Overcoming Calcium Catalysis During the Thermal Reactivation of Granular Activated Carbon (GAC)

D.W. Mazyck and F.S. Cannon
The Pennsylvania State University
212 Sackett Building,
University Park, PA 16803, USA

Introduction

During conventional thermal reactivation, calcium catalysis broadens the small micropores into larger micropores and large micropores into mesopores [1]. The micropores, which constitute about 90 % of the total surface area, are believed to be the most important for removing small organics. Tailored thermal reactivations overcame calcium catalysis by first steam curing spent GAC at 648 K for 60 minutes, before pyrolyzing it in nitrogen under temperatures that ramped up to 1123 K. Pore volume distribution measurements using the density functional theory (DFT) software package revealed that this strategy increased the pore volume between 5.4 and 32 Å when compared to its virgin counterpart, or when compared to spent GACs that were pyrolyzed and oxidized. The steam curing/pyrolysis approach also achieved the same micropore volume as its virgin counterpart, and also more pores between 5.4 to 100 Å in width. The 5.4 to 100 Å pore range represents an important span for removing the full size distribution of organics that enter a GAC bed during potable water treatment.

Experimental

The GAC sample originated from the Hays Mine water treatment plant in Pittsburgh, PA. At the time of sampling it had been in service for three years and it contained 1.8 % calcium. Reactivation experiments conducted in a fluidized bed compared two approaches to thermal treatment: the first employed pyrolysis at 1123 K for 10 minutes and oxidation in steam and CO_2 at 1123 K for 7.75 minutes. The second employed an alternative strategy comprised of steam curing at a moderate temperature (648 K) followed by ramped-up temperature while flowing in N_2 to 1123 K. Pore structures were determined using a Micromeritics ASAP 2000.

Results and Discussion

The mass loss, volume loss and final apparent densities following these reactivations are compared in Table 1. When steam curing plus ramped pyrolysis was employed, the mass loss and volume loss data suggests that there was less gasification of the original skeletal GAC than for the pyrolyzed-oxidized GAC. Indeed, the mass loss for the steam curing plus ramped pyrolysis sample was the same as for the acid leached sample. (Acid-leaching prior to reactivation eliminates most of the calcium and therefore the adverse effects of calcium catalysis would not exist.) Another intriguing result of the steam-curing plus ramped-temperature pyrolysis approach is that it resulted in quite low volume losses (2.3 %), and these were lower than for pyrolyzed-oxidized of the spent (7.4 %) or acid-leached (5.2 %) GACs. This would be a favorable outcome if this approach were to be applied in full-scale operation, and it indicates that this steam-curing plus pyrolysis process caused a higher fraction of the mass loss to occur via gasification within the GAC pores.

When the pyrolyzed-oxidized reactivation is compared to the steam curing strategy, it is clear that the steam curing strategy restores more micropores, as seen in Figure 1. The pyrolyzed-oxidized reactivation drastically lost pore volume in the less than 12 Å width, while the pore volume between 20 and 300 Å gained substantially. This is characteristic of calcium catalysis. The steam curing strategy did not exhibit the same catalytic destruction of micropores.

Comparing the acid leached pyrolyzed-oxidized reactivation to the steam cured plus ramped pyrolysis shows that these two treatments have the same pore volume up to 5.4 Å and they have nearly the same distributions up to 20 Å (Figure 2). This likewise suggests that the steam curing process overcame calcium catalysis. If one compares virgin Hays Mine to steam cured plus ramped pyrolysis, the steam cured has more pores between 5.4 and 30 Å and this pore range is probably the most important for removing all but the very smallest molecules. The virgin GAC has more pore volume in the less than 5.4 Å pore width. However, few if any organic compounds could fit in the less than 5.4 Å pore width. More reactivation and pore characterization data will be included in the presentation

References

1. Cannon FS, Snoeyink VL, Lee RG, Dagois G, DeWolfe JR. Effect of calcium in field-spent GACs on pore development during regeneration. J.AWWA 1993; 85(3): 76-89.

Table 1. Comparison of Mass Loss, Volume Loss and Apparent Density (AD)

	Mass Loss (%)	Volume Loss (%)	A.D. (g/mL)
Pyrolyzed-Oxidized Reactivation	33.4	7.4	0.414
Steam Cured + Ramped Pyrolysis	16.3	2.3	0.496
Acid Leached Pyrolyzed-Oxidized Reactivation	16.1	5.2	0.483
Virgin	-	-	0.503
Spent	-	-	0.570

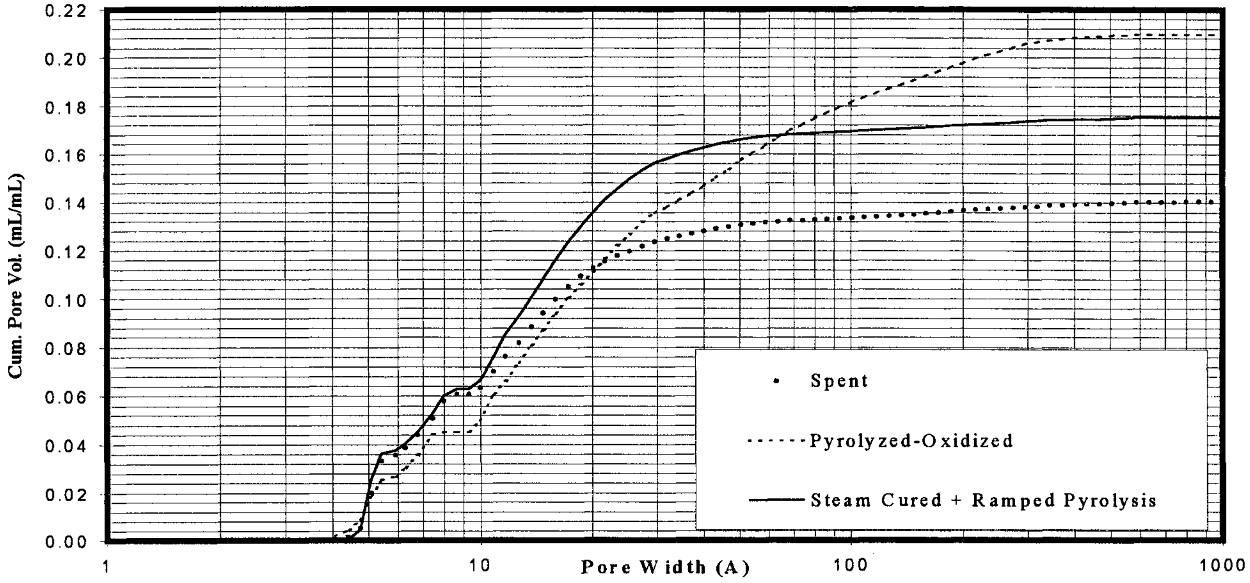

Figure 1. Pore Volume Distribution hat has Experienced Pyrolyzed-Oxidized Reactivation vs. Steam/Pyrolysis

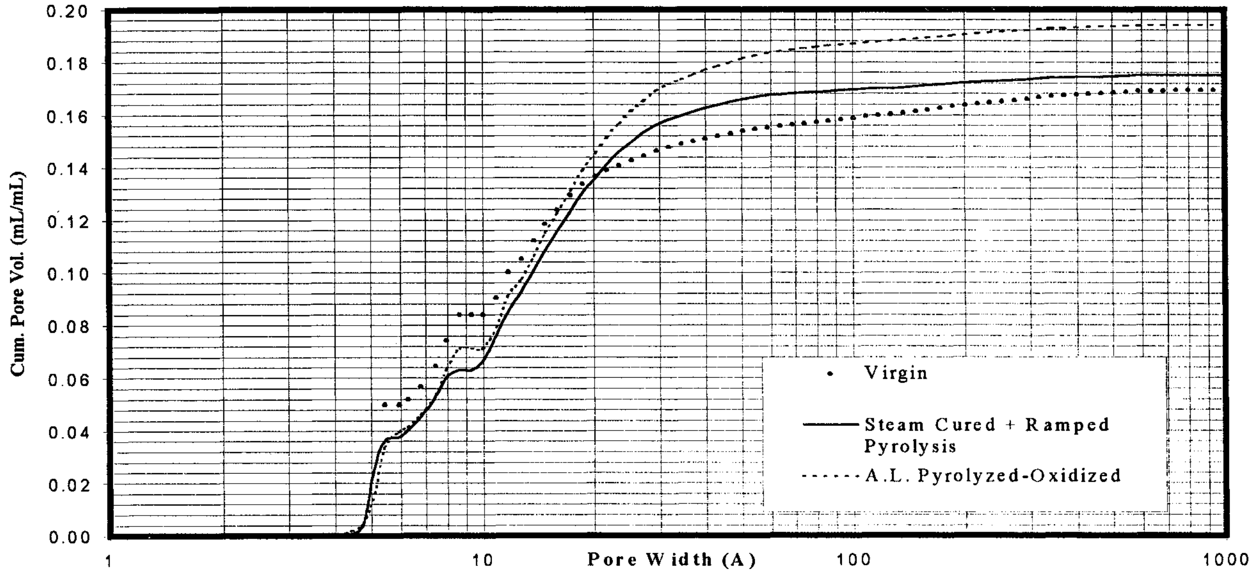

Figure 2. Pore Volume Distribution that has Experienced Steam/ Pyrolysis vs. Acid Leached Pyrolyzed-Oxidized