IMPROVING THE PERFORMANCE OF GRANULAR ACTIVATED CARBON (GAC) VIA PRE-REGENERATION ACID TREATMENT

L. Perry, BSc, PhD*, D. Essex, BSc**, P. Giess, BSc, PhD***

N. Graham, BA, MA, MSc, DIC, PhD (Member)****, K. Kaur, BSc, PhD (Member)*

S. Lambert, BSc, PhD (member)*****and C. Spencer, BSc*****.

ABSTRACT

A lab-scale acid treatment system was developed to investigate the effects of hydrochloric acid on the removal of calcium from field spent GAC (FSGAC). The effects of acid treatment on the subsequent regeneration process and regenerated GAC properties were also investigated using a lab-scale furnace. A linear relationship between calcium remaining on the GAC following acid treatment and GAC mass losses during regeneration was exhibited. FSGAC treated with 0.1N hydrochloric acid resulted in 7.5% lower mass losses than non-acid treated GAC. An increase in total surface area of 7.2% and micropore volume of 3.1% was also noted following acid treatment and regeneration. This was due to a reduction in calcium-catalysed gasification of the GAC structure, which may have occurred in samples, which had not received acid treatment. Improvements in porosity, adsorption capacity and surface chemistry indicate that acid treatment is an effective process, which may be used to provide superior regenerated GAC product.

Key words: **Acid treatment; calcium catalysis; granular activated carbon (GAC); regeneration.**

*WatStech Ltd, The Technology Centre, Wolverhampton Science Park, Wolverhampton, WV10 9RU (formerly University of Wolverhampton) **Grafham Carbons, Foxyards Bean Road, Tipton, West Midlands, DY4 9AQ, UK.

***University of Wolverhampton, Wulfruna Street, Wolverhampton, WV1 1SB.

**** Department of Civil and Environmental Engineering, Imperial College, Exhibition Road, London, SW7 2BU.

*****Water Supply Group, Severn Trent Water Ltd, 2297 Coventry Road, Sheldon, Birmingham, B26 3PU.

INTRODUCTION

The introduction of increasingly stringent legislation such as Water Supply (Water Quality) Regulations, 1989, regarding the control of synthetic organic micro-pollutants has focused research on the development and optimisation of advanced water treatment technologies, such as granular activated carbon (GAC). GAC has long been recognised as a versatile and adsorbent [1,2] medium, due primarily to its highly porous structure and large surface area, as well as its favourable surface chemistry.

Thermal Regeneration

Thermal regeneration is considered to be (in the UK and Europe) the most cost-effective and environmentally sustainable option for the treatment of exhausted GAC[3]. However, this process is itself costly and, in order to achieve a

satisfactory regenerated product, it is important that the reactions, which occur during the process, are fully understood. The regeneration process involves several key stages. Firstly, excess moisture is removed from the GAC as steam, followed by the loss of highly volatile organic compounds at temperatures below 200°C and between 200-500°C, unstable or refractory adsorbates are volatilised. At temperatures between 500-700°C, non-volatile organics, such as humic acids, lignin and phenols are pyrolysed to form an amorphous char[3,4]. At temperatures exceeding 700°C the amorphous char residues that have been formed are then oxidised by the furnace gases (predominantly steam and CO_2). It is also under these conditions that damage to the GAC skeletal structure can occur. During the oxidation stages of regeneration some of the GAC skeletal structure can become gasified leading to micropore widening and GAC mass losses. Accordingly, virgin GAC (VGAC) is used to replace the GAC mass losses, which typically accounts for 20-40% of the total cost of the process[5].

Inorganic species (particularly calcium) accumulate in large quantities on the GAC surfaces due to their ubiquitous nature in raw waters[6,7]. Once adsorbed they may also catalyse the gasification process by facilitating the transfer of oxygen to the surface of the GAC [3,6].

When the oxidising furnace gases (predominantly CO_2) reach the micropores they chemisorb onto the calcium oxide (CaO) crystallites, which are formed from the decomposition of adsorbed calcium complexes, such as calcium carbonate during regeneration. The oxidant gas then diffuses via surface diffusion along the CaO surface to the CaO-carbon interface where it transfers to a free active site to form a C-O functional group. This functional group is then gasified to form CO, which diffuses out of the GAC grain[8].

Calcium is the predominant inorganic species found on field spent GAC. However, metals such as aluminium also accumulate on GAC during service and may undergo molecular changes during regeneration. As a result, aluminium for example has a greater tendency to leach from GAC when it is returned to service[9,10]. The dissolution of metal oxides and peroxides, from the newly regenerated GAC, can also lead to an elevated treated water pH. Therefore, in order that the treated water meets all quality standards, GAC often requires extensive conditioning prior to its return to service.

Pre-regeneration acid washing
Currently, some of the GAC regeneration companies utilise a post-regeneration acid quenching process. This process has the effect of demineralising and cooling the carbon before it returns to service, although it does not prevent damage being caused to the GAC during regeneration. Therefore, the aim of this research was to establish the effectiveness of acid treatment, prior to regeneration, to remove inorganic species from the GAC surfaces. The majority of previous similar investigations[3,6,11] have focused on GAC properties following regeneration. However, there is limited available literature regarding the dynamics of the acid treatment process itself or its impact on GAC properties prior to regeneration, during regeneration and on the subsequent conditioning processes.

METHODS AND MATERIALS
Sample selection and preparation
The field spent GAC (FSGAC) employed in this study was Chemviron Filtrasorb 400 (F400) supplied by Grafham Carbons Ltd. (Tipton, UK). The GAC had been in service for 27 months and had previously undergone two regenerations. It was decided that a 'field-spent' sample be used in this study rather than an artificially loaded virgin GAC since FSGAC would have undergone a natural process of calcium adsorption and thus more realistically represent the process which could be applied to a full-scale system. Virgin F400 GAC (VGAC) was also used for comparison with FSGAC. All GAC samples were dried at 105°C±5°C and sieved to 1-1.18mm prior to analysis, to obtain a homogenous sample.

Lab-scale acid treatment system
A lab-scale system was designed and manufactured to simulate a full-scale application. This system comprised of a 50mm internal diameter glass column (70cm in length) with a porous sintered glass disk at the lower end to support the GAC. Acid was pumped into the top of the column using a centrifugal pump and flow rates were monitored and adjusted using PTFE valves and a flow meter. The system could be operated in both forward rinse and backwash mode.

Prior to acid treatment, pre-weighed masses of FSGAC were soaked overnight in distilled water buffered to pH 7 using 1N potassium di-hydrogen phosphate (KH_2PO_4) and 1N sodium hydroxide (NaOH). Buffered water was used, as it was found that some inorganic leaching occurred when using distilled water only. The FSGAC was packed into the pilot column under buffered water to prevent air from becoming trapped in the GAC grains and within the GAC bed. The GAC samples were then backwashed with 30 litres of buffered water with flow rates adjusted to achieve a 30% bed expansion. This removed fines and loosely attached contamination that may have introduced experimental errors.

The acid type selected for this study was hydrochloric acid, diluted with distilled water to the concentration required for each specific experiment. Hydrochloric acid is typically used for post-acid quenching by a local regeneration company. In addition, other references have indicated that previous use of this acid assisted the removal of the inorganic load[3,6,11].

However, such work has not involved extensive or dynamic lab-scale trials using a controlled acid treatment system, as utilised in this work.

Flow rates used during all acid treatment experiments were controlled to achieve a 10-minute empty bed contact time (EBCT). This approach was used to provide a comparative evaluation of acid concentrations and treatment regimes. Other operational regimes may be more efficient for full-scale processes. However, such regimes were not practical on the lab-scale system due to the volumes of acid required.

Pilot-scale regeneration of GAC

Samples of FSGAC (acid treated and untreated) were regenerated using a Carbolite tilt and quench furnace as shown in Figure 1. This comprised of an electrically heated furnace with a four-stage adjustable temperature profile, controlled via a Eurotherm 91 programmer. The rotation of the ceramic furnace tube was fixed at approximately 12 revs/min. The feed rate of the GAC into the furnace was also controlled via the speed of the Archimedes screw feeder.
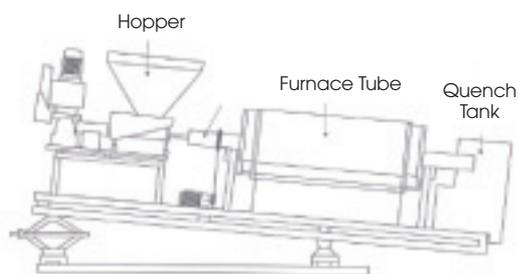

Figure. 1. *Pilot-scale regeneration furnace used in this study (Jackson et al., 1997).*

The furnace comprises of a quench tank, which can be filled manually with distilled water. A port at the rear allows for the internal furnace gases to be sampled and monitored. Nitrogen gas was purged into the lower end of the furnace tube (zone 4) at a rate of 12 l/min. Samples of GAC (approximately 250g) enter the furnace as slurry (GAC and buffered water). An oxidising environment was attained during the regeneration of FSGAC from steam (H_2O). Carbon dioxide (CO_2) was produced from volatilisation of organic species adsorbed onto the GAC. This process is similar to that which occurs in full-scale regeneration. GAC retention time in the tube was approximately 15 minutes.

Temperature settings across the four heated zones of the furnace tube were as follows; 450°C in zone 1, 600°C in zone 2, 750°C in zone 3 and 900°C in zone 4. GAC enters the furnace tube in zone 1 and the tube is tilted at a 2° angle from horizontal, so that GAC moves freely along the heated zones to the quench tank.

Thermogravimetric analysis (TGA)

TGA analysis provides data on the weight change of the GAC with increasing furnace temperatures in nitrogen gas. This instrument can utilise similar pyrolysis conditions to pilot-scale and full-scale furnaces. Samples of acid treated GAC were dried in an oven at 105°C±5°C overnight. Small quantities of sample (10-20mg) were then placed in a ceramic crucible on a microbalance and thermal analysis conducted using a Mettler TG50 TGA. The TGA instrument was programmed from a TC10A processor. Samples were heated in a stream of nitrogen gas (N_2) at a constant flow rate of 60ml/min. The temperature was increased to 900°C at a rate of 10°C/min. Changes in sample weight were logged during the experiment using associated software.

Inorganic analysis

Nitric acid (0.5mls of 70% w/w) was added to 5ml aliquots of acid waste solution (taken from the outlet of the lab-scale acid treatment system). These samples were refluxed for 30 minutes at 105°C. Samples were then diluted and analysed using a Unicam 929 atomic absorption spectrophotometer (AAS) in order to determine the concentration of inorganics such as calcium.

Acid treated GAC samples were dried overnight at 105°C±5°C. Subsequently 1g samples were weighed to the nearest 0.001g and placed into a pre-ignited and pre-weighed crucible before being ashed at 600°C for 12hr. The ash was re-weighed, added to 25ml of 70% nitric acid and mixed for 24hr. The digested ash was then diluted and the concentrations of calcium determined using AAS. Concentrations of aluminium, iron, magnesium and manganese within the samples were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Alkalinity and pH of the acid waste from the lab-scale system were measured periodically throughout the acid treatment trials. pH was measured using a Jenway laboratory pH meter. Alkalinity was determined using a HACH digital titrator and phenolphthalein titration (total carbonate and bicarbonate alkalinity).

Adsorption capacity and surface chemistry

The adsorption capacity of GAC can be determined by aqueous adsorption batch tests using, for example, iodine and methylene blue. The surface chemistry of GAC can also be assessed by titration of the surface functional groups (SFGs).

Iodine adsorption capacity

Determination of iodine adsorption onto GAC is a method used extensively in the carbon industry. Iodine is a molecule similar in molecular radii to organic micropollutants, such as

pesticides found in raw waters. As iodine is cheaper and safer to use than such pesticides and more easily analysed, it was used as a surrogate. The amount of iodine adsorbed as mg per gram of carbon is expressed as the iodine number (ASTM method D4607-94) [12].

Methylene blue adsorption capacity

This method is also used extensively in the carbon industry. Methylene blue is a larger molecule than iodine and might conveniently be used as a surrogate for natural organic matter (NOM) adsorption. A calibration graph plotting pre-determined methylene blue concentrations against visible absorbance (at 650nm) was used to calculate the methylene blue concentration remaining in solution.

Surface chemistry

The adsorption capacity of GAC is also affected by the concentration of surface functional groups (SFGs) present on the GAC surface. Oxygen containing SFGs are produced from the chemisorption of oxygen during GAC manufacture or regeneration. The type and concentration of these functional groups on regenerated GAC samples was determined via an acid base titration developed by Boehm[13].

Porosity development

Gas phase adsorption isotherms are often used to evaluate GAC porosity and surface area. An adsorption model, proposed by Brunaur, Emmet and Teller (BET) is the most commonly used mode for evaluating GAC[14]. In this study nitrogen gas was adsorbed at 77K using an Omnisorp SA3100 nitrogen gas analyser. The BET model was then applied to evaluate the nitrogen monolayer capacity of the GAC, i.e. the volume of gas required to cover the surface of the GAC with a monolayer of nitrogen gas at standard temperature and pressure (STP). As the molecular diameter of nitrogen is known, it is theoretically possible to calculate the surface area of the GAC [14]. The adsorption isotherm produced is plotted according to the BET equation[14]. Samples of dried GAC were analysed and surface areas and micropore volumes determined using this method.

RESULTS AND DISCUSSION

Samples of FSGAC and VGAC were evaluated prior to acid treatment to assess certain quality parameters. These included porosity, adsorption capacity and inorganic content. Table 1 shows a comparison between the FSGAC sample used and a sample of VGAC.

It can be seen that adsorption capacity (determined by iodine and methylene blue adsorption) and surface area (total and micropore) are lower for the FSGAC sample, as a result of the accumulation of organic and inorganic contaminants. The higher ash content of FSGAC sample is indicative of inorganic contamination. Of the inorganic species adsorbed onto FSGAC, calcium was found to have the greatest concentration. Thermal regeneration is required to recover adsorption capacity and surface area of FSGAC.

Effect of acid treatment on removal of calcium from FSGAC

Samples of FSGAC were treated with 20 bed volumes of 0.05N hydrochloric acid. Bed volumes are measured as volume of acid / volume of GAC (measured as the volume occupied by the GAC in a packed pilot column). Samples of the acid waste were taken from the outlet of the system periodically throughout the trial and calcium concentrations determined using atomic absorption spectroscopy (AAS). Figure 2 illustrates the effect of acid on the pH and alkalinity of the acid waste.

At the onset of acid treatment, the system waste had a near neutral pH. However, during acid treatment a significant
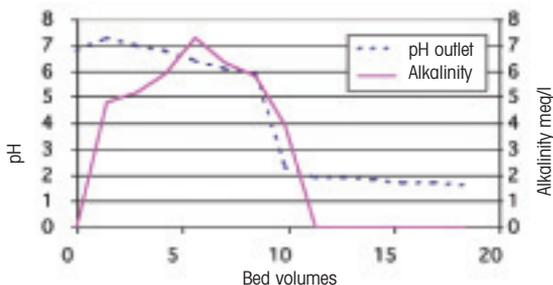

Figure. 2. Effect of acid treatment on pH and alkalinity of acid waste

Table 1 – Comparison of VGAC and FSGAC properties

Sample	Iodine No. (mg/g)	Methylene Blue No. (mg/g)	B.E.T Surface Area (m²/g)	Micropore Surface Area (m²/g)	Micropore Volume (ml/g)	% Ash	Calcium (mg/g)
VGAC	1050	260	1076	900	0.363	8.19	0.99
FSGAC	451	206	637	365	0.132	16.07	32.03

decrease in the pH of the acid waste was observed. This was coupled with a decrease in alkalinity at approximately the same bed volumes of treatment. This was attributed to the reaction and removal of carbonate anions adsorbed onto the GAC. As carbonates are increasingly removed, the pH within the column decreases. Upon removal of carbonates, carbon dioxide gas (CO_2) is evolved as evidenced by gas pockets within the GAC bed and outlet pipe. The evolution of CO_2 on a full-scale process may have several operational implications. For example, in an upflow mode, GAC particles may have a tendency to float. Legislation regarding the release of gases to the atmosphere may also require some consideration.

The effect of acid concentration on the removal of calcium from FSGAC is demonstrated in Figure 3.
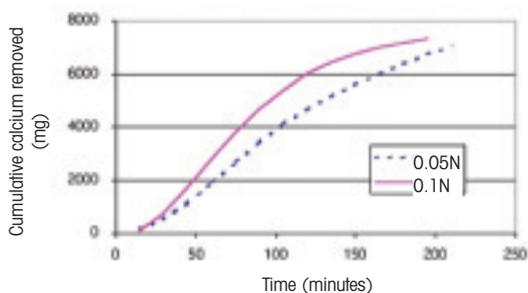

Figure. 3. Effect of acid concentration on the removal of calcium from FSGAC

Results in Figure 3 show that calcium removal in the first 200 minutes of the trial is similar; however, increasing acid concentration increases the rate of calcium removal. The rate of acid diffusion, and thus calcium removal, may be dependent on the concentration gradient of acid surrounding the FSGAC grain. In order that calcium is removed from FSGAC, acid must first diffuse from the bulk solution to the surface of the GAC grain and then into the GAC pores. Diffusion of acid will be from a high concentration, surrounding the GAC grain, to a low concentration within the GAC grain. It is probable that calcium will diffuse in the opposite direction from high concentrations, inside the GAC pores, to a lower concentration in the solution surrounding the GAC grain. The reactions, which take place at the surface of the GAC are believed to involve the reaction of H^+ ions with either carbonate anions or calcium ions.

The effect of flow was also investigated. Figure 4 illustrates the impact of increased acid velocity on calcium removal with 0.1N hydrochloric acid.

It can be seen that, in the initial 7-7.5 bed volumes, calcium removal curves are similar. However, the removal appears to increase at 8 bed volumes with a higher flow rate. As calcium in solution is transported out of the media bed (i.e. away from
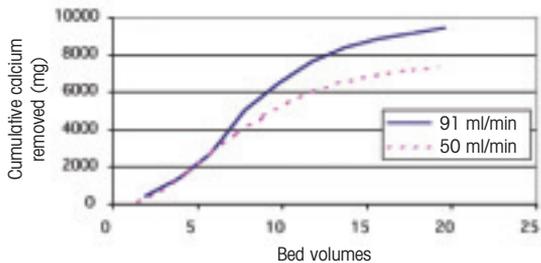

Figure. 4. Effect of acid flow on the cumulative removal of calcium from FSGAC

the GAC grains) fresh acid entering the bed re-establishes the concentration gradient. Therefore, it can be suggested that increasing the flow through the system will increase the rate at which bulk diffusion proceeds.

Figure 5 illustrates that there may be a relationship between acid concentration and calcium remaining on the FSGAC following treatment whereby increasing acid concentration generally resulted in GAC with reduced calcium concentrations.
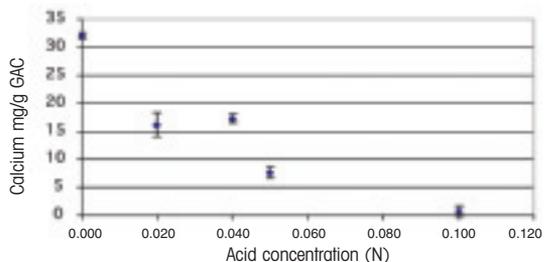

Figure. 5. Impact of hydrochloric acid concentration on calcium remaining on FSGAC

Effect of calcium removal on GAC regeneration

FSGAC samples treated with hydrochloric acid at various concentrations were regenerated using the pilot-scale furnace. This furnace was commissioned to mimic full-scale regeneration. The gases produced within this furnace allowed for catalytic oxidation and subsequent gasification of the
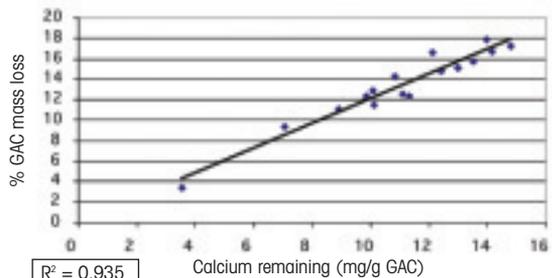

Figure. 6. Relationship between calcium concentration and % mass losses

GAC to occur as it would during full-scale regeneration. Figure 6 illustrates the relationship between calcium concentration remaining on the acid treated FSGAC samples and GAC mass losses, which occurred as a result of regeneration.

Whereas other studies have stressed the importance of calcium distribution over absolute concentrations, in this study a strong linear relationship between calcium concentration and % GAC mass losses during regeneration was found. In agreement with the literature [3,6,8,9,11,16,17], calcium appears to act as a catalyst for the gasification of the GAC skeletal structure during regeneration. Treatment of FSGAC with 0.1N hydrochloric acid reduced mass losses by 7.5%, compared to field spent GAC, which has not received acid treatment.

Calcium carbonate adsorbed on GAC decomposes to calcium oxide rapidly above 700°C in an inert environment and is displaced to slightly higher temperatures in an oxidising environment[7,9,14]. This decomposition results in the evolution of carbon monoxide (CO). During TGA trials, a notable reduction in sample mass loss (attributed to CO evolution) was observed at approximately 700°C, with all acid treated samples compared to untreated samples. When steam is used as an oxidant in regeneration, it can react with CO (via the water-gas shift reaction) to produce CO_2, which can contribute to gasification. It is also well documented that metal carbonates are the most catalytic of the inorganic anions adsorbed onto FSGAC. Therefore, the removal of carbonate anions as well as calcium during acid treatment was found to improve regeneration of FSGAC via reduction of gasification.

Impact of acid treatment on regenerated GAC quality

As discussed previously, the properties of the GAC and its inorganic composition prior to regeneration will influence the quality of the regenerated GAC product. Results for the carbon properties following regeneration are presented in Table 2.

Table 2 – Differences in regenerated GAC properties for acid treated and untreated FSGAC

Regenerated GAC sample	Calcium loading on GAC (mg/g)	Total surface area (m2/g)	Micropore volume (ml/g)	Iodine adsorption capacity (mg/g)	Methylene blue adsorption capacity (mg/g)
VGAC	0.99	1076	0.363	1050	260
No acid treatment	32.03	762.2	0.157	710	214
Hydrochloric acid treatment (0.1N)	0.802	821.7	0.162	740	233

It can be seen from Table 2 that hydrochloric acid treatment, followed by regeneration, has resulted in an increase in total surface area and micropore volume of GAC by 7.2% and 3.1% respectively. Better adsorption capacities were also observed. Adsorption capacity is perhaps one of the most important indications of GAC quality following regeneration, as the majority of target micropollutants adsorb in the narrower micropores. Maintaining micropore volume, and particularly micropore adsorption capacity, is therefore crucial to GAC performance.

In this study it was found that there was a direct relationship between calcium concentration of GAC and iodine adsorption following regeneration. The results presented in Figure 7 are taken from acid treated FSGAC samples following regeneration.

R² = 0.8113
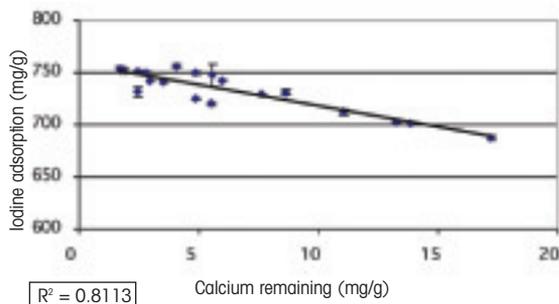
Figure. 7. *Relationship between calcium remaining on FSGAC and iodine adsorption following regeneration.*

Figure 7 highlights an inversely linear relationship between calcium concentration and iodine adsorption. This would suggest that the removal of calcium via pre-regeneration acid treatment will retain and possibly improve micropore adsorption capacity.

Another important GAC quality indicator is surface chemistry. The presence of surface functional groups (SFGs) can influence the adsorption characteristics of the GAC[16]. The presence of carboxylic functional groups, in particular, are believed to reduce the adsorption capacity of the GAC, particularly for natural organic matter (NOM)[17]. It was found that the concentration of carboxylic groups on regenerated GAC was reduced via pre-regeneration acid treatment. This can be seen in Figure 8.
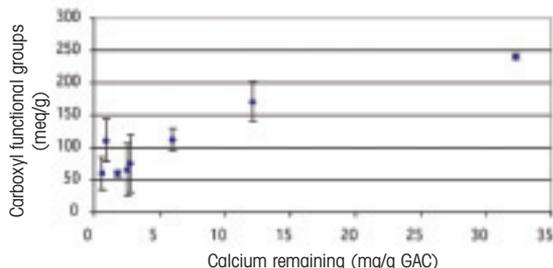
Figure. 8. *Relationship between calcium remaining on FSGAC following acid treatment and concentration of carboxylic functional groups following regeneration.*

Impact of acid treatment and regeneration on conditioning prior to returning the GAC to service

Leaching of metals such as aluminium from newly regenerated GAC is a common problem for water treatment companies. The results presented in Table 3, illustrate that acid treatment reduced aluminium contamination of FSGAC prior to regeneration and that this resulted in a decrease in aluminium leaching from the regenerated GAC almost to virgin GAC levels.

Table 3 – Effect of acid treatment on leachable aluminium following regeneration

Treatment received	Aluminium leached (mg/g GAC)
FSGAC regeneration only	0.055
VGAC no regeneration	0.028
FSGAC 0.1N Hydrochloric acid and regeneration	0.029

Another common problem encountered with newly regenerated GAC is an elevated pH of the treated water. This is overcome, in some cases, by extensive conditioning prior to returning the GAC to service. In order to assess the impact of acid treatment and regeneration on the return to service conditioning process, the lab-scale system was operated in backwash mode. Samples of acid treated, regenerated GAC, were backwashed with 20 bed volumes of buffered distilled water and outlet pH was monitored. Preliminary results showed that pH of the treated water was lower than would be expected for newly regenerated GACs, which had not received acid treatment.

CONCLUSIONS

1. This study has shown that hydrochloric acid treatment is an effective option for the removal of inorganic species such as Ca^{2+} and CO_3^- from FSGAC.
2. Removal of calcium resulted in lower GAC mass losses during regeneration and an improved regenerated GAC product, in terms of surface area, micropore volume, surface functional groups and adsorption capacity.
3. Increasing acid concentration and acid flow rate resulted in higher calcium percentage removal and rates. This would have benefits for full-scale operation in terms of process time and costs.
4. The originality of this work has been in the development of a lab-scale acid treatment system. This has provided data regarding the dynamics of the acid treatment process using different acid concentrations and treatment regimes. This system has also allowed for the assessment of conditioning protocols for the GACs following regeneration.
5. It is hoped that the findings of this study may contribute to the development and optimisation of a full-scale regeneration treatment process and also benefit the water companies who would utilise the GAC produced.

REFERENCES

1. LI, P.H., BRUCE, R.L., HOBDAY, M.D. A pseudo first order rate model for the adsorption of an organic adsorbate in aqueous solution, *Journal of Chemical Technology and Biotechnology*, 1999, **74,** 55.
2. PELEKANI, C., AND SNOEYINK, V.L. Competitive adsorption in natural water: Role of activated pore size, *Water Resources*, 1999, **33**, (5), 1209.
3. CANNON, F.S., SNOEYINK, V.L., LEE, R.G., DAGOISE, G., DEWOLFE, J.R. Effect of Calcium on field spent GAC's Pore Development during regeneration, *Journal of the American Water Works Association*, 1993, **85**, (3), 76.
4. SUZUKI, M., MISIC, D.M., KOYOAMA, O., KAWAZOE, K. Study of thermal regeneration of spent activated carbons: Thermogravimetric measurement of various single component organics loaded on activated carbons, *Chemical Engineering Science*, 1978, **33**, (3), 271.
5. ADAMS, J.Q. & CLARKE, R.M. Cost estimates for GAC treatment systems, *Journal of American Water Works Association*, 1989, **81**, (1), 35.
6. SEBASTIANI, E.G., SNOEYINK, V.L., ANGELOTTI, R.W. Thermal regeneration of spent and acid-washed GAC from the upper Occoquan Sewage Authority, *Water and Environment Research*, 1994, **63**, (9), 199.
7. SAN MIGUEL, G., LAMBERT, S.D., GRAHAM, N.J.D. The Regeneration of Field-Spent Granular Activated Carbons. *Water Resources*, 2001, **35**, (11), 2740.
8. CANNON, F.S., SNOEYINK, V.L., LEE, R.G., DAGOIS G., , Reaction Mechanism of Calcium Catalysed Thermal Regeneration of Spent Granular Activated Carbon, *Carbon*, 1994, **32**, (7), 1285.
9. LAMBERT, S.D., SAN MIGUEL, G., GRAHAM, N.J.D., , Deleterious Effects of Inorganic Compounds during Thermal

Regeneration of GAC -A Review, *Journal of American Water Works Association (AWWA)*, 2002, **94,** (12), 109.

10. JACKSON, P.J., CRANE, R.I., NORRIS, M.W. Influence of regenerated GAC on Drinking water quality, Report No. PT2034, *Water Research Centre.* 1997.

11. PILARD, M., DAGOIS, G., CHESNEAU, M., LEVY, P.J., , Impact of mineral elements on the regeneration process of activated carbon used in potable water treatment, *Water Supply*, 1995, **13,** (3), 1.

12. ASTM *Annual Book of ASTM methods*, *Refractories; Carbon and Graphite products; Activated carbon; Advanced Ceramics*, Vol 15, American Technical Publishers Ltd. 1999

13. BOEHM, H.P. Chemical identification of surface groups, in Eley, D.D., Pines, H. and Weisz, P.B., (Eds), Academic Press, New York, *Advances in Catalysis*, chpt. 16, p.179. 1966.

14. GREGG, S. J., AND SING, K.S.W. *Adsorption Surface Area and Porosity*, 2nd Ed., Academic Press: London. 1982.

15. PERRY, L.G. Acid washing of granular activated carbon (GAC) and its impact on drinking water quality. PhD Thesis, University of Wolverhampton, UK. 2003.

16. CAZORLA-AMOROS, D., LINARES-SOLANO, A., SALINAS-MARTINEZ DE LECEA, C., , Assessment of the CO2- Carbon gasification catalysed by calcium. A transient isotopic study, *Carbon*, 1994, **32,** (3), 423.

17. MCKEE, D. Catalytic Effect of Alkaline Earth Carbonates in the Carbon-Carbon Dioxide Reactions, *Fuel*, 1980, **59**, 308

18. KARANFIL, T., KITIS, M., KILDUDD, J.E., WIGTON, A., , Role of Granular Activated Carbon Surface Chemistry on the Adsorption of Organic Compounds 2. Natural Organic Matter, *Environmental Science and Technology*, 1999, **33,** 3225.