximately once per week. The total investment cost (2001 values) was EUR 30,400. There is no extra filter for fine particles before the water network.

Figure 3 | Limestone grinders in the Haukipudas groundwater treatment plant. The black tanks each contain 28 rock wool cartridge filters.

The pH of the raw water treated in the Haukipudas plant is approx. 6.3, the CO_2 content 7–11 mg L^{-1} and the alkalinity 0.35 mmol L^{-1}. There is a side flow of 6 m^3 h^{-1} through the limestone grinder. Before installation of the limestone grinder system, the pH of outflow water from water plant was approximately 7.0. After grinder and contact tank the pH rises to 8.0–8.5. Limestone consumption is approximately 300 kg per week (~20 g m^{-3}), which is close to the practical limestone consumption in limestone filters, 2.5 mg $CaCO_3$ mg^{-1} CO_2.

Experiences from the system have been positive to date. Running costs are low. The limestone supply lasts for 1.5–2 years and the electricity consumption of the system is approximately 20 kWh per day. The only maintenance work needed has been removal of impurities from the grinder four times per year, which takes 2 h each time. Impurities in the contact tank have been removed twice per year, which takes 4 h each time. The clear water tank is cleaned once every 2 years, as it was before grinder installation. The grinder axle suffers some wear and has been changed every 5 years. The introduction of limestone grinding has had some negative effects on the UV disinfection after the clear water tank. Lamps have been cleaned approximately once per month. No limestone particles have been observed in the water network.

The Kangasala water treatment plant added the same kind of limestone grinder system to one of their groundwater treatment units in 2008. However, they used it for only 3 years before changing to soda alkalisation. The main reason for this was negative feedback from industry and customers about increased limescale formation in heat exchangers and boilers. There were also problems with the first grinder axle, which broke after a short period of use owing to some factory defect or material fault. There were no problems with the second axle. Another reason was that when the pH of the water was raised to over 7.5, some turbidity could be seen in the treated water, so turbidity was the limiting factor for pH elevation.

DISCUSSION

By mechanical grinding of limestone, the space requirements, and thus the capital costs, of limestone alkalisation can be substantially decreased. Some of those savings are cancelled out by the machinery, storage space for limestone and maintenance requirements, but the savings on plant area are so great that they far exceed the additional costs of the grinding system. For example, in a water plant for 40,000 people with a planned flow of 220 L $person^{-1}$ day^{-1} and an EBCT of the limestone filter of 1.5 h, the volume of limestone needed in the filter would be 1,000 m^3, which means approx. 1,200 m^3 tank capacity as a whole. Incorporating a grinder into this kind of alkalisation plant would reduce the filter volume required to only 50 m^3 for the contact tank, plus the storage tank for limestone.

The use of fine limestone slurry, micronised $CaCO_3$, for water alkalisation has been studied previously by Gude *et al.* (2011). They found that it was impossible to dissolve the powered $CaCO_3$ products currently on the market completely in a contact tank with acceptable contact times (less than 30 min). Thus some $CaCO_3$ always remained in the suspension, which had a detrimental impact on the turbidity and sediment load in consumer water tanks and the distribution system. These negative impacts of small particles in the treated water have not been found at the Haukipudas plant. However, at Kangasala, problems with small particles were experienced when ground limestone was used for alkalisation and attempts were made to increase the pH to over 7.5, but not in other cases. Some impurity sediments have also accumulated in the contact tank at Haukipudas and it has been cleaned twice per year, but no negative effects have been reported in the consumption network. At Haukipudas, the groundwater quality, low pH and alkalinity and suitable amount of CO_2 further shorten the contact time. In addition, the lower targets as regards increases in pH and hardness add to the suitability of the grinding system at this plant.

When using a grinding system as opposed to a limestone filter, the Fe and Mn removal effect of the limestone filter is lost. In Finland, problems with Fe and Mn in groundwater are very common and such problems sometimes increase with long-term use of groundwater wells. However, when comparing the ground limestone alkalisation system with use of NaOH, it has the positive effect of raising the hardness of the water and poses no risk of very high pH due to overdosing. If necessary, the Fe and Mn can be removed in a sand filter after alkalisation.

CONCLUSIONS

For soft and corrosive waters, use of limestone is a very popular method of alkalisation. By using a slow rotating auger grinder for mechanical grinding of limestone, it is possible to obtain approximately 4,500-fold larger specific surface area of limestone particles and thereby much faster chemical reactions. The retention time for groundwater alkalisation using limestone can thereby be reduced substantially and the investment costs and space requirements can also be reduced. The retention time required in the water tank after the grinder depends on water quality, degree of grinding, water mixing and groundwater treatment targets.

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