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AN UNUSUAL "THUCHOLITE" FROM ELLIOT LAKE, ONTARIO

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ABSTRACT

Shiny black nodules of carbonaceous material, believed to have occurred in a haulage drift of the Milliken Lake mine, contain a small amount of radioactivity concentrated in a thin layer at the surface of the nodules. The nodules consist of about 80% carbon and differ from thucholite in that they contain no inclusions of radioactive material. Radiometric analysis (gamma spectrometry) indicates that the surface radioactivity is due to radium; low-energy gamma radioactivity disseminated inside the nodules is thought to be due to radon daughters. It is suggested that the nodules formed during mining operations by the agglomeration of fine carbon particles from diesel exhaust smoke.

SOMMAIRE

Des nodules noirs brillants d'un matériau charbonneux, qui semblent avoir été trouvés dans une galerie de roulage de la mine de Milliken Lake, contiennent une faible quantité de radioactivité concentrée dans une mince couche à la surface des nodules. Ces nodules sont constitués d'environ 80% de carbone et diffèrent de la thucholite par l'absence d'inclusions de substance radioactive. Une analyse radiométrique (spectrométrie par rayons gamma) indique que la radioactivité de la surface est causée par du radium; la radioactivité gamma à faible énergie disséminée dans les nodules semble être causée, elle, par le radon. Nous sommes portés à croire que les nodules se sont formés, pendant l'extraction, par l'agglomération de fines particules de carbone provenant des fumées d'échappement diésel.

INTRODUCTION

A uranium- and thorium-bearing hydrocarbon occurring in a pegmatite dyke was named thucholite by Ellsworth (1928). A carbonaceous material, also referred to as thucholite, is a minor constituent of the radioactive conglomerate ores of the Elliot Lake district of Ontario. This material usually consists of carbon with fine inclusions of uraninite. Joubin (1954) reported that thucholite occurs in the Quirke ore as glassy "bubbles" up to 0.6 cm in diameter, encrusting the walls of small open fractures. Roscoe & Steacy (1958) referred to the occurrence of a weakly radioactive hydrocarbon with marcasite, sphalerite and galena in small calcite veins and as a coating with molybdenite on walls of some fractures. Robertson & Steenland (1960), and Robertson (1962) described very faintly radioactive globules of hydrocarbon in open joints in Blind River orebodies. Robertson (1968) stated: "Thucholite, and (or) slightly radioactive hydrocarbon, both of which are younger than the main mineralization are definitely crosscutting and may be seen surrounding pebbles, filling joints, or filling fissures in either quartzite or conglomerite" and Robertson (1970): "A mixture of radioactive hydrocarbons with uraninite and coffinite that is found in post-ore fractures as either massive or botryoidal bodies is generally considered to be the mineraloid thucholite".

In deposits of Shinarump channel conglomerate in Utah and Arizona, Bain (1952) noted the presence of nodular hydrocarbon in which the outer rim is enriched in uranium.

At the Milliken mine, in the Elliot Lake district, Ontario, uraniferous carbon occurs in fracture zones and vugs, and is considered to be secondary. It is closely associated with sphalerite and galena and appears to replace uraninite grains: those grains in which the uraninite has been largely replaced tend to be nodular (Kaiman 1960). Under the microscope the carbon is seen to be anisotropic and to contain inclusions of radioactive minerals, mainly uraninite. An isotropic variety of carbon, which contains no visible inclusions of radioactive minerals, is also present in the Milliken ore as well as in other Elliot Lake orebodies (see Other Occurrences). It is the latter type of carbonaceous material that is described here. Since this "thucholite" contains no thorium and very little uranium, a better name is carbon and it will be referred to thus in this paper. A similar conclusion was recently reached for the Witwatersrand carbon by Feather & Koen (1975).

A previous unpublished study had been made by the first author on a sample of nodular carbon which occurred with gouge derived from

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fractures and minor slips in the Quirke mine. This carbon was isotropic and had a density of 1.2. Analysis of concentrates (Table 1) had shown that the ash content was low as compared to that of pegmatite thucholites reported by Ellsworth (1928) and that little or no thorium was present. To obtain additional material for a comparison study, a sample of the carbon was requested from the Milliken mine, Rio Algom Mines Ltd., during a visit to the property in 1959. The concentrate of nodular material subsequently supplied by the mine geologist, the late Mr. David A. Keyes, was found to be very weakly radioactive, and further study revealed that the radioactivity in the nodules was of an unusual type.

TABLE 1. COMPOSITION OF CARBON

Source	Milliken		Quirke		
Sample No.			1	2A	2B
Moisture Condition	As Rec'd	Dry	Dry	Dry	Dry
Proximate Analysis:					
Moisture.....%	2.70	0.00	0.0	0.0	0.0
Ash.....%	0.84	0.86	1.4	0.9	0.9
Volatile Matter...%	31.75	32.63	27.6	29.7	28.7
Fixed Carbon.....% (by difference)	64.71	66.51	71.0	69.4	70.4
Ultimate Analysis:					
Carbon.....%	78.14	80.31	79.0	85.2	80.2
Hydrogen.....%	4.99	5.13	4.1	4.4	4.6
Sulfur.....%	4.81	4.94	1.1	1.1	1.2
Nitrogen.....%	0.15	0.15	1.4	0.8	1.2
Ash.....%	0.84	0.86	1.4	0.9	1.5
Oxygen.....% (by difference)	8.27	8.61	13.0	7.6	11.6

The mode of occurrence of the sample of Milliken carbon was not recorded at the time of its receipt, and after Mr. Keyes' fatal accident it appeared that there was no way to ascertain the source. Little could be inferred about the original mineralogical association of the nodules because the material supplied consisted of a concentrate containing only small proportions of other minerals. Fortunately, a description of the occurrence has recently been provided by a former Senior Mine Geologist at the Milliken mine, Mr. Dale M. Hendrick. Mr. Hendrick reveals (pers. comm. May 1975) that during the summer of 1959 a student sampler observed on the wall of the haulage drift, on the 2960 level, black "buckshot-like" beads of radioactive material which were identified then as thucholite. It was the opinion of the mine geological staff that they were being formed at the time that mining was being carried out: uranium-bearing, acidic mine water seeping down through cracks and fractures, along the faulted contact of a steep-dipping diabase dyke and bedded flat-dipping quartzite, deposited the radioactive black beads by precipitation in a reducing environment in the haulage drift below. The atmosphere of the drift contained damp air and diesel oil exhaust fumes. The exposure site was located 15 to 18 m below a mined-out stope that once contained typical Elliot Lake conglomerate. During that year, according to Mr. Hendrick, the samplers at the mine harvested the exposure at regular intervals and filled numerous jars with the material, some of which was sent to the Mines Branch (now Canada Centre for Mineral and Energy Technology) in Ottawa.

Description of Nodules

The carbon nodules are black, with smooth shiny surfaces, and they resemble pitch. The carbon is brittle, has a conchoidal fracture and no cleavage, and is black when pulverized. It consists of globular nodules and blebs (Fig. 1) which are up to 3 or 4 mm in diameter but generally smaller; some elongate masses, however, are up to 13 mm in length. The nodules

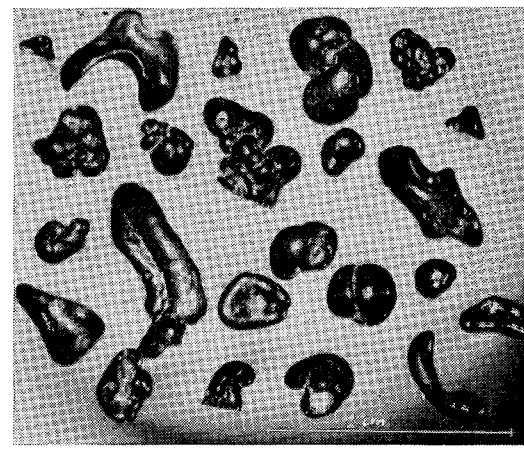

FIG. 1. Carbon nodules from Milliken mine.

vary widely in shape; in addition to round or spherical ones, some are flat, dimpled, twisted or elongate and they assume complicated forms including those resembling an ear, kidney, saddle, tear-drop, boomerang, and a bunch of grapes. Some consist of two or more blebs stuck together and many appear to have been rolled, squeezed, and twisted while in a plastic condition.

The nodules are amorphous to X-rays. When ignited they burn slowly and leave a very small amount of grey ash. They are insoluble in methyl alcohol, benzene, ether, acetone and toluene.

Specific gravity determinations were made on

six nodules weighing between 6 and 17 mg and gave an average value of 1.20±0.01.

In polished section the nodules are homogeneous, opaque and optically isotropic. Fine sulfide inclusions, generally less than 2 μm in diameter, are sparsely disseminated in the carbon. No other inclusions are visible microscopically.

Attached to the nodules are small amounts of other minerals. Sulfide minerals, including pyrrhotite, chalcopyrite and cubanite, occur as small crystals embedded in the surface of the nodules, and in the depression at the junction of curved surfaces. In addition, a small amount of flexible, fibrous, waxy, asbestos-like mineral occurs attached to some nodules and occasionally encapsulates nodules in cocoon-like sheathes. The X-ray diffraction pattern of the fibres corresponds to that of a hydrous magnesium aluminum silicate which has been called pilolite (Heddle 1879) but has not been established as a valid species. Nevertheless, the term "pilolite" will be retained here for convenience. SEM examination of the fibres shows that they closely resemble chrysotile asbestos. Very fine pyrite crystals often occur with the "pilolite". A small number of unattached, irregular grains of quartz, feldspar and calcite are also present in the sample.

SEM photographs of nodule surfaces show that they are generally smooth and featureless except for a uniform distribution of surface pits or depressions. The pits are usually circular and vary in size and depth: many are between 5 and 15 μm in diameter. A small number of pits show hexagonal outlines.

An autoradiograph of a sample of 24 nodules placed in random contact with photographic film showed that all but one of the nodules darkened the film. Autoradiographs of polished sections of nodules exposed to photographic film or to alpha-sensitive nuclear plates (Ilford, type K-2) show that the amount of radioactivity in the nodules varies from low to very low. This radioactivity is concentrated in a thin layer on the outside of the nodules (Fig. 2) but no discrete inclusions of radioactive material are indicated, i.e., the radioactivity is disseminated in the thin surface layer. Although some nodules appear to contain a small core of radioactivity or to have some radioactivity dispersed throughout the section, these are believed to represent sections of involuted material or near-surface material, respectively. Broken surfaces are usually not radioactive. The depth of the radioactive layer, as measured on autoradiographs of sections nearly normal to the nodule surface, is approximately 70-120 μm. Inside this layer the radioactivity decreases abruptly.

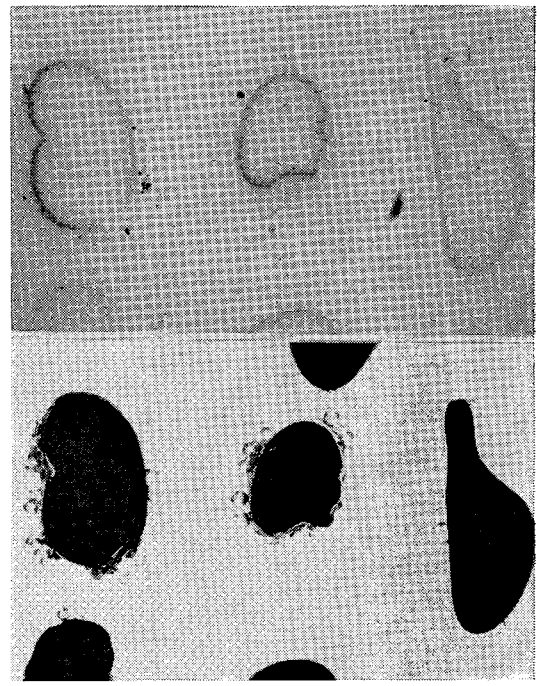

FIG. 2. Photomicrographs of polished section (bottom) and of alpha autoradiograph (top) of carbon nodules to show distribution of radioactivity. Note chipped surface and discontinued radioactivity in lower right area of nodule on the left. Width of Figure is approximately 1 cm.

CHEMICAL COMPOSITION

Proximate and ultimate analyses of a purified sample of the carbon, estimated to contain less than 1% by weight of contaminants (mainly sulfide inclusions), gave the results shown in Table 1. For comparison, results of analyses of 3 concentrates of carbon nodules from the Quirke Mine (made in 1957) are included in the Table.

The analyses in Table 1 illustrate the similarity in composition of the nodules from the two mines. Both contain approximately 80% carbon but the sulfur content of the Milliken nodules is more than four times that of the Quirke nodules.

Analyses of ash of ignited nodules, by optical fluorescence and by alpha spectrometry, showed that they contain 0.0045% U and 19 pCi Ra-226 per gram.

Electron microprobe analysis (using an expanded beam and a reduced voltage to prevent decomposition of the sample) failed to reveal

U or Th but showed that about 7 wt. % S is apparently evenly distributed in the carbon.

Isotopic Composition

The carbon isotope composition of the nodules was determined by Dr. P. Fritz of the University of Waterloo. The analysis gave a $^{13}C/^{12}C$ ratio of −24.1 per thousand (PDB). This value falls in the range for terrestrial plants, −22 to −30 per thousand, which differs markedly from that for marine plants as shown by Hallbauer (1975, after Laporte 1968) and suggests a terrestrial or freshwater origin for the carbon in the nodules. However, the same compilation by Hallbauer (1975) shows that Devonian crude oils have a similar range of carbon isotope ratios. Thus the carbon isotope evidence, while not unequivocal, does not preclude the possibility of crude oil having been the source of the carbon.

Radiometric Analysis Using Energy Discrimination

A gamma-ray spectrometer was used to analyze the radioactivity of the nodules. The spectrometer employed a Nuclear Data 512-channel analyzer; half of the channels were used to store data from the sample or standard reference materials, and half for background radiation which was subtracted to provide a net spectrogram of the sample. During counting, the sample was enclosed in a 3-ton lead shield (Hawkings & Edwards 1958) having a double lining (copper and cadmium) to suppress X-rays which could interfere at low gamma-ray energies.

Because the nodules are only weakly radioactive it was necessary in some cases to use counting periods of several days. To ensure optimum counting efficiency, the nodules were spread in a single layer behind a window of thin plastic sheeting in contact with the gamma-ray detector. The latter was a 75-mm-diameter sodium iodide crystal mounted in a housing of 380 μm aluminum.

A preliminary spectrogram, in the energy range 80 to 3000 keV, indicated radium and its daughter elements, of which Bi-214 is the predominant gamma-ray emitter. There was evidence of a small amount of uranium but no indication of thorium or its daughter elements. Uranium, free of radium, emits only low-energy (soft) gamma radiation, mostly in the range 50 to 250 keV (Fig. 3).

A spectrogram (Fig. 3) was obtained from a 16.6 gram sample of nodules, by counting in the energy range 20 to 700 keV for 3800 minutes. Spectrograms of related reference materials are also shown for comparison and to facilitate interpretation. In the decay series of natural uranium, only elements following radium make a significant contribution in the range of energies above 250 keV. Thus, count yields obtained at these energies represent the radium content of a sample and may be used to determine the uranium content only if the sample is in secular (100%) equilibrium, or if the percentage or degree of equilibrium is known (Eichholz *et al.* 1953). The spectrogram of the present sample indicates a radium content

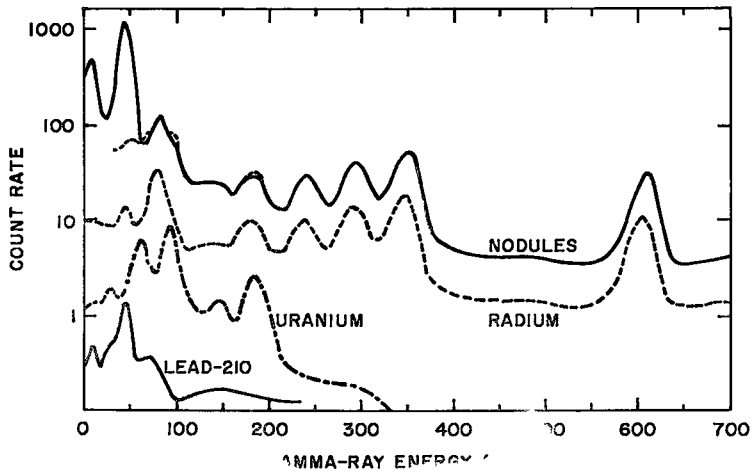

FIG. 3. Spectrogram of nodules and comparison materials. Dotted portions of the top curve show modifications necessary to match natural uranium. Comparison materials are shown separated vertically for clarity.

which would be associated with 0.005% uranium, provided that 100% equilibrium prevailed. However, since the principal peak between 50 and 100 keV is much narrower than in the case of natural uranium and closer to that of uranium-free radium, the actual uranium content is estimated to be closer to 0.002%.

An additional feature in the spectrogram — one not normally encountered in natural radioactive samples — is the anomalously high peak in the low-energy range centred just below 47 keV: this peak is at least 25 times higher than any peak of similar energy obtained from uranium or radium. The peak was identified using an expanded low-energy scale, 0.66 keV per channel, and calibrated with the following known emitters: Am-241, at 59.5 keV, Pb-210 at 46.52 keV, Cs-137 (Ba K X-ray) at 32.0 keV, and Cd-109 (Ag K X-ray) at 22.1 keV. The peak from the nodules coincides on the energy scale with the 46.52 keV peak from Pb-210; this reference emitter was contained in the residue from depleted radon needles. A sample containing natural thorium and its daughters produced no peak near this energy; natural uranium produced a small peak, but closer to 40 keV; only radium, free of uranium, produced a clearly-defined peak near 47 keV.

The 21-year half-life of Pb-210 is of significance in formulating a theory to explain its origin in the nodules. All of the natural decay products between Ra-226 and Pb-210 have very short half-lives: minutes or less except for radon (Em-222) which has a 3.8-day half-life. Thus, nearly complete equilibrium, 99.8% in one month, is quickly established over this part of the series; the gamma radiation from Bi-214 therefore accurately provides a measure of the radium content of the nodules. Only 4% or less of the Pb-210 in the nodules can be accounted for by the radium/radon content of the sample. Because the remainder was probably introduced from a different source its distribution in the nodules might well differ from that of the radium-derived activity, shown by autoradiography to be a surface effect.

It was suspected that radon gas had been the source of the excess of Pb-210. It was hypothesized that the solid nuclei formed by the decay of radon attached themselves to carbon particles and these became incorporated in the nodules as they formed. This resulted in an even dissemination of Pb-210 throughout the whole volume of each nodule.

To test this hypothesis the surface layers of a test group of about 900 nodules, weighing initially 1.3 g, were ground away in three stages by propulsion against the walls of a ring-shaped cavity using an air jet; equivalent periods of grinding were used during each stage. It is important to note that most concave surfaces of the nodules could not be ground away by this method and therefore only about 50% of the total surface area (visual estimate) was affected by the grinding. Approximately 3% of the weight was removed in each stage of abrasion. These changes are plotted in Figure 4 together with the related changes in gamma-ray intensity. In the case of the 47 keV peak, there was sufficient activity to plot peak height as the measured parameter; however, the radium daughters did not produce well-defined peaks so that count yield in a broad band of energies

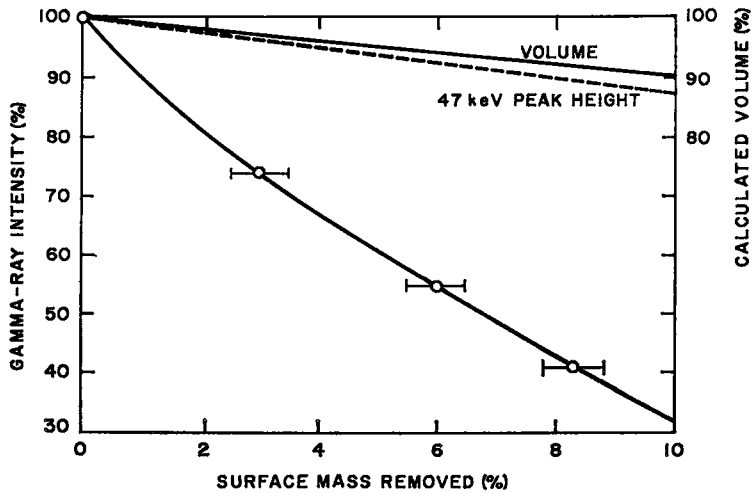

FIG. 4. Effect of surface grinding on gamma-ray intensity, and volume.

from 120 to 480 keV was plotted in the latter case. It is obvious from the curves that the radon-derived activity is a volume-related effect, whereas the change in radium-derived activity is related much more directly to removal of surface material.

Other Occurrences

Recent study has shown that carbonaceous nodules from the Denison mine resemble those from Milliken in that they are usually associated with "pilolite" and show weak radioactivity on some surfaces. R. J. Gunning, mine geologist, points out (pers. comm. October 1975) that the Denison nodules occur in open fractures, faults, and small vugs and are found only along that portion of the wall of a stope or drift that exposes a section of a fault plane. Similar nodules from the New Quirke mine are often embedded in a felted mass of "pilolite" and exhibit weak radioactivity on some surfaces: not all of the surfaces of any one nodule are radioactive.

Discussion

The nodules are composed mainly of carbon; significant amounts of oxygen, hydrogen, and sulfur are also present and less than 1% of ash remains after ignition. Most of the sulfur is evenly disseminated in the nodules.

The nodules show no evidence of biogenic origin; rather, their occurrence in the mine, on the walls of a drift and at the exposure in the drift of a steeply dipping fracture zone, and also their nodular form and lack of crystallinity suggest colloidal deposition in open spaces. The optical properties and radioactive characteristics of the carbon differ markedly from those of normal "thucholite" found in Elliot Lake conglomerates and it is therefore considered probable that these materials were formed at different times. Radioactive black seams of normal "thucholite", up to 6 mm thick, contain angular grains of uraninite inclusions. The weakly radioactive, glossy, carbon nodules, on the other hand, are of late origin, according to Robertson & Steenland (1960) who suggested that they may have been formed in open joints by reprecipitation from solutions of first-formed "thucholite".

The authors believe, however, that formation of the nodules occurred as a concomitant of mining operations. This is based on the evidence of the anomalously high peak in the low-energy range of the gamma spectrum, which has been attributed to an excess of Pb-210 derived from radon and which clearly indicates that the radon and its daughters were introduced into the nodules not more than several decades ago. It is hypothesized that the nodules formed on the moist walls of the haulage drift by coagulation of colloidal particles of carbon. Particulate decay products of radon in the mine atmosphere, as well as air-borne sulfide particles, were attracted and adsorbed by fine, fluffy, porous carbon particles in the exhaust fumes of diesel engines used underground. Some of these particles settled on the wet walls of the drift and particularly near the fault zone intersection, where descending acidic mine waters, carrying small amounts of radium, uranium, iron and other elements, seeped into the drift. As the number of carbon particles in suspension increased, they aggregated to form a gel which dried and hardened into rounded masses under the influence of surface tension, when the solution evaporated. The occurrence of radium, and possibly uranium, in the outer layer of nodules may have resulted from migration of the solution toward the surface as the particles coalesced, and the ensuing concentration there of radioactive elements as the nodules dried.

Diesel exhaust is believed to be a more likely source of the carbon than re-mobilized uraniferous carbon. The range of radon recoil ions in air is about 600 times that in water, and the concentrations of diesel carbon in mine atmosphere during mining operations could be expected to be much higher than that of carbon from the ore, transported in suspension or in solution by meteoric water. Therefore the possibility of attachment of recoil ions to airborne particles is much more probable than to particles in water, and the formation of nodules from diesel carbon is strongly favored.

If the nodules were in radioactive equilibrium the ratio of uranium to radium would be that of their half lives, i.e., $4.5\times10^{9}/1620=2.8\times10^{6}$. The actual ratio, $U/Ra = 0.0045/19\times10^{-10} = 2.4\times10^{6}$, indicates a slight excess of radium (or deficiency of uranium) relative to equilibrium proportions. If the nodules were old enough to be in secular equilibrium this variation might be attributed to experimental error in the analyses. Since the nodules are of recent age, however, and since the U/Ra ratio of Elliot Lake mine waters is at least two orders of magnitude greater than the equilibrium ratio, the actual proportions of these elements in the nodules probably reflect selective absorption by the carbon of radium rather than of uranium or thorium.

The asbestos-like mineral, "pilolite", was probably a product of rock faulting; where it is present in the fractured rock the descending solutions may carry loose fibres in suspension

which become cemented around the nodules as the solutions evaporate or during periods of reduced seepage.

The tendency of radon progeny to attach themselves to airborne particles was studied by Duggan & Howell (1969). Tests in an operating Cornish tin mine showed that 80–90% of the RaA produced became attached; the radon level was fairly constant at about 700 pCi/l and the concentration of condensation nuclei was about 10^4 particles/cm^3. Their study indicated a concentration in one urban environment of $2x10^4$ to $8x10^4$ particles per cm^3; therefore, it seems reasonable to expect that in a confined space in the presence of diesel smoke an attachment in excess of 90% would be achieved.

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