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PULMONARY RETENTION OF COAL DUSTS¹

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ABSTRACT

The principal objectives of this study were: to determine, quantitatively, coal dust retention times in the dog lung; to test the appropriateness of a pulmonary retention model which incorporates first order rate coefficients obtained from *in vitro* and *in vivo* experiments on neutron-activated coal; to acquire a temporal description of the pulmonary disposition of the retained coal dust, and to compare the behavior of two different Pennsylvania coals in the foregoing regards. The principal findings include: retention half-times for both coals of approximately 2 years following single, hour-long exposures; a vivid association of the retained coal dust with the pulmonary lymphatics; and a general validation of the retention model.

INTRODUCTION

Background

Coals arise from compacted plant materials after aging for aeons under reducing conditions in a milieu of waterborne elements and sediments. Consequently, coals contain most naturally occurring elements with a preponderance of the alkali metals, alkaline earths, aluminum and iron. The inorganic fraction of coals includes silicates, clays and other metal-associated minerals which are typically rich ($> 5 \mu\text{g g}^{-1}$) in such trace elements as chromium, manganese, cerium, fluorine, barium, mercury, zinc, bromine, nickel, lead and strontium. The organic fraction of coals contain phenolic, carboxylic and amino linkages which bind certain trace metals preferentially, e.g., beryllium, boron, antimony, vanadium and selenium. Thus, trace metals were originally incorporated into coal (a) either as detrital minerals or metals originally present in the plant matter; or (b) sequestered syngenetically by humates and/or precipitated *in situ* during coal formation; or (c) adsorbed or fixed by organic groups on the coal or lignite surfaces, or laid down by other epigenetic processes derived from waterborne minerals (Filby and Khalil, 1978).

The porosity of coals undoubtedly affects the epigenetic incorporation of metals, and contributes to the leaching characteristics of coal-associated metals. Debelak (1979) found coal porosity to involve a broad spectrum of pore sizes, e.g., $6\text{\AA}$ to $\sim 300\text{\AA}$. Many of the pores are "plugged" by water, CO_2 , and/or volatile hydrocarbons (Thomas and Damberger, 1976). When coal dusts are formed, specific surface areas $> 100 \text{ m}^2 \text{ g}^{-1}$ are not uncommon. Thus, the complex mineralogical disposition of metals in coals, the peculiarities of associated epigenetic minerals, and the intrinsically high internal surface areas of coals all contribute to the leaching characteristics and bioavailability of metals in coal dusts as they are normally encountered (Akers, 1978; Christian and Nelson, 1978; Nord and Bingham, 1973; Cavallaro, *et al.*, 1978).

Bases for Present Study

Our interest in these relationships is based principally on the possible utilization of neutron-activated coal contaminants, such as the trace metals, as tracers for the study of the biological behavior of coals, especially their pulmonary retention.

Although much progress has been made in the study of trace elements in coal, many of the metals of interest fall ambiguously into a mixed-affinity category (both inorganic and organic) as far as their disposition in coals is concerned. A few metals, e.g., iron, lead and arsenic, are predominantly of epigenetic origins and exist in pyritic sediments and other clastic materials which often can be physically separated from coals (Filby, Shah and Sautter, 1976; Filby and Khalil,

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1978). There are few reliable generalizations of this type available, consequently, each coal must be evaluated experimentally.

In our first study of coal dust retention in the lungs (Morrow et al. 1979), we used a Gasflammkohle from the Ruhr Valley which exhibited two slowly-leachable radionuclides, after neutron activation. Scandium-46 and cesium-134 were present in sufficient amounts to permit their use as radioactive labels for the coal. When combined with *in vitro* leaching studies and retention studies of the free (non-coal associated) radionuclides, we estimated the pulmonary retention half-time of the coal in dog lungs following brief (1 hr) exposures to 40 mg m^{-3} (MMAD $2.4 \text{ }\mu\text{m}$, σ_g 1.7) to be about 4 years. In shorter term rat studies, we found the pulmonary retention half time was approximately 1.5 years.

Heppleston et al. (1971) quantitatively recovered the coal dust from rats sacrificed serially after chronic, high level exposures. Their lung retention data appear to give 380 and 430 day half times for a high and low rank coal, respectively.

Skidmore et al. (1965) also studied high and low rank coals in rats following either inhalation or intratracheal injection at 10^1 - 10^2 milligram levels, and found no differences in retention due to rank. However, one cannot assign a retention half-time to their data.

A post-mortem investigation of coal miners' lungs from miners having no, or minimal, pathology, indicated that the total lung dust retention was consonant with a 4.9 yr biological half life (Stober et al. (1967).

Because of the scarcity of quantitative coal retention data, and our dependence on two less-than-ideal radionuclides in the first study for estimating such a protracted retention time for coal, we began a new study in dogs using the same pharmacokinetic model and the same general experimental design (Morrow et al., 1979). In distinction to the earlier study, we utilized both bituminous and anthracite coals for which there were abundant biologic and epidemiologic data (Carlberg, et al, 1971; Crable, et al, 1967; Lainhart, et al, 1969; McBride, et al, 1963; Lieben, et al, 1961; Baier and Diakun, 1963; Fairman, et al, 1977; Kober, et al, 1976). Also we selected coals which, upon neutron activation, contained more than two useful radionuclides. Finally, we undertook a more extensive investigation of the microdistribution of the coal dusts and histopathology in the lungs. In the latter regard, we exposed additional dogs to the same coal dusts without neutron activation as well as having non-exposed controls.

METHODS AND MATERIALS

Coal Dusts: Activation and Selection

After a group of coals from West Virginia, Pennsylvania and Utah were neutron activated and examined, we selected a high rank bituminous coal from the Lower Kittanning seam, Cambria County, Pennsylvania and a Tamaqua anthracite coal from Schuylkill County, Pennsylvania.¹ Both lump and finely ground specimens were activated to determine if the milling process contributed to the trace element content. The milling was accomplished in two stages: The first was performed before the coal was provided and reportedly used an "air comminution process" designed to foster coal-to-coal collisions (W. D. Wagner, 1975); in the second stage, we ground the coal several days in a zirconium oxide roller mill. Both excess iron and zirconium were found in the neutron-activated, milled specimens, consequently, the coal dust for the dog study was washed with 10N HCl, rinsed with distilled water and vacuum-dried before neutron activation.² The washing procedure unquestionably dissolved some of the clastic minerals present in the mine dust.

Approximately 1 week after neutron activation, isotopic analysis of the coals was begun using two 500 mm² intrinsic germanium detectors. See Fig. 1. An 18-month assessment identified the characteristic photon energies and decay rates of approximately twenty radionuclides, but only 8 appeared to be present in sufficient quantities to follow their biological retention, viz., Cs-134, Co-60, Sc-46, Fe-59, Hf-181, Cr-51, Cd-109, Hg-203. Additionally Sb-124, Ta-182, Co-57, Co-58, Tb-160 and Zn-65 were present in lesser amounts which made their retention measurements uncertain, but worthy of investigation. Finally, Hf-182, Th-234, U-235, Ra-226 and Zr/Nb-95 were detectable. See Figure 2. These various radio-isotopes were not equally useful in terms of their half-life considerations and on the basis of other information concerning their physical disposition in the coal (See Results). For the biological studies, additional lots of the same coals were activated and utilized within 1 month.

Inhalation Exposures

The coal dusts were dispersed using a Wright Dust Feed Mechanism (Model GA 180), into a 30 liter chamber from which two dogs were exposed simultaneously (Figure 3). During exposure the

¹These coals and the other specimens studied were generously provided by the Biological Support Branch (W.D. Wagner), National Institute of Occupational Health and Safety, Cincinnati, Ohio.

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subjects were maintained in a body plethysmograph with their heads exteriorized through a neck seal, while anesthetized (26 mg kg⁻¹ i.v. pentobarbital sodium). The plethysmographs were fitted with Wright Respirometers (BOC, England) which were calibrated by injecting known amounts of air into the plethysmographs through a 3-way stopcock while the dogs were at functional residual volume. To avoid external contamination and upper airway deposition, the dogs were intubated with balloon-cuffed endotracheal tubes (Fr 36) which were directly connected to the Rudolph respiratory valves (V in Figure 3).

Exposure times varied from 60-150 minutes. Coal dust concentrations emerging from the respiratory valves ranged from 80-100 mg m⁻³. The average mass median aerodynamic diameter (MMAD) was 1.85 μ m (σ_g = 2.8) for the bituminous coal and 1.90 μ m (σ_g = 2.4) for the anthracite coal; these determinations were made with an 8-stage inertial impactor (Mercer 1970). The radioactivity of the dominant radionuclides, e.g. Sc-46 and Co-60, ranged from 1 to 14 μ Ci g⁻¹ of coal 1 week after activation. These conditions led to initial lung burdens which averaged <10 mg with respect to coal and < 0.1 μ Ci for any specific radionuclide.

At the completion of the coal exposures, additional dogs were exposed to ⁵⁷Co labelled CoCl₂ and Co(OH)₂, inasmuch as the available pulmonary retention data on cobalt were very limited (Kreyling and Kracke, 1979). Also, two dogs were exposed to ¹¹⁸HfO₂ to determine if the extremely avid whole body retention of hafnium after parenteral administration (Riedel et al., 1979) was also typical of the inhaled material. These exposures made use of the same exposure apparatus as that depicted in Figure 3 with the exception that the aerosol generation was accomplished by a modified De Vilbiss 45 nebulizer using suspensions or solutions of the respective radionuclide compounds. Otherwise, pulmonary retention data for all remaining radionuclides of interest were obtained from previously reported studies (op. cit.).

Experimental Subjects

Female beagle dogs (6-8 kg) were obtained from commercial sources. These young adult dogs ventilated typically 1.5 to 2.5 l min⁻¹ under pentobarbital anesthesia. Eight dogs were exposed, four to each type of neutron-activated coal. Four additional dogs were exposed: two to each of the non-activated coals. Also 3 dogs never intentionally exposed to any dust served as unexposed controls. For the study of the free radionuclides, an extra four dogs were utilized.

Radioactive Assessments

Serial chest counts on the four dogs exposed to bituminous coal were continued for 113, 237, 285 and 301 days after exposure, respectively, at which times one dog was sacrificed. The corresponding anthracite coal group was measured for 73, 183, 385 and 392 days, respectively, before sacrifice. During *in vivo* measurements, the dogs were lightly anesthetized and placed in a shielded dog holder which restricted the thoracic field of measurement to the 1st to 5th intercostal spaces. The shielded dog holder was placed in a lead-filled steel counting chamber where two 2" x 4" dia NaI (Tl) scintillation detectors were positioned on either side (Figure 4).

The serially-taped data were "stripped" into the component radionuclides using a modified ALPHA-M program (Schonfield, 1969) and a Prime P-500 computer via a Tracor Northern EIA Interface. Standardized amounts of each radionuclide were placed into the lung fields of an Alderson beagle phantom and the spectra recorded in the ALPHA-M library. The library used for stripping was adjusted during the study so that only those radionuclides constituting 5% or more of total spectral activity were maintained in the program.

In vitro counting, e.g., samples from leaching studies, was performed with a single 3" x 3" sodium iodide scintillation detector coupled to the same MCA system used for the dog measurements (Figure 4). Collectively, the two radioactive coals exhibited 11 prominent photopeak areas when measured by either NaI detector-MCA system. See Figure 5. Although each of these 11 areas did not represent a specific radionuclide, they provided a convenient basis for digital printouts and experimental comparisons. Accordingly, these 11 areas of interest (AOI) encompassed the following photon energies in MeV: (1) 0.029-.068; (2) 0.078-.102; (3) 0.107-.147; (4) 0.175-.235; (5) 0.285-.360; (6) 0.410-.524; (7) 0.555-.635; (8) 0.683-.762; (9) 0.785-.902 (10) 1.015-1.152 and (11) 1.190-1.309, respectively.

Coal Leaching Methods

A number of dialysis and ultrafiltration methods were tested and two were selected for the leaching study of both coals. For the first, about 500 ml Gambles interstitial fluid simulant was prefiltered through a 0.45 μ m pore size molecular filter and placed in a sterile 1 liter 3-neck flask. Approximately 1200 mg coal dust and 1 ml benzyl alcohol (as a preservative) were added to the Gambles. The flask was placed in a water bath at 35° C and stirred with a magnetic stirrer. A stream of 5% CO₂-95% oxygen was used to purge the flask continuously. For studies up to about 2 weeks duration, 1-2 ml samples were taken periodically with a syringe and filtered through a molecular filter for counting. The AOIs in these filtrates were compared to the AOIs in the unfiltered aliquots taken initially and at the completion of the test. Loss of sterility was the usual basis for discontinuing the flask studies. Two studies each of 2 weeks duration were accomplished for each coal.

Longer leaching time studies were possible using a dialysis cell (Technilab Model E10) separated into two parts by a cellulose membrane (-14,000 MW cut-off). Using a protein-free acetate-modification of Gambles fluid, and an infusion pump (Braun Type 1850), fluid was forced

through one-half of the cell at $\sim 1.5 \text{ ml hr}^{-1}$, while $\sim 150 \text{ mg}$ coal dust was suspended in the other half of the cell with the aid of a small magnetic stirrer. The entire cell was sealed and submerged in a water bath at 35° C . The collected dialysate was counted in the same manner as the flask filtrate and the results expressed as percentages of the initial AOI activities in the cell. Four studies each of at least four weeks duration were completed on each of the coals.

Coal Retention Model

The model used in the previous study (Morrow et al. 1979) and the current effort is given in Figure 6. This depicts the main physical, chemical and biological processes which contribute to the coal retention estimation.

For dust retention data, especially with materials, such as coal, which tend to persist in the lungs for months or years, a multiphasic exponential model of the following form appears generally appropriate:

$$R = \sum_{i=1}^n a_i e^{-\lambda_i t}$$

where R is the fractional retention at time t , a_i is the mass or activity fraction following clearance rate λ_i , and n is the number of clearance components. Inasmuch as this study of coal retention is directed basically at the long term, alveolar component, the early rapid clearance phases which are influenced by bronchial deposition can be ignored. Similarly the retention data for the free radionuclides which are required for the model can be truncated. Moreover, we found that the leaching rates were not constant during the first week (See Results). Thus, a considerable simplification was introduced into the analysis in that single exponential rate constants were used for k_1 , k_2 and k_4 in the model and time "zero" was set at 6 days postexposure. The retention constants (k_{eff}) for the various radionuclides associated with coal were determined by a least square regression analysis of the lung field gamma spectra using the stripping routine of the ALPHA-M program. The k_2 and k_4 values were determined by regression analyses of the appropriate leaching and retention data. The values for k_1 were taken from the radionuclide decay data of Hawkins, Edwards and McLeod (1961). Using the MLAB program (Knott and Reece 1977), the values for k_3 were finally computed from the retention relationship implicit in the Figure 6 Model:

$$R = \frac{(k_4 - k_3)}{(k_4 - k_3 - k_2)} e^{-(k_2 + k_3)t} - \frac{k_2}{(k_4 - k_3 - k_2)} e^{-k_4 t}$$

Histopathology

Sections were taken from each lobe of the dog's lungs at sacrifice so that the pleural surface, and the tissue surrounding the peripheral and central airways were examined not only with respect to any pathologic changes, but also for a microdistributional description of the retained coals. Since the dogs were sacrificed at various times during the post exposure year, we hoped to gain some insight into the relative importance of various alveolar retention pathways from these > 400 pulmonary specimens, all prepared at $\sim 8 \mu\text{m}$ thickness and stained with hematoxylin-eosin.

The lymph nodes serving the dog lungs were carefully collected and several sections made from each. Mesenteric and mediastinal nodes were also taken and examined. In addition, liver and spleen sections were routinely taken. Dogs receiving comparable exposures to the stable (non-activated) coals were included to determine if the radionuclide radiations might have produced some tissue changes. Their tissues were also of value in the pulmonary microdistributional assessment. As a control for coal dust effects, tissues from unexposed dogs were acquired and examined in an identical manner. These dogs were also used for ascertaining the degree to which pigmented deposits were normally present in the lung tissues of dogs of similar age.

RESULTS

Coal Retention Estimations

Both coal aerosols, when subjected to aerodynamic size fractionation using a cascade impactor, revealed inhomogeneities in radionuclide distributions. In terms of the 11 AOI analyses, the major discrepancy was associated with AOI 1 in both coals; see Figure 7. The bituminous coal also exhibited a significant inconsonance in AOIs 2 and 3 of the Stage VIII fraction which represents particles below $0.2 \mu\text{m}$ equivalent aerodynamic diameter. There were several other borderline cases, e.g., AOIs 9 and 10 of the Stage VII fraction in bituminous coal; however, except for the clear anomalies in the AOI 1 photon yield, which were mainly derived from uranium, thorium and cadmium, the mechanical comminution of the coals did not produce nor reveal disparate volumetric (mass) distributions of most radionuclides.

The leaching studies also revealed some inconsistencies in the radionuclide behavior which would not have been expected if all were ideally distributed within vitreous coal matrices, e.g., vitrinites. These are exemplified by leachate data from an anthracite coal sample (Figure 8). Both coals showed substantially greater leaching rates for all radionuclides over the first 5 or 6 days. Whether this reflects the so-called disturbed layer effect or not is unclear. Also in the specific coal sample shown, AOI 11 (dark circles) did not reach the same degree of steady state dialysis

during the 6 days as did the other AOIs. In Figure 9, where longer term dialysis data were acquired on the same coal, the peculiar behavior of AOI 11 is again illustrated in that more than 15 percent of its initial activity was removed in 28 days of continuous dialysis (most of this in the first few days), whereas the balance of the AOIs changed by an order of magnitude less, on the average.

On the basis of these findings, the amounts and physical half-lives of the radionuclides present, and the k_{eff} data acquired from the ALPHA-M stripping routine, only Cd-109, Cr-51, Hf-181, Cs-134, Sc-46, Co-57, Hg-203, Fe-59 and Co-60 were deemed useful for the estimation of coal retention. The cogent data obtained on each of these radionuclides are summarized in Table 1:

TABLE 1. RADIONUCLIDE DATA FOR RETENTION MODEL

Radionuclide (probable antecedent)	Decay-Corrected Rate Coefficients (day ⁻¹)					
	k_1	$k_2(A)$	$k_2(B)$	$k_{eff}(A)$	$k_{eff}(B)$	k_4
Cadmium-109 (Cd-108)	0.00147	0.00818	0.00230	0.00736	0.00212	0.01034 ⁵
Cesium-134 (Cs-133)	0.00092	0.00440	0.00310	0.00546	0.00480	231 ^{6,7}
Chromium-51 (Cr-50)	0.02493	0.00030	0.00069	0.00137	0.00184	0.00277 ⁶
Cobalt-60 (Co-59)	0.00036	0.00225	0.00600	0.00197	0.00220	0.00772 ⁸
Cobalt-57 ¹ (Ni-58)	0.00257	0.00540	0.02580	0.00423	0.01554	0.00772 ⁹
Hafnium-181 ² (Hf-180)	0.01554	0.00488	---	0.00059	---	0.00007 ^{*9}
Iron-59 ³ (Fe-58)	0.01537	0.01857	0.00300	---	0.00269	0.01066 ⁶
Mercury 203 ⁴ (Hg-202)	0.01477	---	0.00092	---	0.00252	0.11550 ⁶
Scandium-46 (Sc-45)	0.00826	0.00048	0.00067	0.00074	0.00110	0.00094 ⁷

Footnotes:

- ¹ k_{eff} data are from 3 anthracite dogs and only 1 bituminous dog.
- ² k_{eff} data are limited to 4 anthracite dogs.
- ³ k_{eff} data are from 1 bituminous dog.
- ⁴ k_{eff} data are limited to 3 bituminous dogs.
- ^{*} ¹⁸¹HfO₂ used for the k_4 studies was made at Brookhaven National Laboratory by neutron activation of 99+ percent enriched hafnium-180.
- ⁵ Oberdoerster et al., 1979
- ⁶ Morrow et al., 1968
- ⁷ Morrow et al., 1979
- ⁸ Kreyling and Kracke, 1979
- ⁹ This study: see Results

In the Table 1 data, the k_2 values for each type of coal fall generally into one of 3 categories, viz., those which infer leaching half times of about 1 month, several hundred days, or greater than 2 years, respectively. Most of the radionuclides in both coals fall into the intermediate group: anthracite mean $T_{1/2} = 164$ da (S.D. 84) $n = 5$; bituminous mean $T_{1/2} = 195$ da (S.D. 83) $n = 5$. The least leachable group, consisting of scandium and chromium in both coals, averaged over 1000 days in all cases. Mercury-203 in the bituminous coal, also appeared to belong to this category but the k_2 value must be considered provisional because of the short physical half life and the extremely low levels of ²⁰³Hg detected. The remaining two radionuclides, iron-59 in the anthracite coal and cobalt-57 in the bituminous coal, gave leaching half times of 32 ± 5 days; as previously discussed, these trace metals may have been associated with pyrites or other clastics. Thus, there is a general picture of reasonably consistent k_2 values in Table 1 which would be expected if the radionuclides had a common mineralogical disposition.

From the data in Table 1 and the retention relationship cited in the section, Coal Retention Model, the pulmonary retention half times for the two coals were computed and these are summarized in Table 2.

The Table 2 data reveal that several of the coal-associated radionuclides were not successfully applied to a k_3 estimation; this was usually due to insufficient data for a satisfactory k_{eff} determination, i.e., where the standard error of the estimate was 20% or less than the estimate per se and was associated with inadequate activities. Since the reliability of the k_3 estimates varies some weighting must be applied. On this basis we believe that coal retention half times of 767 days and 637 days are appropriate for the anthracite and high rank bituminous coals studied.

TABLE 2. COAL RETENTION ESTIMATIONS

Anthracite Coal:		Bituminous Coal:	
Radionuclide used for k_3	Coal Half time ($0.693/k_3$) days	Radionuclide used for k_3	Coal Half Time ($0.693/k_3$) days
Cadmium-109	(107)	Cadmium-109	n.a.
Cesium-134	621	Cesium-134	452
Chromium-51	642	Chromium-51	775
Cobalt-57	852	Cobalt-57	n.a.
Cobalt-60	n.a.	Cobalt-60	n.a.
Hafnium-181	762	Hafnium-181	n.a.
Iron-59	n.a.	Iron-59	934
Mercury-203	n.a.	Mercury-203	417
Scandium-46	956	Scandium-46	609

n.a. not available (See Discussion)

A different type of analysis was undertaken using the relationship of the 11 AOIs in the NaI counter gamma spectra. In this case, a comparison was made between the AOI ratios among the coals as measured in the exposed dogs and in samples of coal maintained in the laboratory for comparable post activation times. See Table 3 for representative examples.

Table 3. CHANGES IN AOIs WITH TIME.

AOI	Bituminous Coal (% of total activity/AOI)										
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
B Coal Stnd +6da	11	5	11	11	10	10	6	5	15	13	3
B Coal Dog +6a	11	6	11	12	11	9	6	5	15	13	1
B Coal Stnd +238 da	12	6	10	11	10	9	6	5	16	13	2
B Coal Dog +238 da Δ	15**	4	11	8**	10	9	7	5	16	13	2
AOI	Anthracite Coal (% of total activity/AOI)										
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
A Coal Stnd +6 da	17	5	17	9	11	17	3	5	8	6	2
A Coal Stnd +72 da	15	5	15	9	11	16	4	5	9	8	3
A Coal Dog I +72 da Δ	16	4	12*	8	12	15	5	6	10	9	3
A Coal Stnd +176 da	12*	5	10*	10	11	12*	5	7	11	12*	5
A Coal Dog II +182 da Δ	14*	4	11*	9	11	12*	5	7	11*	12*	4

* $p < 0.05$ when compared to +6 day standard. + $p < 0.05$ when compared to coal standard of equal age
Δ Lung spectrum

Both Table 2 and Table 3 data indicate that the dominant radionuclides are well associated with and retained by the coal dust. In Table 3, for example, the AOIs for anthracite coal undergo considerable change with time, but the in vitro and in vivo spectra remained insignificantly different.

Histological Examinations

Since quantification of the coal dusts in microscopic sections was not feasible, an arbitrary scoring system (0, +, ++, and +++) was devised to describe the relative amounts of black pigmentation in various anatomical localizations. Pathologic evaluations were also undertaken on both pulmonary and visceral tissues from all of the control and exposed animals.

Unexposed Control Dogs: Beagles acquired from the same commercial sources, having the same general age as the experimental group, and living in our vivarium for comparable times, exhibited very little or no lung pigmentation. Even our beagles of considerably older age (13-14 yrs) rarely showed more than + pigmentation which was defined as less than 15 particulate aggregates in any lung section. Consequently, the correspondence of dark pigmentation with retained coal dust could be presumed.

Dogs Exposed to Stable Coals: These four dogs, which received identical time-concentration exposures as those receiving the neutron-activated coals, typically manifest numerous small aggregates of coal dust throughout the interstitial spaces of the lung tissue in all of the sections taken. In some alveoli, a few macrophages were seen to contain particles at all postexposure times. However, most of the coal dust conglomerates were subpleural, around small airways, and/or around small blood vessels (See Figure 10). These deposits were not associated with either inflammatory or fibrotic changes, although they were frequently foci for lymphocytes. The localization of coal dusts within connective tissue spaces implicates active lymphatic translocation. No significant distinctions in lung tissue disposition and responses were evident in the two dogs exposed to anthracite and the pair exposed to bituminous coals at either 173 or 377 days postexposure, the two times selected for serial sacrifice of both pairs. The tracheobronchial lymph nodes from all animals appeared normal and contained moderate amounts of coal dust mainly within medullary macrophages. Omental and mesenteric lymph nodes were completely free of coal particles. The liver and spleen were also free of coal dust and normal in appearance.

Dogs Exposed to Neutron-Activated Coals: These 8 dogs showed a qualitatively and quantitatively similar picture of coal particle distribution in pulmonary tissues as described for the dogs exposed to stable coals. The histopathology was different, however, in two anthracite dogs which were sacrificed at 385 and 392 days postexposure. Both dogs, but the latter dog in particular, showed changes consisting of hyaline thickening of the walls of small blood vessels and of patchy groups of alveolar septa. These changes were seen in all lung lobes generally in accord with the scale of pigmentation. The two dogs cited received the highest radioactive exposures of the group of 8 dogs, so the evidence suggests that these changes were derived from the exposure and not coincidental. Since the dog exposed to stable anthracite coal and sacrificed at 376 days postexposure showed comparable pigmentation without hyalinization, we tentatively conclude these pathologic changes were either radiation-induced or radiation-potentiated.

The tracheobronchial lymph nodes in these dogs were found to be quite similar in all respects to those from the stable coal exposures. The lack of coal dust and pathologic changes in other lymph nodes and visceral tissues were also substantiated in the dogs exposed to radioactive coals.

Thus, except for the lungs of the two dogs receiving the highest doses of radioactive anthracite coal, all of their tissues were qualitatively indistinguishable from each other or from the dogs exposed to either stable coal dust. In other words, we found no distributional nor pathological basis for differentiating between the anthracite and bituminous coals.

DISCUSSION

Coal is not a single chemical specie; on the contrary it is an immensely complex mixture whose exact nature has not been determined for a single coal type. Furthermore it is known that even the mechanical comminution of coal can not only result in mineralogical fractionations, but can even disrupt chemical linkages among organic macromolecules (Lebedev, 1977), consequently biological studies must consider the coal's heterogeneity and the possible effects of coal dust preparation, activation and aerosolization methods on any given specimen.

The variations we found in coal retention estimates are disappointingly large mainly because the absolute radionuclide levels were generally lower than ideal. The use of relatively short term leaching rates obtained from *in vitro* studies is intuitively unsatisfactory and this may have yielded higher k_2 values than are appropriate for coal retention times in excess of a year. Presumably this would apply to all the radionuclides and tend thereby to cause all of the coal retention half times to be slightly overestimated. In other words with a smaller value of k_2 , k_4 becomes less important and the value of k_3 must increase to account for a given k_{eff} ; restated, the smaller the value of k_2 , the better is the radionuclide label for the coal and the closer the identity of the decay corrected k_{eff} to the value of k_3 .

The k_4 values are also subject to criticism if changes in the chemical state of a radionuclide are known to produce major changes in its pulmonary retention. Fortunately, for most of the radionuclides studied, this is not a problem. Perhaps the soundest model for a k_4 estimate would be a retention study of the carrier-free radionuclide; this would best approximate the trace element levels involved with the *in vivo* leachate and minimize the role of polymeric forms produced by

hydrosolation and similar in vivo conversions. Our determination of the hafnium retention half-time may have involved these problems.

Collectively, the most serious limitation in this investigation of the coal retention model seems to be technical not conceptual; it was the lack of radionuclides having suitable absolute activities and long physical half lives. Nevertheless, the neutron-activated coals used in this effort were a vast improvement over those in our earlier study. Possibly studies of other dusts, e.g., neutron-activated fly-ash where trace element enrichment occurs, will prove more amenable to analyses and test the retention model more rigorously. In this regard, it may also prove beneficial to utilize, where appropriate, more complex kinetic descriptions than simple first order rate constants for k_2 , k_3 , k_4 and/or k_{eff} .

Several of the failures to compute k_3 values, viz: Co-57 (A) and Co-60 (A,B) in Table 2 were not wholly related to the radionuclide activity. The MLAB program gave negative values for these k_3 's and further work is required to ascertain the basis for this enigma.

Removal of coal dust deposited in the lungs has been described by Morgan and Lapp (1976) as first involving macrophage recruitment. This leads to phagocytosis and cellular translocation via mucociliary transport through the bronchial airways. This view of alveolar dust clearance is not novel for coal dust, nor is it necessarily adequate, for it lacks quantitation and neglects other active dust removal processes. The quandary is compounded by evidence that dust clearance pathways may change with dust loading, presence of cofactors or disease, and type of dust. Our studies of single short term exposures utilized much lower lung levels of coal than were present in most other experimental and human studies; moreover, the histologic studies verified the absence of significant pathology. They provide clear evidence of active coal dust removal via the pulmonic lymphatics, as well as removal by alveolar macrophages via the airways. No distinctions in tissue responses were detectable between the anthracite and high rank bituminous coals studied and their retention times appear to be of the same order. Perhaps the rank of the two coals is too similar to affect biological distinctions. The available epidemiology (op. cit.) attests to the relatively high propensity of both coals to produce coal workers pneumoconiosis in accord with other studies which have associated rank with the incidence of CWP (Bennett et al. 1979; Walton et al., 1977).

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FIGURES DUAL INTRINSIC GERMANIUM SYSTEM

Figure 1. Germanium system for isotopic identification.

The outputs of the Princeton Gamma Tech cryogenic detectors (IGP Model 510) are coupled to a Tracor Northern Multichannel Analyzer, Model TN 1710-4, and a Texas Instruments Model 733 AR Data Terminal.

Figure 2. Representative spectra from isotope assessment study.

Using the intrinsic germanium detector system, the counting times for these spectra were varied to compensate for differences in age and activity of samples.

Figure 3. Coal aerosol exposure unit.

Dogs were connected to the bag-in-box chamber (C) by endotracheal tubes via Rudolph valves (V); their expired aerosol was collected by absolute filters (M) adjacent to the 3-way valves (T). The airflow through these filters was adjusted by varying the couplings (L) so that the Rudolph valves were not unseated. The aerosol output (W) was diluted by air through flow regulator (F₂) and passed through deionizer (D). Excess aerosol passed through chamber port (E) into electrostatic precipitator (P) and its backup filter. Screen (G) keeps the bag (B) (used to vacate box and keep the box at ambient pressure) from closing off the several exhaust ports and chamber connections.

Figure 4. NaI Scintillation counters.

The detector outputs are directed to a Tracor Northern Model 710 Pulse Height Analyzer from which data are recorded using a Superscope Model CS 200 tape recorder, a Model 3320 Teletype and a Moseley Model 2FRA X-Y Plotter.

Figure 5. Scintillation counter spectra from activated coals.

These X-Y recorder plots of gamma spectra from both coals at 1 month (Right) and 12 months (Left) post activation, were adjusted to favor reproduction and cannot be directly compared. For example, the anthracite spectrum at 1 month, (below 0.2 MeV) was recorded at 50,000 cts full scale for 60 sec whereas the balance of this spectrum was recorded at 10K full scale for 60 sec (See upper right figure). The scale and time factors for the other spectra are noted above the respective plots.

Figure 6. Pulmonary retention model for neutron-activated coal dusts.

In the above model, k_1 is the radioactive decay coefficient for the specific radionuclide; k_2 represents the *in vitro* leaching rate from coal of that particular radionuclide; k_3 is the lung clearance coefficient for the same radionuclide determined independently from coal; and k_4 is the lung clearance coefficient for the coal dust per se. The measured retention characteristic of the coal-associated form of the radionuclide is termed k_{eff} , as it is controlled to various extents by k_1-k_4 . All of the rate coefficients are measured directly except k_3 .

Figure 7. Radionuclide distributions as a function of aerodynamic particle size.

Using an eight-stage inertial impactor (Stages 0-VII incl and a terminal absolute filter: VIII), the anthracite and bituminous coals were size-fractionated and the gamma spectra of each fraction compared in terms of 11 AOIs (abscissa). The aerodynamic "cut off" diameters for stages 0-VII (ordinate) were as follows: 4.8, 3.3, 1.9, 1.1, 0.61, 0.31 and 0.17 μm , respectively.

Figure 8. Coal leachability study: representative early dialysis data.

These data were taken from a continuously dialyzed sample of anthracite coal in a E10 Cell using a modified Gamble's solution equilibrated with 5 percent CO_2 . The short-term behavior of the radionuclides, represented by AOI 2 (dark squares), 5 (open squares), 8 (open circles), and 11 (dark circles), are depicted. Only AOI 11 manifests a changing dialysis rate after 6 days.

Figure 9. Coal leachability study: representative long term results.

This sample of anthracite coal was dialyzed for 28 days in the same manner as that described in Figure 8. The total leachate activity includes the activity recovered in the first 6 days which was greater than during steady state, consequently these results are approximately 30 percent greater than the 6-28 day data used for k_2 estimates. Nevertheless, they clearly demonstrate the marked difference in the AOI 11 activity due to the highly leachable iron (^{59}Fe). The upper graph shows the change in total coal activity attributable to each AOI whereas the lower histogram pertains to the change in each AOI with time expressed as a percentage of the initial AOI value (decay corrected). The downward trend in these data (right to left) probably indicates some uncorrected contributions of the higher energy gammas to the lower energy channels.

(WILL APPEAR IN PUBLISHED PROCEEDINGS)

Figure 10. Histopathological Sections.