

Looking back on 45 years in nuclear air cleaning activity.

J. Louis Kovach

Nucon International Inc. Columbus OH USA

I. Introduction

When one is asked to be a key-note speaker at a conference which he attended in the past many times, it generally means that he is expected to depart and leave the field to the younger generation. Well, it is time for me to do that, but not before I gather up some thoughts and pass them on to you. Perhaps, all of you can learn from my experiences or from my perception of them and do much better work than I did, at least by avoiding my mistakes.

The problems of nuclear air cleaning, while not overcomplicated, were rather tortuous during my activity in the field, and so mostly due to fragmented product and not process driven research studies and often because of misleading regulatory emphasis established too early and on questionable preliminary data. I will discuss a few examples not necessarily in order of importance but more as a demonstration of scope. I am sure, there are many who will disagree with me on their significance. The examples represent only my personal opinions and recollections and are by no means official NUCON opinions!

II. Source Term and Adsorbent Fires

One of the early nuclear air cleaning problems I was asked to work on related to the ignition temperature of activated carbon for the SRP air cleaning systems.(1) The study established the impacts of air velocity, particle size, ash content, ash constituent, gas composition etc. The background reason for studies was the AEC fear that the activated carbon adsorbers would catch on fire from the adsorbed radioiodine released in case of an accident. The fear originated from the Windscale graphite fire. There was no technical evaluation of the dissimilarity between the two events and the amount of iodine that could be loaded on the carbon adsorbent. However, it was found that the carbon adsorber beds once ignited, (by a gas torch) could not be extinguished by water deluge or even by liquid nitrogen deluge as long as the air flow was maintained.

The evaluation of the carbons showed that the best radioiodine retention is obtained, even at elevated temperatures, by carbon types that have high alkalinity, however those same carbons have the lowest ignition temperatures, while carbons that have low alkalinity or are acid treated do not hold radioiodine but have elevated ignition temperatures. Thus, a compromise is required for carbon selection for optimum application, from a radioiodine retentivity standpoint. Many of the tested carbon properties were not clear to even to the principal investigators, because carbons were identified only by manufacturer's grade

numbers and very few investigators were aware of the additional important properties of the tested carbons.

However, all of the carbons, even those with high radioiodine retentivity are incapable of holding onto sufficient radioiodine in flowing airstreams to reach their ignition temperatures. Thus, as the decay heat of the adsorbed radioiodine heats the carbon, the carbon's iodine retentivity will decrease at some temperature significantly below its ignition temperature.

While, neither water nor liquid nitrogen deluge was capable in extinguishing artificially ignited carbon beds the "regulatory" and the subsequently the insurance approach both required installation of water deluge systems which resulted in significant economic damage and potential non-availability of safety related equipment. At the same time, simple shut down of air flow, isolation of the carbon bed containing housing, which results in the consumption of the available oxygen and extinguishment of the fire still escapes the attention of those selecting fire extinguishing methods.

Furthermore, it is important to understand that long before the carbon ignites, surface oxides that exist on the carbon surface will start to decompose at a faster rate than they are forming and the condition leading to eventual fire can be detected and the actual fire be prevented by monitoring carbon monoxide downstream of carbon beds. This is well demonstrated on Figure 1, where data is shown developed for the Seabrook justification to omit water deluge from the air cleaning systems. Of course, in deep carbon beds, the carbon has to be cooled before any air flow is resumed through the carbon bed.

Naturally, the quantity of iodine released in an accident also affects its chemical form. This fact is not clear for the official NRC source term. In the primary system the radioiodine is present in elemental form, however, in the location of the release the potential conversion will be dependent on the presence of the organic material capable of forming organic iodides and its partitioning into the gas phase. The investigators who work on the iodine partitioning have disappeared from the air cleaning conferences in the past 20 years and have their own international meetings under the aegis of the NEA - CSNI. I have not seen input from their meetings being considered by this group since their departure. The front end of the iodine behavior knowledge slipped away from the "air cleaning" activity group, without being noticed by those who are presumable working on the design of the hardware to ameliorate the problem caused by that same source term.

In my opinion, for many reasons, both in operating and in post accident mode, outside the containment, the challenge to the air cleaning systems will be primarily organic iodides, and the main reason for the operation of the air cleaning systems will be to provide satisfactory environmental conditions for the operating and recovery personnel. Iodine loadings would never reach conditions would which could result in any elevated temperatures. The last event needed in those circumstances would be "accidental" initiation of water deluge systems.

It is time to resolve this make believe “ignition” issue once and for all.

II. Adsorption-Chemical Reaction-Isotope Exchange

Adsorption capacity in all cases increases with increasing concentration, no exceptions. However, this does not mean that adsorptive or isotope exchange based removal efficiency is decreasing with decreasing inlet adsorbate concentration, one should not mix-up adsorption equilibrium with dynamic adsorption, the latter being influenced by all of the typical packed bed mass transfer gas phase contact process steps. Furthermore, the pure physical adsorption rules are no longer valid, if either chemical reactions or isotope exchange steps take place in addition to physical adsorption on the surface.

Even in case of typical amine impregnated carbons, the primary iodine decontamination is by isotope exchange because there is a very significant excess of stable iodine in the ambient air stream, and even in the uranium decay product, thus the I-131 is always greatly overwhelmed by stable iodine and the impregnate amine is first converted to a stable amine/iodide complex which subsequently exchanges with the influent I-131.

Isotope exchange, being a form of chemical reaction, is always improved by temperature increase (as long as the impregnant is retained on the adsorbent surface) thus; organic iodide decontamination efficiency is improved with increasing temperature. The current radioiodine decontamination beds are not designed based on proper adsorption technology principles, but frozen in the regulatory conditions based on mid 1960s knowledge.

Adsorption unit operations also clearly indicate, that turbulent flow is advantageous for accelerating the chemical reaction, i.e. the isotope exchange in the adsorbent beds. Thus higher than 40 fpm velocity and deeper than two inch deep bed would result in improved performance even at the same 0.25 second residence time. Furthermore, the currently used two inch deep bed is barely adequate to contain the mass transfer zone even for new adsorbent material.

At TMI, with limited exposure to radioiodine, out of the four air cleaning units each with two inch deep beds, three have reached breakthrough, one significantly because of high flow (due incorrect flow balancing), the fourth which was not penetrated operated at the unbalanced, reduced flow.

There is no current indication that the new generation reactors would utilize adsorbent technology based on improved knowledge, but only more defined and rigid standards based, dusted off frozen technology of the 1960s.

III. Wall Effect.

Wall effect, as it relates to packing and velocity impacts near the interior wall of the adsorbers or test beds has been well treated in mass and heat transfer even in the nuclear industry, (2) (3) but it appears to have periodic resistance to its understanding in the nuclear air cleaning industry. This effect is completely separate and opposite from any entrance velocity differences due to empty duct or pipe wall effects, where the velocity in fact is lower next to the wall than in the interior of the pipe or the duct. In packed beds, the bed porosity is always lower next to wall and therefore the velocity is higher in that region. It is best illustrated by data for uniform spheres, when the impact is maximum. In case of irregular shapes of various size particles, the impact is less, but depending on the particle size to bed diameter ratio, it can be still significant. Figure 2 shows the increased porosity toward the wall of bed when packed with uniform spheres.

The understanding or misunderstanding of the wall effect in packed beds is a recurring problem in air cleaning activities last demonstrated here at the 26th Air Cleaning Conference. It would be helpful for all investigators to review the extant literature regarding this problem before evaluating flow related results through packed beds.

One unique misunderstanding of the wall effect in heat transfer is externally heated deep carbon beds. If the bed's surface temperature is measured lower temperature will be shown due to the lower bed porosity than further away from the vessel wall, where the carbon bed temperature will be higher. In general, external, spot heating of carbon beds, particularly by infrared heaters should be avoided.

The wall effect can be greatly attenuated in any non- rigidly packed horizontal bed, where even minute movement of the particles can result in significant additional air flow velocity increase along the wall. Particularly for testing purposes horizontal test beds should be avoided.

IV. Aging and Weathering of Radioiodine Adsorbents.

The aging studies on impregnated carbons are well known from the military gas mask applications and are appropriate for carbons for nuclear applications also. Most of these studies were initiated in the UK using activated carbons which were activated in large pieces, ground, sieved to size and impregnated. Activated carbons produced in this manner are somewhat unique in that there is only a limited surface oxide build-up on their freshly cleaved surfaces. The natural surface oxide build up takes place from humid air during storage of the product changing the surface conditions whether the carbon is impregnated or not. Figure 3 shows the typical equilibrium surface oxides on activated carbon exposed to humid air.

Most of the activated carbons, but not all, used in the US were and are activated in the particle size range in which they are impregnated, thus the surface oxides are well established prior to impregnation. In general, this oxidation process lowers the isotope exchange performance efficiency of carbons that are surface oxidized post impregnation. However, the somewhat high “aging” deterioration reported from the UK caused alarm in the US and data generation was initiated in the US also, albeit somewhat intermixed with “weathering” information, the latter meaning performance deterioration due to exposure to contaminants present in the atmosphere of the operating air cleaning systems.

Unfortunately, many of these studies, were performed in laboratories which were incapable of generating reproducible methyl iodide test results, furthermore did not adequately identify the adsorbent base properties and the preparation methods of the adsorbents and therefore contributed very little to the general understanding of the life cycle properties of radioiodine adsorbents.

A few extant, industry sponsored, studies indicate that the effect of various contaminants known to be present in nuclear facilities can range from major to no impact on the organic iodide exchange properties of currently used adsorbents based on the currently accepted test methodology, but there is no comprehensive useful aging and/or weathering data available in spite of the extensive NRC funded aging and weathering work of 1970s and 80s at the NRL.

V. The Plethora of Irreproducible Methyl Iodide Test Data

Upon reviewing the test rig descriptions, all of the data reported at 99 % RH but at “laboratory” air temperature in the 20 to 30 C range can be safely discarded as totally unreliable. It is impossible to control relative humidity at 99 % RH, without very extensive temperature control, in ambient laboratory air. (Setting laboratory air thermostat to the “desired” temperature just does not do it!) Even data reported under “ambient laboratory” temperature conditions at 95 % RH is suspect because the slight temperature variations can result in more than +/- 2 % RH variation which have a major impact on the measure methyl iodide penetration. Lax control of temperature (+/- 2 C) permits tests only around 90 % RH and below.

The problems of the inadequate laboratory test conditions were first demonstrated by an OECD round robin and subsequently confirmed by both a CONAGT and two NRC round robin test series. These round robin tests resulted in both a significant tightening of both the test parameter tolerances and improvements in the understanding of sample preparation handling and counting methodology. At the same time, they shed light on the questionability of most of the data generated previously, which encompassed, with a very few exception, (the latter from KfK Germany), the parametric data information on organic iodide removal by adsorbents.

The NRC needs to be commended for funding the work at INEL regarding the intricacies of obtaining reproducible results of methyl iodide exchange efficiency at high humidity, in the course of the last round robin test series. Perhaps, one of the important lessons learned from that work is that it is futile to expect reliable, reproducible methyl iodide exchange results above 95 % RH even under carefully monitored conditions.

Perhaps it is considered adequate that the utilities obtain the test results regulated by the NRC on their particular schedule and no “research” data is generated which would permit future improvements in system design or life cycle improvement. Although, it is sad that now, when the test conditions and parameters are refined to be much better capable to generate good parametric design data, such data generation dried up.

VI. Filtration, Adsorption and the Void in between.

Having been “cross-trained” in the last fifteen years in liquid phase application both at Hanford and at Yucca Mountain, the somewhat intriguing borderline area between filtration and adsorption occupied my attention. As the “particle” of interest decreases in size what happens when it is not filtered anymore, particularly if it is radioactive. My esteemed aerosol expert colleagues always assured me, that such small particles would agglomerate so fast that there would be little reason to worry about them, but. At the same time they place radioactive sources in size measuring instruments to avoid agglomeration.

In liquid phase systems, what is not filtered out by the best of the filters, is simply assumed to be “dissolved” and therefore liquid, but in case of many radioactive, particularly plutonium solutions this solubility appears to be time dependent and in the presence of some other colloidal material observations are made that the plutonium is attached to submicron size clay particles. Is it filtered or is it adsorbed? Where does filtration stop and where does adsorption start? Perhaps it is easier to determine this in liquid phase than in gas phase, but the question exists for gas phase application also. Just a teaser question on this subject, as shown on Figure 4.

VII. Who is Responsible for Radioactive Process Off-Gas System Codes Standards?

The lack of adequate design standards for radioactive off-gas processing, have been identified, at least in the ASME CONAGT Committee, for the last 20 years. The results, so far have been nil. If ASME is not interested or capable of doing this work, then it should clearly state so, maybe other ANSI consensus standard groups or even the DOE would undertake the development of minimum requirements for these systems. In my opinion, it is not fair for any group to “play” code development in such an important field, without achieving anything in 20 years.

VIII. In-Service Inspection Schism.

There is still a large gap in the applicability of nuclear air cleaning test standards and codes for air cleaning systems which, are normally uncontaminated and are in a standby mode, i.e. operated only in case of an accident and those which are continuously treating radioactive or other hazardous contaminants and therefore for not freely accessible to inspection personnel. In the design of the new radioactive material processing facilities, while nominal adherence to the mostly power reactor oriented ASME AG-1 Code is indicated, it is generally compromised, because its applicability can not be directly correlated to the particular design case, and testability is in fact applied only to part of the system. Currently, the DOE methodology of many tiered contractor system is not amenable to delegate personnel to code and standard writing groups, therefore “designated” experts are used who at most attend one or more seminars, but do not participate in the development of applicable standards and codes. Often, far more cost and time is used to explain why something was done incorrectly than to do it correctly the first time.

IX. Summary.

I do believe in the renaissance of the nuclear power industry and even in the renaissance of the US nuclear industry. I am not so hopeful that the US nuclear air cleaning industry will be up to the challenges of this new industry with new improved technology solely based on the frozen rigid standardization of the 1960s technology. Perhaps, I should be more optimistic, but I have not seen significant new innovations in this field in the past decades. I wish the younger generation success in innovation and doing better and more innovative work than I did in the past, and success in the coming new nuclear industry field. The path will not be smooth; there will always be events and people who will not cooperate with your progress. Do not give up!

Thank you for your invitation and letting me share some of my thoughts with you.

X. References.

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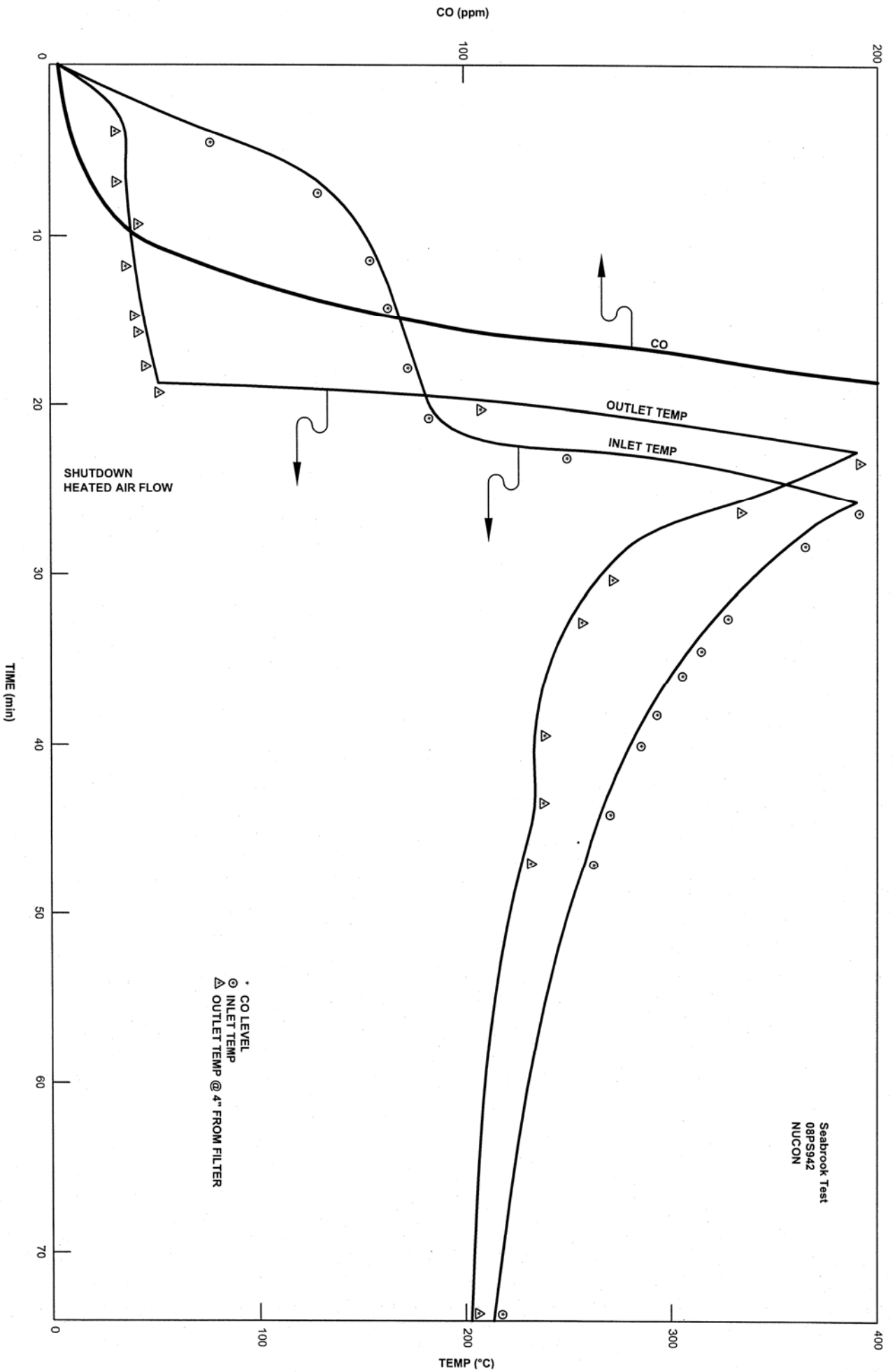


Figure 1

J.L.K.

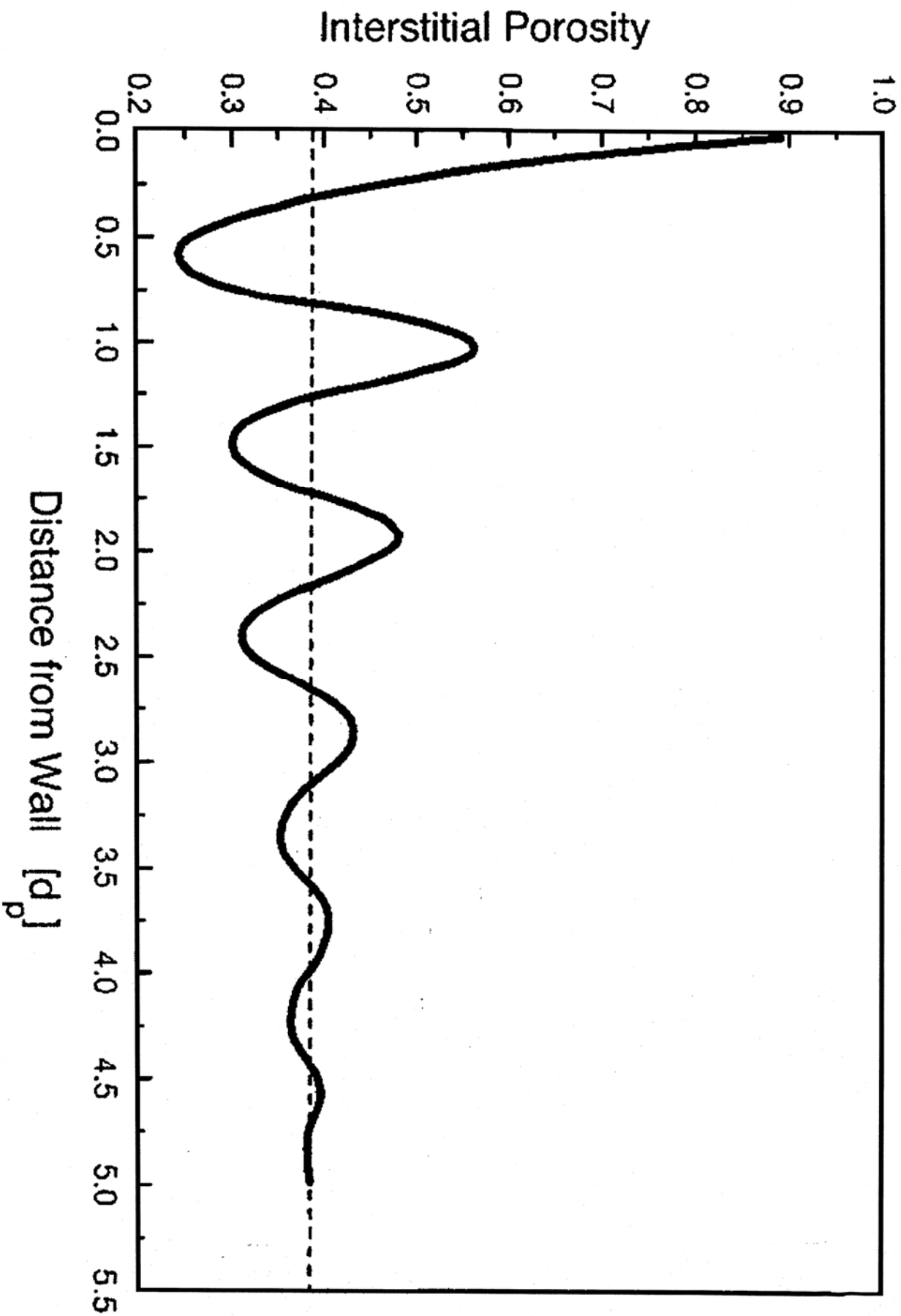
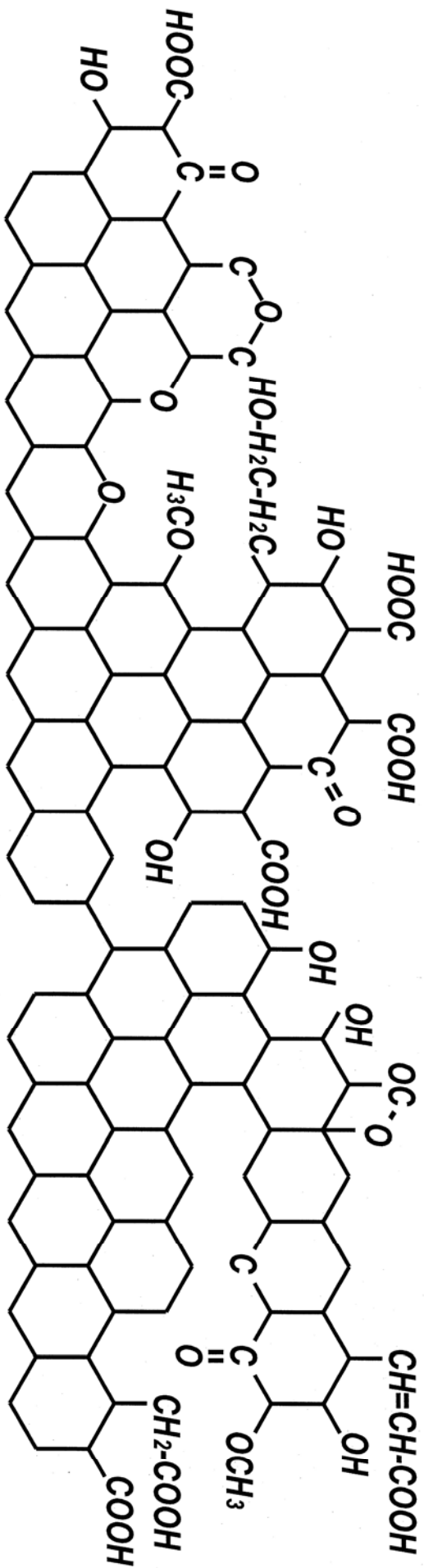


Figure 2. The radial porosity distribution function $\epsilon_{\text{inter}}(r)$ for fixed beds of monodisperse particles with perfect spherical shape and smooth surface. Experimental data column-to-particle diameter ratio $d_c/d_p = 14.1$



Carbon Surface Oxides

Figure 3

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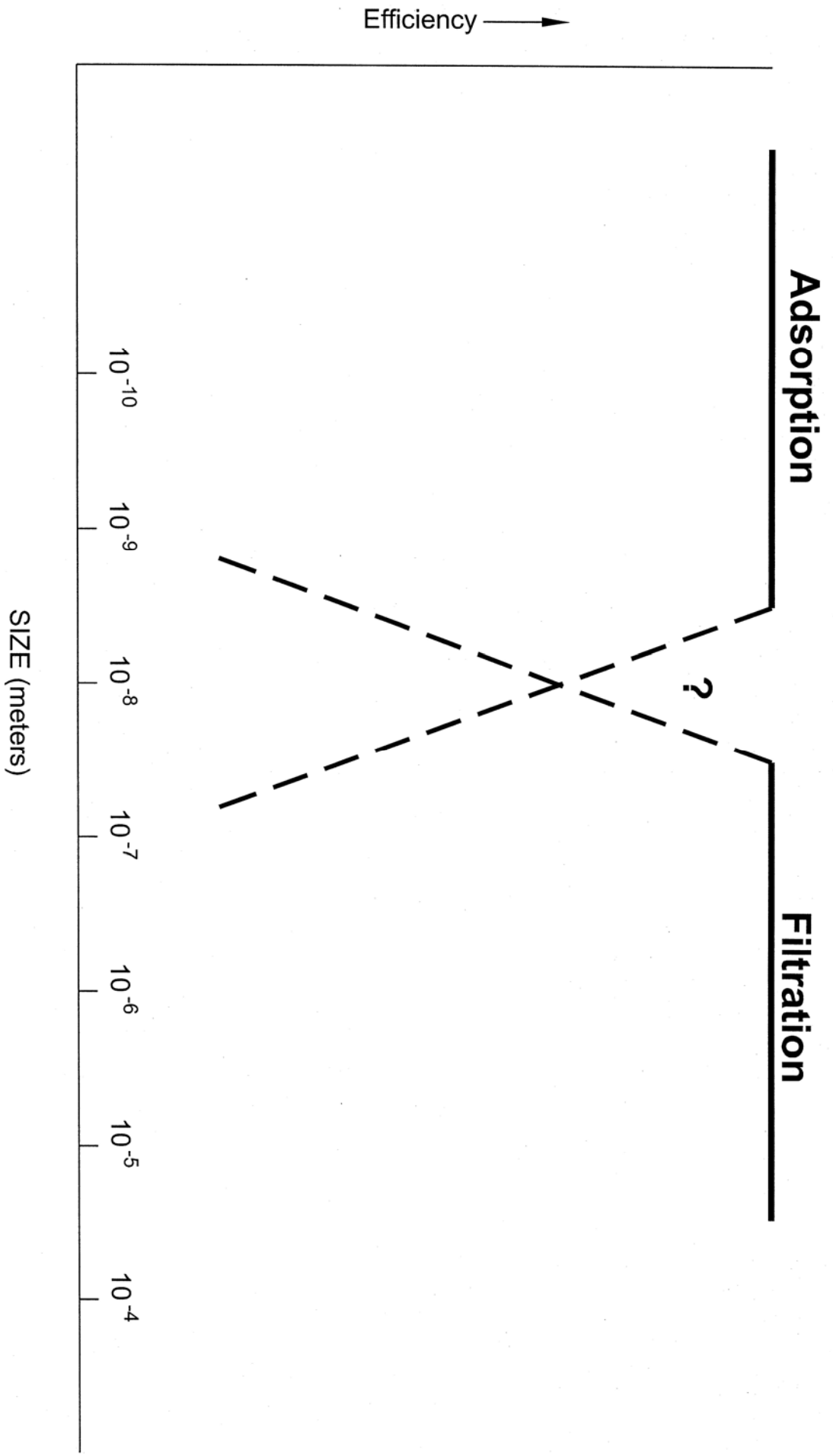


Figure 4

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