Reprinted from AMERICAN INDUSTRIAL HYGIENE ASSOCIATION JOURNAL
Volume 28, September-October, 1967

Exposure to Metals in the Manufacture of Asbestos Textile Products

L. J. CRALLEY, R. G. KEENAN, and J. R. LYNCH

Occupational Health Program, National Center for Urban and Industrial Health, U. S. Public Health Service, 1014 Broadway, Cincinnati, Ohio

Asbestos textile workers processing chrysotile were exposed, in the past, to significant airborne levels of nickel, chromium, and manganese. Limited studies indicate that other metals were also involved. It is likely that the phenomenon shown in asbestos textile manufacturing is also true in other asbestos mining, milling, and processing operations. Sufficient evidence is presented in this study to indicate that the role of metals in the etiology of disease associated with asbestos inhalation should not be ignored. It is no longer tenable to look only for asbestos fibers or bodies in biological tissue and by their presence assume a cause and effect relationship with the disease.

Introduction

IT WAS KNOWN around the turn of the century that excessive exposure to asbestos gave rise to a disabling and fatal pneumoconiosis.[1,2,3] More recently, a number of investigators have related a higher prevalence of pulmonary and other cancer to asbestos workers.[4-8] It was generally assumed that the asbestos fiber was the causative agent since the rate of pulmonary cancer was much higher in persons having asbestosis.[9,10,11]

A further look into the environmental exposures of workers processing asbestos revealed potential exposures to hazardous materials other than asbestos, not generally appreciated during the earlier investigations. Also, the latent period of 20 years and longer from initial exposure to the onset of disease made retrospective assessment of pertinent exposures very difficult. This is especially true of the period before World War II when dust control was much less effective and high dust exposures were common at many operations. The carcinogenic agent(s) may have been one or more types of the asbestos fibers, trace minerals and polycyclic aromatic oils associated with the asbestos fibers, other additives in processing (such as coal-tar, pitch, oils, and metals), tobacco smoke, community air pollutants, or some combination of these factors.

Even though it was known in the early 1900's that asbestos minerals contained small amounts of metals,[12] no significance was given to their presence. These metals may exist independently as minerals or native alloy metals associated with the asbestos ore body and may form a minor part of the crystalline structure of the fiber.[13,14] Harington,[15] in single sample analyses, further attested to the presence of these metals in three types of asbestos and speculated on the meaning of their presence.

The present investigation was undertaken to define the nature and extent of exposure to metals in the manufacture of asbestos textile products. In addition to the metals in the form of minerals associated with the asbestos fiber, it was realized that a second source of exposure to metals may be alloy particulates abraded and liberated into the air during the processing of the asbestos. These have never been studied as potential sources of exposure of asbestos workers.

TABLE I
Designated Metals in Mine-milled
Asbestos Fiber by Type and Source of Asbestos*

Type	Source	No. Samples	% Ni	% Cr	% Co	% Mn
Chrysotile	Canada	27				
	Range		0.01-0.20	<0.01-0.12	<0.01-0.01	0.03-0.08
	Average		0.10	0.04	<0.01	0.04
	Median		0.10	0.03	<0.01	0.04
	Africa	8				
	Range		0.12-0.29	0.06-0.17	<0.01	0.03-0.09
	Average		0.14	0.09	<0.01	0.05
	Median		0.15	0.09	<0.01	0.05
Crocidolite	Africa	3				
	Range		<0.01	<0.01	<0.01	0.01-0.03
	Average		<0.01	<0.01	<0.01	0.02
	Median		<0.01	<0.01	<0.01	0.02
Amosite	Africa	4				
	Range		<0.01	<0.01	<0.01	0.14-1.48
	Average		<0.01	<0.01	<0.01	0.79
	Median		<0.01	<0.01	<0.01	0.77

*Adjusted to the nearest 0.01%, 0.01% = 100 μg/gm.

The samples collected during the investigation were analyzed quantitatively for designated metals; atomic absorption spectrophotometry was used for the determination of nickel, chromium, cobalt, and manganese, and emission spectrography for other metals. This report covers only the preliminary findings on nickel, chromium, cobalt, and manganese since these are known to be present as minerals in many of the asbestos ores and are also present in the alloys of processing equipment. A subsequent report will be made on the full spectrum of metals tested.

Metal Content of Milled Fibers

The nickel, chromium, cobalt, and manganese content of mine-milled asbestos fibers is shown in Table I. In Canadian chrysotile the nickel ranged from 0.01 to 0.20% with an average of 0.10%; chromium <0.01 to 0.12% with an average of 0.04%; cobalt <0.01%; and manganese 0.03 to 0.08% with an average of 0.04%. The nickel and chromium were around 50 to 100% greater in the African than in the Canadian chrysotile. The cobalt and manganese content were about the same in chrysotile from both sources.

The nickel and chromium content of the crocidolite and amosite ranged under 0.01%, less than a tenth of that found in chrysotile. The cobalt remained around the same level, under 0.01%. The manganese showed a 50% decrease in crocidolite compared to the chrysotile while the amosite showed around a twentyfold increase. Additional samples of crocidolite and amosite fibers will be analyzed to verify the values presented since they are from a limited number of samples. The spectrum of metal exposures is being extended to include other metals in different types and sources of asbestos.

The mine-milled chrysotile was further examined for major differences in metal content by grade and source of fiber. These data are given in Table II. The percentage of metals in Canadian grades 1, 2, and 7 showed little change between grades and source of fiber, with nickel averaging 0.15 to 0.18%: chromium 0.05 to 0.08%: cobalt, under 0.01%; and manganese 0.03 to 0.05%. Grade 3, however, showed a marked difference in that the nickel and chromium were only approximately one-fourth of that present in grades 1, 2, and 7. Grade 4, with the exception of one high value sample, showed nickel and chromium values approximately one-half of grades 1, 2, and 7. The metal content of the African fiber was generally higher than the Canadian fiber for the same grade. Since only limited samples were analyzed in some grades, additional work needs to be done to confirm these reported relationships.

In the earlier years, the fibers in grades 1 and 2 were only partially opened at the mines. Although the fibers of grade 3 were opened more fully at the mines, the milling in the earlier years was less exacting, so that

TABLE II
Designated Metal in Mine-milled Samples of Chrysotile by Grades and Source*

Fiber Grade	No. Samples	Source		% Ni	% Cr	% Co	% Mn
1—3/4"	3	Canada	Range	0.15-0.16	0.05-0.08	0.01	0.03-0.08
			Average	0.15	0.06	0.01	0.05
		Africa	—	—	—	—	—
2-3/8" to 3/4"	5	Canada	Range	0.13-0.16	0.08-0.12	<0.01-0.01	0.03-0.04
			Average	0.15	0.08	<0.01	0.03
	5	Africa	Range	0.12-0.29	0.04-0.12	<0.01-0.01	0.03-0.09
			Average	0.17	0.09	<0.01	0.05
3—spinning	10	Canada	Range	0.01-0.06	0.01-0.10	<0.01-0.01	0.03-0.06
			Average	0.04	0.02	<0.01	0.04
		Africa	—	—	—	—	—
4—shingle	5	Canada	Range	0.05-0.21	0.02-0.03	<0.01-0.01	0.04-0.05
			Average	0.11	0.02	<0.01	0.04
	1	Africa		0.20	0.07	<0.01	0.05
7—shorts	2	Canada	Range	0.16-0.20	0.05-0.06	0.01	0.05-0.06
			Average	0.18	0.05	0.01	0.05
	1	Africa		0.16	0.17	0.01	0.05

*Adjusted to nearest 0.01%; 0.01% = 100 μg/gm.

TABLE III
Comparison of Designated Metal Levels in Mine-milled Chrysotile from Same Source by Grades According to Size Fractions

	Micrograms of element per gram of sample			
Asbestos Sample	Ni	Cr	Co	Mn
7TF (milled 1950)				
A[a]	1756	371	34	574
B[b]	2008	546	103	602
B/A[c]	1.1:1.0	1.5:1.0	3.0:1.0	1.0:1.0
7TF (milled 1965)				
A	1184	238	66	360
B	1686	564	96	538
B/A	1.4:1.0	2.4:1.0	1.4:1.0	1.5:1.0
4T (milled 1948)				
A	706	103	42	289
B	1718	529	95	627
B/A	2.4:1.0	5.1:1.0	2.3:1.0	2.2:1.0
4T (milled 1965)				
A	861	68	52	248
B	1665	441	94	515
B/A	1.9:1.0	6.5:1.0	1.8:1.0	2.1:1.0

[a] A is size fraction retained by 200 mesh sieve.
[b] B is size fraction passed through 200 mesh sieve.
[c] B/A is the ratio of the designated elements concentrations in these two size fractions.

the fiber carried a great excess of fines. This likely was also true of grades 4 and 7. The grade 3 analyzed in this study represents a much cleaner milled fiber than that of the pre-World War II period.

Since different grades of mine-milled chrysotile showed contrasting differences in the nickel and chromium content, two grades of chrysotile from the same source but from different processing years were separated into two size fractions, over and under 200 mesh (approximately 74 microns) and analyzed for metals. These data are shown in Table III. The metal content of the smaller size fraction was appreciably greater than that in the larger size fraction for both grades. The ratio of metal content of the smaller size fraction of grade 4T was much greater than that in grade 7TF with chromium five to six times greater in the smaller size fraction than in the larger size fraction of the same sample.

In a further effort to determine the source of the metals in the mine-milled asbestos, samples of chrysotile ore were fractionated into different cross-sectional zones, and these zone samples were then analyzed for metals.

TABLE IV
Designated Metal Content of Chrysotile Ore by Cross-sectional Zone Areas

Ore Zone	No. Samples		Micrograms of metal per gram of sample Ni	Cr	Co	Mn
Cleaned fiber	6	High	1420	510	50	360
		Low	120	—	23	210
		Average	282	101	36	293
		Median	190	19	36	310
Fiber ends	4	High	1600	1100	75	445
		Low	145	25	31	290
		Average	606	329	50	375
		Median	240	95	48	382
Magnetic concentrate (fiber)	3	High	420	270	110	565
		Low	180	100	—	260
		Average	267	177	37	415
		Median	200	160	—	420
Magnetic concentrate (serpentine)	2	High	3150	12530	230	1960
		Low	1100	520	87	655
		Average	2125	6525	158	1307
		Median	2125	6525	158	1307
Wall rock (serpentine)	3	High	2450	2330	110	565
		Low	1240	390	60	320
		Average	1835	1027	80	465
		Median	1815	510	69	510
Ratio of metal in wall rock to cleaned fiber			10:1	27:1	2:1	2:1
Ratio of metal in wall rock magnetic concentrate to cleaned fiber			11:1	343:1	4:1	4:1

These data (Table IV) show that the nickel content of the cleaned fiber, fiber ends, and fiber magnetic concentrate remained fairly constant, 190 μg to 240 μg/gm. The nickel content of the adjoining serpentine rock (1815 μg/gm) and its magnetic concentrate (2125 μg/gm), however, were 10 and 11 times higher, respectively, than that of the cleaned fiber. The cleaned fiber showed a median chromium content of 19 μg/gm compared to 510 μg/gm in the adjoining wall rock and 6525 μg/gm in the wall rock magnetic concentrate. The latter data, however, are based on only two samples in one of which the chromium content was extremely high. The adjoining rock and its magnetic concentrate had two and four times as much cobalt as the cleaned fiber. The manganese content of the wall rock was two times greater and its magnetic concentrate four times greater than that of the cleaned fiber. Additional information is being obtained on the variation in metal content of different types of asbestos ore from separate geographical areas as well as on the metal content and relative solubility as the ore bodies change from surface to deeper sites. It is known that minerals from surface ores often have different characteristics from those of ores at deeper levels of the same ore body.

Data in Table I show that mine-milled chrysotile contains an appreciable amount of nickel, chromium, and manganese. The levels of cobalt were consistently low. Tables II, III, and IV indicate that considerable portions of these metals are concentrated in the smaller size fraction of the milled asbestos and that the wall rock and magnetic concentrate are a major source. It is not known, however, to what extent metals in the milled fiber may have also resulted from the abrasive action of the asbestos fiber on the metal alloys in the milling equipment or from different milling procedures. The extent to which the metals may be distributed between the respirable size grains or fibers is also unknown.

Levels and Sources of Airborne Metal Exposures

In our study of the extent and source of metal exposures in asbestos textile manufacturing, an asbestos textile manufacturing plant cooperated in setting up a special test run in which the same batch of asbestos fiber of known metal content was followed through successive stages of asbestos textile manufacture, including fiber preparation, carding,

TABLE V
Levels of Designated Metals in Bulk Chrysotile Fiber and in Airborne Dust During Textile Manufacturing with Exhaust Ventilation Off

Operation	Sample	Metal in Sample[a] % Ni	% Cr	% Co	% Mn
Fiber preparation					
Pan grinding	Crude ore after opening	0.02	<0.01	<0.01	0.04
Blending	Blending fiber	0.16	0.09	0.01	0.03
Blending and screening	Blended and screened fiber	0.16	0.08	<0.01	0.03
Fiberizing	Fiberized asbestos	0.10	0.06	<0.01	0.03
Combing	Combed fiber	0.07	0.03	<0.01	0.03
	Airborne dust from combined fiber preparation operations	0.16	0.13	<0.01	0.06
	Ratio of metal in airborne dust to metal in combed fiber	2.3:1.0	4.3:1.0	—	2.0:1.0
Carding	Bulk fiber entering carder	0.07	0.03	<0.01	0.03
	Roving leaving carder	0.08	0.04	<0.01	0.03
	Airborne dust at carder	0.22	0.17	0.01	0.07
	Ratio of metal in airborne dust to metal in roving	2.7:1.0	4.2:1.0	—	2.3:1.0
Spinning	Roving before spinning	0.08	0.04	<0.01	0.03
	Yarn from spinner	0.08	0.04	<0.01	0.03
	Airborne dust at spinner	0.13	0.11	0.01	0.07
	Ratio of metal in airborne dust to metal in yarn	1.6:1.0	2.7:1.0	—	2.3:1.0
Twisting	Yarn before twisting	0.08	0.04	<0.01	0.03
	Twisted yarn	0.09	0.04	<0.01	0.03
	Airborne dust at twister	0.12	0.07	0.01	0.06
	Ratio of metal in airborne dust to metal in twisted yarn	1.5:1.0	1.7:1.0	—	2.0:1.0
Weaving[b]	Filler yarn	0.14	0.06	<0.01	0.02
	Warp yarn	0.14	0.06	<0.01	0.02
	Woven asbestos	0.14	0.06	<0.01	0.02
	Airborne dust at loom	0.16	0.07	<0.01	0.04
	Ratio of metal in airborne dust to metal in woven asbestos	1.1:1.0	1.2:1.0	—	2.0:1.0

[a]Adjusted to nearest 0.01%; 0.01% = 100 $\mu g/g$
[b]Filler and warp yarn different batch than the special run

spinning, and twisting. Ventilation was turned off during the tests, and operations were conducted to simulate procedures used in the 1930's. Samples of bulk fibers were collected as they entered and left each process. At each process, airborne dust was also collected on membrane filters by means of high volume air samplers. These data are shown in Table V.

The special test batch was made up of approximately 60% of a commercially milled fiber of the type presently used in textile manufacture blended with 40% pan ground No. 2 crude fiber added to simulate weaving grades of fiber of the mid-1930's.

Since a blend of two grades of asbestos with different trace metal contents was used in fiber preparation, it was impossible to relate specific trends in metal contents of the test batch of asbestos previous to fiberizing and combing. The metal content of the bulk fiber remained fairly constant as it passed from blending, fiberizing, and combing through successive operations of carding, twisting, and spinning, nickel 0.07 to 0.09%, chromium 0.03 to 0.04%, cobalt <0.01%, and manganese 0.03%.

The airborne dust from the fiber combing operations showed the following ratio increases of metal contents over that of the combed and blended fiber: nickel 2.3:1.0, chromium 4.3:1.0, cobalt, no difference, and manganese 2.0:1.0. Data in Tables II, III, and IV indicate that a major source of the metals was the fines carried with the milled fiber. It is not known to what extent this source may have been supplemented by the abrasive action of the chrysotile on the processing equipment in fiber preparation.

As the chrysotile passed through the successive operations of carding, spinning, and twisting, the ratios of metals in the airborne dust to the bulk fiber were: carding — nickel 2.7:1.0, chromium 4.2:1.0, cobalt, no difference, manganese 2.3:1.0; spinning — nickel 1.6:1.0, chromium 2.7:1.0, cobalt, no difference, manganese 2.3:1.0; twisting — nickel 1.5:1.0, chromium 1.7:1.0, cobalt, no difference, manganese 2.0:1.0.

It was impossible to follow processing of

TABLE VI
Designated Metals in Metal Alloy of Processing Equipment*

Processing Equipment	% Ni	% Cr	% Mn	% Co
Pan Grinder				
Bottom of pan	0.01	0.01	0.40	0.01
Roller	0.02	0.01	1.04	0.02
Carder				
Finisher wire	0.01	0.03	0.65	0.01
Finisher leader wire	0.01	0.02	0.56	0.01
Breaker wire	0.02	0.03	0.61	0.01
Breaker leader wire	0.02	0.03	0.34	0.01
Leather apron	0.06	4.60	0.03	<0.01
Mule spinner				
Spinner guide wire	0.05	0.02	0.24	0.01
Ring spinner				
Spinner traveler	0.03	0.04	0.51	0.01
Spinner guide	0.10	2.27	0.19	0.01
Loom				
Drop wire beddle	0.32	17.00	0.50	0.03

*Adjusted to nearest 0.01%; 0.01% = 100 μg/g.

TABLE VII
Airborne Levels of Designated Metals in Seven Asbestos Textile Plants, 1961-65, by Operation

Operation	Micrograms of element per cubic meter of air			
	Ni	Cr	Co	Mn
Fiber preparation				
Range	0.50-1.41	0.10-0.79	0.01-0.28	<0.01-0.70
Average	0.87	0.44	0.10	0.33
Median	0.71	0.39	0.09	0.31
Special run (ventilation off)	26.00	20.50	1.19	10.30
Carding				
Range	0.69-8.36	0.44-1.87	<0.01-0.37	<0.01-1.28
Average	2.99	1.15	0.16	0.91
Median	2.14	1.43	0.09	0.69
Special run (ventilation off)	23.60	18.00	1.08	8.94
Spinning				
Range	1.15-7.17	0.60-4.29	0.07-1.10	<0.01-2.45
Average	3.31	1.66	0.26	1.00
Median	2.64	1.41	0.12	1.00
Special run	1.25	0.88	0.07	0.52
Twisting				
Range	1.02-39.0	0.35-3.00	0.02-0.81	<0.01-2.47
Average	8.14	0.97	0.22	1.05
Median	1.54	0.60	0.10	1.07
Special run (ventilation off)	3.66	2.13	0.18	1.89
Weaving				
Range	<0.01-4.26	0.03-1.75	<0.01-0.17	<0.01-2.37
Average	0.72	0.38	0.06	0.39
Median	0.01	0.13	0.03	0.04
Special run (ventilation off)	1.74	1.21	0.08	0.66

the same batch of asbestos through weaving because of the great amount of asbestos required for this operation. A separate test showed ratio increases of metal in the airborne dust over the woven asbestos of 1.1:1.0 for nickel, 1.2:1.0 for chromium, no change for cobalt and 2.0:1.0 for manganese. It was noted, however, that little dust was produced at this operation during the test period, and the operation may not have represented weaving during the mid-1930's.

It is likely there was continued release of the fines in the bulk chrysotile being processed beyond the blending and combing state and that this constituted one source of the metals in the airborne dust. However, since the percentage of metals in the bulk chrysotile at subsequent processing stages remained fairly constant and the ratio of metals in the airborne dust to bulk asbestos at carding was equal to that at fiber preparation, it is apparent that a supplementary source contributed metals to the air.

We studied the abrasive action of the asbestos on the processing equipment as a potential source by testing for designated metals in representative metal parts of the processing equipment having harsh contact with the

TABLE VIII
Estimated Past Levels versus Current Levels of Designated Metals in Airborne Dust in Asbestos Textile Plants by Operations

	Micrograms of element per cubic meter of air				Total Metals
	Ni	Cr	Co	Mn	
Fiber preparation					
pre 1930-35	210.0	160.0	9.0	80.0	460.0
1935-45	100.0	80.0	4.5	40.0	230.0
current (average)	0.87	0.44	0.1	0.33	1.7
Carding					
pre 1930-35	330.0	250.0	15.0	120.0	720.0
1935-45	160.0	130.0	7.0	80.0	380.0
current (average)	3.0	1.1	0.16	0.91	5.2
Spinning					
pre 1930-35	10.0	7.0	1.0	4.0	22.0
1935-45	10.0	7.0	1.0	4.0	22.0
current (average)	3.3	1.7	0.26	1.0	6.2
Twisting					
pre 1930-35	29.0	17.0	1.0	15.0	62.0
1935-45	7.0	4.0	—	4.0	15.0
current (average)	8.1	0.97	0.22	1.1	10.4
Weaving					
pre 1930-35	52.0	36.0	2.0	20.0	110.0
1935-45	17.0	12.0	1.0	7.0	37.0
current (average)	0.72	0.38	0.06	0.39	1.5

asbestos. These data are shown in Table VI. The presence of these metals in the alloy of the processing equipment and the plant maintenance experience of frequent replacement of equipment parts having immediate contact with asbestos indicate that the abrasive action of asbestos on the equipment is a supplementary source of airborne metal exposure. This is further substantiated in that the fines from under the processing equipment had an appreciably greater metal content than the bulk chrysotile being processed through the equipment.

Present and Past Levels of Airborne Metals

Airborne levels of designated metals in seven asbestos textile plants, 1961–65, are shown by operations in Table VII. The low levels of metals in the air and the large air sample volumes required made it necessary to use stationary high volume sampling equipment. These samplers were placed near a number of operating units and in the immediate vicinity of the worker so as to be representative of the worker's exposures. For comparative information, the airborne metal concentrations of the special test run are also shown. Although the data presented in Table VII represent limited samples in that all types of processing, including different grades and blends of asbestos, are not covered, it is believed that they represent realistic exposure levels. Supplemental data on this will be reported later.

The average airborne levels for nickel in the seven textile plants combined ranged from 0.72 $\mu g/m^3$ at weaving to 8.14 $\mu g/m^3$ at twisting. The maximum values, however, ranged from 1.41 $\mu g/m^3$ at fiber preparation to 39.0 $\mu g/m^3$ at twisting. Average values for chromium ranged from 0.38 to 1.66 $\mu g/m^3$ with maximums from 0.79 to 4.29 $\mu g/m^3$. Both average and maximum values for cobalt were under 1.1 $\mu g/m^3$. Average values for manganese ranged from 0.33 to 1.05 $\mu g/m^3$ with maximums of 0.70 to 2.47 $\mu g/m^3$. The increase in maximum over average values largely represented differences in the dust control programs, housekeeping, and maintenance between the different plants as well as operating practices and the nature of the product being manufactured at the time of the study. Additional sampling will be done to supplement these data and further define current exposures to metals in the manufacture of asbestos textile products.

It is important to note the sharp increase in metal content of the airborne dust when the ventilation was turned off. Table VIII shows estimated levels of metals in airborne dust of asbestos textile plants, by operations, during different periods of time.

Past exposures were estimated as follows: Total dust concentrations were determined at each operation of the special test run with the impinger-light field dust counting technique. Ratios of dust levels were estimated by contrasting concentrations at designated

TABLE IX
Levels of Designated Metals in Mine Milled Chrysotile Before and After Laboratory Grinding

Grinding Equipment			Micrograms of metal per gram of chrysotile Ni	Cr	Co	Mn
Mixer mill (cemented tungsten carbide using cobalt as a binder) Grinding 10 minutes	Sample 1	(a)*	365	197	37	270
		(b)*	360	193	73	280
		(c)*	—	—	2.0:1.0	—
Grinding 10 minutes	Sample 2	(a)	630	170	47	510
		(b)	555	165	215	430
		(c)	—	—	4.5:1.0	0.8:1.0
Grinding 10 minutes	Sample 3	(a)	1670	1550	53	425
		(b)	1500	1500	113	405
		(c)	—	—	2.1:1.0	—
Hammer mill (chrome steel) Recycle Grinding (continuous)	Sample 1	(a)	90	38	12	not determined
		(b)	245	153	22	not determined
		(c)	2.7:1.0	4.0:1.0	1.8:1.0	—
Grinding 10 hours	Sample 2	(a)	630	170	47	510
		(b)	680	590	38	420
		(c)	—	3.5:1.0	0.8:1.0	0.9:1.0
Ball mill (chrome steel) Grinding 8 hours	Sample 1	(a)	90	38	12	not determined
		(b)	134	114	8	not determined
		(c)	1.5:1.0	3.0:1.0	0.8:1.0	—

*(a) Before grinding; (b) After grinding; (c) Ratios of metal in ground to preground chrysotile.

operations of the test run with concentrations reported in past studies at the same operations. The metal concentrations found in the airborne dusts during the test runs were multiplied by these ratios to predict past exposures to metals. It is realized that this procedure for estimating past exposure has many limitations, since the relation of dust counts to mass values is quite variable and the information on respirable mass of past airborne dust at the operations studied is unavailable. However, with the finding that the metals of the airborne dust around processing equipment rose sharply when the ventilation was turned off, it is important that estimation be made of past levels of exposures to metal during the periods when dust control was lacking or less effective.

Data in Table VIII show that a rather uniform ratio existed between the airborne levels of nickel, chromium, and manganese at different operations with chromium representing 70 to 80% and manganese 40 to 50% of the nickel values: exposure to cobalt was minimal.

In the past, the greatest levels of airborne dust occurred at carding and fiber preparation, followed by weaving, twisting, and spinning. In the pre-1930-35 period, levels of exposure were conservatively estimated, at carding, to be: 330 $\mu g/m^3$ for nickel, 250 $\mu g/m^3$ for chromium, and 120 $\mu g/m^3$ for manganese; fiber preparation: 210 $\mu g/m^3$ for nickel, 160 $\mu g/m^3$ for chromium, and 80 $\mu g/m^3$ for manganese. The values for corresponding metal exposures at weaving, twisting, and spinning were considerably lower. The massive dust during the earlier years at fiber preparation and carding are known to have contaminated the ambient air at subsequent operations so that the predicted values at spinning, twisting, and weaving are somewhat low.

The values for metals in airborne dust for the period 1935–45, during which dust control programs were generally initiated, were estimated at around 50% of those during the previous period. After World War II, there was greater emphasis on dust controls and levels gradually were reduced to the values found during 1961-65.

In contrasting exposures of the pre-1930-35 period with those of today, the exposures to the total metals reported were greater by a conservative factor of 270 at fiber preparation, and 140 at carding. Although the data show factors of 70 at weaving, 7 at spinning, and 6 at twisting, these are undoubtedly quite low due to the gross contamination of the general ambient air which, in the past, existed throughout all operations.

Grinding of Asbestos for Laboratory Research

In preparing asbestos for animal dosing studies, it is often the practice to grind the larger size fibers to the lower micron range using equipment such as the hammer mill and the mixer mill. To test the extent to which metal contamination may occur during the breaking down of the asbestos fibers through laboratory milling, chrysotile with a known percentage of designated metals was reduced in a hammer mill and a ball mill, made of a chrome steel alloy, and in a mixer mill made of cemented tungsten carbide with cobalt as a binder. It was found that chrysotile, after being ground for ten minutes in a cemented tungsten carbide mixer mill, picked up increased cobalt in ratios ranging from 2 to 4.5 over that in the preground asbestos. In the hammer mill, the increase of chromium ranged from 3.5 to 4.0 over the amount present in the preground asbestos. The ball mill showed about the same relationship with increases of 1.5 for nickel and 3.0 for chromium over the preground chrysotile. It is apparent that the asbestos abraded the metal in which it was ground. This supports the premise that the abrasive action of asbestos on processing equipment metal may be an unsuspected source of airborne metal exposure.

Discussion

The data presented show that workers in the asbestos textile manufacturing industry, in the past, were exposed to airborne dust containing significant levels of nickel, chromium and manganese. Limited studies indicate that other metals are also involved. These metals come from minerals and native alloys associated with the asbestos mineral body and from the abrasive action of the asbestos fiber on metal components of the processing equipment and raise a number of important questions involving areas in which additional research is needed. What other metals are associated with the mining, milling, and processing of asbestos? In what precise chemical forms are these metals present and what is the pattern of exposure to metals in processing other types of asbestos? What is the distribution of these metals in the respirable grains and fibers? It is plausible that the phenomenon observed in asbestos textile manufacturing will also occur in other processing of different types of asbestos. This being true, the metals associated with the asbestos may have a different qualitative and quantitative pattern depending on the type, grade, and source of the asbestos, the equipment in which it is milled and processed, and the subsequent treatment of the milled fiber.

Also, the qualitative and quantitative pattern of the metals in the airborne dust at asbestos processing operations may vary significantly from the metal content of the asbestos crude and milled fiber since the metals appear closely associated with low micron size fraction of the particulates and fibers.

In simulating past procedures of grinding asbestos for animal studies, it has been shown that chrysotile abrades and incorporates portions of the metal alloy in which it was ground. These factors of extraneous metal exposures should be reassessed in terms of past animal research, especially since much of the evidence of the carcinogenicity of asbestos is based on animal research data.

We need much more information on the levels of metals in tissues from deceased workers known to have had asbestosis, and also from lung cancer and mesothelioma cases with and without known exposure to asbestos. Information is also needed on the levels of metals in the blood and urine of workers with prolonged heavy and light exposures to asbestos.

The significance of the presence of these metals in past exposures is not clear. It is reasonable to consider their relationship with the increased pulmonary and other cancers observed in asbestos workers.[16-22]

In addition to the fact that the nature and source of the metals associated with airborne dust exposures in the processing of asbestos are important with respect to exposure evaluation and contamination control. Harington[12] showed that serum elutes significant quantities of metals from different types of asbestos. The presence of these metals and other associated materials should be studied in relation to variations of chest roentgenographic and the health patterns of workers as observed from one group of asbestos workers to another.

The specific role of the asbestos fiber, *per se*, in relation to disease observed in asbestos workers needs redefining. Although asbestos fiber was considered in the past to be the primary etiologic agent, it may have been only an arbitrary index concealing a spectrum of undefined agents and relationships. Its role must be reassessed as a co-factor acting with other agents.

Summary

Asbestos textile workers processing chrysotile were exposed, in the past, to significant airborne levels of nickel, chromium, and manganese. Limited studies indicate that other metals were also involved. It is likely that the phenomenon shown in asbestos textile manufacturing is also true in other asbestos mining, milling and processing operations. The qualitative and quantitative pattern of these airborne metal exposures may vary significantly from the metal content of the crude asbestos ore and milled fiber.

The relationship should be investigated between these metal exposures and the increased pulmonary and other cancer observed in asbestos workers. Other varying patterns of pathology including altered chest roentgenograms, pulmonary function tests and worker health patterns should be considered in relation to these exposures.

Sufficient evidence is presented in this study to indicate that the role of metals in the etiology of disease associated with asbestos inhalation should not be ignored. It is no longer tenable to look only for asbestos fibers or bodies in biological tissue and by their presence assume a cause and effect relationship with the disease.

Acknowledgments

The authors acknowledge, with appreciation, the technical assistance of Richard E. Kinser, Theodore D. Martin, and Patricia A. Mauer, who set up the atomic absorption spectrophotometric procedures and performed the analyses for nickel, chromium, cobalt, and manganese, and to George H. Edwards and Douglas L. Johnson, who assisted in collecting and preparing the environmental samples.

References

1. MARCHAND, F.: Über Eigentümliche Pigmentkristalle in Den Lungen. *Verh. Dtsch. Path. Ges. 10:* 223 (1906).
2. FAHR, T., and E. FEIGEL: Demonstrationen: Preparate und Mikrophotogramme von einem Falle von Pneumoconiose. *Munch. Med. Wschr. 61:* 625 (1914).
3. COOKE, W. E.: Pulmonary Asbestosis. *Brit. Med. J. 2:* 578 (1929).
4. DOLL, R.: Mortality from Lung Cancer in Asbestos Workers. *Brit. J. Indust. Med. 12:* 81 (1955).
5. MANCUSO, T. F., and E. J. COULTER: Methodology in Industrial Health Studies. *Arch. Environ. Health 6:* 210 (1963).
6. SELIKOFF, I. J., J. CHURG, and E. C. HAMMOND: Asbestos Exposure and Neoplasia. Presented at a Joint Meeting of the Sections on Radiology and Diseases of the Chest of the American Medical Association and the American College of Chest Physicians on June 17, 1963, at Atlantic City, N. J.
7. WAGNER, J. C., C. A. SLEGGS, and P. MARCHAND: Diffuse Pleural Mesothelioma and Asbestos Exposure in the North Western Cape Province. *Brit. J. Indus. Med. 17:* 260 (1960).
8. ENTERLINE, P. E.: Mortality Among Asbestos Products Workers in the United States. *Annals N. Y. Acad. Sci. 132:* 156 (1965).
9. LYNCH, K. M., and W. A. SMITH: Carcinoma of Lung in Asbestos-silicosis. *Am. J. Cancer* 24:56 (1935).
10. GLOYNE, S. R.: Squamous Carcinoma of Lung Occurring in Asbestosis: Two Cases. *Tubercle 17:* 5 (1935).
11. EGBERT, D. S., and A. J. GEIGER: Pulmonary Asbestosis and Carcinoma. *Amer. Rev. of Tuberc 34:* 143 (1936).
12. DANA, E. S.: A Textbook of Mineralogy. John Wiley & Sons, Inc., New York (1905).
13. BERGER, H.: Asbestos Fundamentals: Origin, Properties, Mining, Processing, Utilization. Translated from the German by Ralph E. Oesper. Chemical Publishing Co., Inc., 212 Fifth Ave., New York (1963).
14. NICKEL, E. H.: The Occurrence of Native Nickel-Iron in the Serpentine Rock of the Eastern Township of Quebec Province. *The Canadian Mineralogist 6:* 307 (1959).
15. HARINGTON, J. S., and F. J. C. ROE: Studies of Carcinogenesis of Asbestos Fibers and Their Natural Oils. *Annals N. Y. Acad. Sci. 132:* 439 (1965).
16. MASTROMATTEO, E.: Nickel: A Review of Its Occupational Health Aspects. *J. Occup. Med.* 9: 127 (1967).
17. DOLL, R.: Occupational Lung Cancer: A Review. *Brit. J. Indust. Med. 16:* 181 (1959).
18. ROE, F. J. C., and M. C. LANCASTER: Natural, Metallic and Other Substances, as Carcinogens. Mechanisms of Carcinogenesis: Chemical, Physical and Viral. *Brit. Med. Bull. 20:* 129 (1964).
19. SUNDERMAN, F. W., Jr.: Inhibition of Induction of Benzopyrene Hydrolase by Nickel Carbonyl. *Cancer Research* (To be in press in May 1967 issue).
20. SUNDERMAN, F. W., Jr.: Nickel Carbonyl Inhibition of Cortisone Induction of Hepatic Tryptophan Pyrrolase. *Cancer Research* (in press).
21. HACKETT, R. L., and F. W. SUNDERMAN, Jr.: Acute Pathologic Reaction to Parenteral Administration of Nickel Carbonyl. *Arch. Environ. Health* (in press)
22. HEUPER, W. C., and W. W. PAYNE: Experimental Studies in Metal Carcinogenesis. *Arch. Environ. Health 5:* 445 (1962).

Received June 5, 1967