

CHARACTERIZATION AND RESTORATION OF PERFORMANCE OF "AGED"  
RADIOIODINE REMOVING ACTIVATED CARBONS

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Abstract

The degradation of radioiodine removal performance for impregnated activated carbons because of ageing is well established. However, the causes for this degradation remain unclear. One theory is that this reduction in performance from the ageing process results from an oxidation of the surface of the carbon. Radioiodine removing activated carbons that failed radioiodine removal tests showed an oxidized surface that had become hydrophilic compared with new carbons. We attempted to restore the performance of these "failed" carbons with a combination of thermal and chemical treatment. The results of these investigations are presented and discussed with the view of extending the life of radioiodine removing activated carbons.

Introduction

Experience has shown that the performance of activated carbons for radioiodine removal decreases with time by a process known as ageing. This ageing process can occur in storage and has led to the recommended shelf life of five years currently accepted in the U.S. after which the carbon should be retested for radioiodine removal. Carbons that do not meet the retesting requirements and thus cannot be used though "new" have become known as "spinster" carbons. It is generally believed that these "spinster" carbons fail after prolonged storage due to a change in the surface oxides present on the carbon. NUCON<sup>®</sup> and others<sup>1,2</sup> have used a combination of thermal and chemical treatments to restore the performance of these "failed" carbons. The results of these investigations are presented and discussed.

Methodology

Except where noted, ASTM D3803-89<sup>3</sup> was used to determine the methyl iodide removal efficiency at 30°C and 95% relative humidity. Heat treatments were performed using a rotary kiln. Carbon impregnations were performed using the incipient wetness technique.

Presentation of Results

Results of tests performed in the NUCON<sup>®</sup> laboratory are shown in Table 1 for treatment of "spinster" carbon. Shown in Table 2 are results of treatments of a spent carbon from a German plant<sup>2</sup>.

Discussion of Results

The German test results in Table 2 show the methyl iodide removal efficiencies after different types of treatment techniques performed on a spent ( i.e., a carbon that has seen service) carbon sample. These treatments included; desorption with steam at 130 °C, with nitrogen at 200, 300 and 450 °C and with carbon dioxide at 180 °C; extraction with hexane and heptane at 25 °C and extraction with supercritical carbon dioxide at 40 and 60 °C; and desorption with nitrogen at 450 °C followed by potassium iodide impregnation. Although their radioiodine test method differs from the ASTM method, the success of their thermal treatment using N<sub>2</sub> at 450°C with or without a following impregnation, prompted similar treatments in our laboratory on “spinster” carbon samples.

The results of these tests with “spinster carbons”, shown in Table 1, indicate that desorption at 850°C with nitrogen followed by impregnation with TEDA restores the carbon to a greater than 99% efficiency. This is NUCON<sup>®</sup>'s lower limit for an acceptable test result using ASTM D3803-89. Hydrazine treatment of spent carbons has also been suggested as a treatment to restore the performance of aged carbons<sup>1</sup>. However, as shown in Table 1, hydrazine gave no improvement over TEDA impregnation.

This high temperature treatment with N<sub>2</sub> has been shown to drive surface oxides off the carbon<sup>4</sup> and, following impregnation, restores the carbon to “new” carbon performance. This treatment method may be a cost-effective way to restore the performance of “spinster carbons” especially when compared with new carbon replacement costs.

References

1. Deitz, V. R., “ Charcoal Performance Under Accident Conditions in Light- Water Reactors”, NUREG/CR-3990, NRL Memo Rpt 5528 (March 1985)
2. Lasch, M., et al, “ Exhaustion of activated carbon for iodine retention in nuclear power plants”, *VGB Krartwerkstech*, 1994, 74(11) 988-90
3. ASTM D3803-89, “Standard Test Method for Nuclear-GRade Activated Carbon”, *Annual Book of ASTM Sandards*, Vol 15.01
4. Boehm, H. P., “Chemical Identification of Surface Groups”, *Institute of Inorganic Chemistry, University of Heidelberg, Germany*

<b>TABLE 1</b> <b>Methyl Iodide Removal Efficiency After Treatment of "Spinster" Carbon</b>		
Sample ID	Treatment	Methyl Iodide Removal Efficiency, %
4501	As Is	90.7
4501	N <sub>2</sub> , 450 °C, KI+TEDA	98.0
4501	N <sub>2</sub> , 700 °C, KI+TEDA	98.4
4501	N <sub>2</sub> , 800 °C, KI+TEDA	98.6
4501	N <sub>2</sub> , 850 °C, TEDA	99.3
I122	TEDA	97.1
I416	Hydrazine, TEDA	97.0

Radioiodine Test Conditions: ASTM D3803-89, 30 °C, 95% Relative Humidity

**TABLE 2**  
**German Studies of Depleted Carbon for Iodine Retention**

Sample #	Treatment	Methyl Iodide Removal Efficiency, %
1	Steam, 130 °C	98.86
2	N <sub>2</sub> , 200 °C	99.27
3	CO <sub>2</sub> , 180 °C	98.86
4	Supercritical CO <sub>2</sub> , 40 °C	99.97
5	Supercritical CO <sub>2</sub> , 60 °C	99.87
6	n-Hexane, 25 °C	99.83
7	n-Heptane, 25 °C	99.90
8	N <sub>2</sub> , 300 °C	99.978
9	N <sub>2</sub> , 450 °C	99.999
10	N <sub>2</sub> , 450 °C, KI	99.999+

Radioiodine Test Conditions: 30 °C, 0.42 m/s, 1.2 sec. Residence Time

DISCUSSION

**RICKETTS:** I wonder if you could comment about how long these regeneration processes take and whether there are any significant differences between the various processes as far as costs go?

**KOVACH, L:** Yes, certainly there are differences. I do not know how familiar everybody is with how activated carbon is made. You process activated carbon at high temperature and at best the residence time may be from 1-3 hours in rotary furnaces but you may also be dealing with 10 - 24 hours residence time at these temperatures for some products. In the case discussed in the paper residence times are much shorter, a half-hour at temperature for the nitrogen treatment. If we are looking at supercritical extraction with carbon dioxide it becomes more complicated because there has been a significantly more strict controlled pressure boundary on the system than just a straight rotary furnace with an inert gas. Organic extractions are again more expensive because you have to recover the organic from the material and then you have to dry it again. So the lowest cost products are still made by nitrogen treatment. I would say by almost an order of magnitude lower cost than any of the other ones. Temperature is nothing other than an energy cost, it is really not significant. It is just as easy to run at 850°C as at 450°C, the residence times would be the same for all cases. In the US, straight impregnation cost is probably somewhere in the neighborhood of \$0.50/lb for labor and material but excluding the cost of carbon used. The nitrogen treatment is the one that looks most promising, both from a cost and a benefit standpoint.

**RICKETTS:** Are you passing nitrogen through the carbon during the regeneration process?

**KOVACH, L:** It is not directly passed through, although we are currently doing some tests where we are passing it through the carbon. In a rotary furnace you are dealing with partial exposure, i.e., carbon is scattered up on the walls and it falls back so there is exposure partly to the nitrogen stream. But it is not continuous, so it is not like a fixed bed with hot nitrogen going through it, it is a rotating bed and it falls back in the tube while it is exposed to nitrogen.