Bull. Environ. Contam. Toxicol. (1990) 45:789–795

Bulletin of Environmental Contamination and Toxicology

Exposure to Non-Asbestos Refractory Materials: Morphological Changes of Airborne Particulate Following Attrition and Recrystalization

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Nonasbestos refractory blankets (NARB) belong to a group of man made materials which find increasing use in homes, business and industry as insulating materials, sound proofing and more. Currently there are no known chronic health effects in humans from long term exposure to fibers released during NARB use. In industrial uses, the ILO (International Labor Organization) has recommended to governments that all potential substitute materials for asbestos should be thoroughly evaluated for their potential harmful effects on health (Ignatov 1987). The development of alternative fibrous materials which would perform similarly to asbestos with respect to their insulation characteristics, results from the possibility of producing very long (several mm) and relatively thick (2-3 um) fibers (The Carborundum Co. 1989). These would be hardly inhalable and accordingly, would show very low pathogenic activity (Woitowitz 1985).

During industrial use at a plant which produces primary aluminum, NARB are submitted to various degrees of attrition and exposure to high temperatures. The material undergoes partial recrystalization and cristobalite-mulite is found in blankets exposed to over 1100-1200 deg C. These result in changes in the morphology (length, diameter) of the released fibers, up to the point where they are no longer fibers but more or less isodiametric particles. According to these, there is an interest in establishing the morphological characteristics of fibrous materials to which workers handling NARB are potentially exposed.

In this contribution, some morphological characteristics of fibrous materials used for the insulation of baking furnaces in the aluminum industry are described with reference to the different phases of the operation. It is shown that the morphology of the fibers released from NARB varies depending on the phase of a normal industrial use cycle of the blanket. The morphological changes occur in a range of hygienic interest, because changes in inhalability and or pathogenicity can be expected following the aerodynamic changes of the fibrous particulate. The results will be used in a following contribution where individual worker exposures to fibers will be corrected taking due account of the potential inhalability and pathogenicity of the transient morphological fiber types.

MATERIALS AND METHODS

The observations here reported were performed during regular hygienic surveillance of the operations at a primary aluminum plant. The anodes used for the electrolytic Hall-Heroult process at the plant are pre-baked in closed top vertical furnaces. Each furnace consists of several chambers which share the heated gases and which are loaded sequentially with fresh anodes. After each baking cycle which lasts about 350 h at about 1100-1200 deg C, the cover of each individual chamber is removed, the baked anodes are unloaded and the chamber pit walls and bottom are submitted to minor maintenance. This implies renewing expansion joints both at corners and at the pit walls, inspection for broken wall bricks, etc. Bands of NARB are used to seal the seat of covers on the furnace chambers and the expansion joints at the corners of the chamber pit walls and pit bottom. This occurs in an operation cycle where the NARB from first use at the cover seal goes in double bands to a second cycle of cover seals. After this, the bands are finally used to fill expansion joints at the interior of chamber pits. This third use is destructive, since after the baking cycle the joint filling must be torn into pieces to be removed from the joint channel. As a consequence of this operation cycle, workers performing the different installation and maintenance tasks could be exposed alternatively and in various degrees to new, first, second or third use NARB fibers. These exposures are not expected to be completely separated from one another, since they occur in adjacent places of the same furnace shop. Table 1 defines four operation stages which differ with respect to the degree of attrition and the length of time during which the NARB is exposed to high temperatures.

At Stage **a**, new NARB bands are cut along the main axis, unrolled and stretched along cover seals. Also, some 2nd. use cover seals are also replaced. The attrition is reduced to handling, rolling-unrolling and half cutting, and is considered low. At Stage **b**, only 1st. use cover seal bands are removed and used in double pads for a next baking cycle. At Stage **c**, new bands are used to fill expansion joints at the chamber pit

Table 1. Operation stages at the anode baking furnace where use of NARB occurs, and its estimated degree of exposure to high temperature (1100-1200 deg C) and attrition.

Stage	Expected prevailing type of NARB material					
	New	1 use	2 use	3 use	Attr.low	Attr.high
a	x	x	x		x	
b		x	x		x	
c	x	x				x
d			x	x		x

corners, all joint fillings being removed at the same time, with high attrition on the NARB material. Stage **d** is the same as **c**, but here the worker starts with 2nd. use material, removes 3rd. use and exerts high attrition on NARB.

Samples of airborne particulate were obtained at randomly (80) selected time intervals during the whole work shift. During this time, work was done with NARB at the four stages in Table 1. Air samples (5 cc) were obtained at each time point by shooting a ZEISS 10 Conimeter in the vicinity of the worker´s facial respiratory protection. The instrument consists of a calibrated cylinder pump which can be loaded against a spring and is triggered instantaneously. The aspired air-particulate sample is projected against a glass platine where the particulate material remains adhered through an adhesive covering the platine, and can be later inspected through a 200x microscope mounted in the same conimeter. A fiber is here defined as any elongated particle (long sides parallel) exceeding 5 um length and a relation length/diameter > 3. Fibers down to 0.3 um diameter can be measured with a reticule mounted in the microscope ocular. All collected fibers were counted and their length-diameter individually registered. The counts were in many cases verified with a second inspection of the platine under a 400x monochromatic slanting incident xenon lamp beam (Leitz MM6 inverted microscope) where also photographs could be obtained from fibers down to 0.2 um diameter.

Crystalization was verified in used NARB by inspection of the material with a Phillips 9920 X-ray diffractometer and comparison with adequate difraction standards.

RESULTS AND DISCUSSION

Table 2 summarizes the X-ray diffraction spectral

Table 2 Results of X-ray diffraction analysis of first use NARB.

Absolute intensity	2 theta angle	Interplanar distance (armst)	Identity
60	16.4	5.400	Mulite
35	21.6	4.100	Cristobalite
150	26.2	3.398	Mulite
35	31.0	2.882	Mulite
50	33.0	2.712	Mulite
70	35.3	2.540	Mulite
20	37.0	2.427	Mulite
25	39.2	2.296	Mulite
85	40.8	2.210	Mulite
30	42.7	2.116	Mulite
15	44.5	2.034	Cristobalite
10	49.4	1.843	Mulite
20	53.9	1.700	Mulite
20	57.6	1.599	Mulite
55	60.7	1.524	Mulite
10	63.7	1.460	Mulite

characteristics of a first use NARB. The results confirm the fact that exposure of this material to temperatures in the range 1100-1200 deg C results in the formation of cristobalite and mulite. It is reported that the amount of those compounds formed depend on the temperature attained and the length of the time during which the blanket remains at temperatures above 1100 deg C (The Carborumdum Co 1989).

Figure 1a shows the typical morphology of air suspended fibrous particulate when handling NARB at Stage **a**. Most fibers are thick, short and are probably generated by simple attrition of long, thick amorphous fibers. Figure 1b shows the morphology and variety of fiber dimensions of a sample obtained while a worker was handling NARB at Stage **c**. Shaking the blanket band to fix it into the expansion joint produced the release of long thick (1-2 um) and thin (< 1 um) fibers.

Although it is hard to find such image in the photographs, the direct observation of samples from Stage **c** and **d** revealed frequent cracks transversal to the longer axis of the fiber, which are most probably future points of breakage through attrition. The frequency of these cracks are higher in 2nd and 3rd use fibers. It is probable that those fibers which are cracked and broke afterwards may contain cristobalite-mulite.

a.

b.

Figure 1a. Air suspended fibers from NARB (Stage **a**). 1b. From Stage **d**. Small dark particles are carbon dust.

The statistical analysis of fiber lengths indicated that the averages of samples corresponding to Stages **a** to **d** were all significantly different as estimated with a two sample pairwise mean test. Figure 2 shows the cumulative relative frequencies of all four types of samples. It is observed that during Stage **a** most of the fibers released from the blanket are of short dimension, the upper limit found being 30 um. At Stage **b**, the NARB releases very long fibers which can attain a length of 200-250 um. Microscopic observations indicate that these fibers are still relatively stable

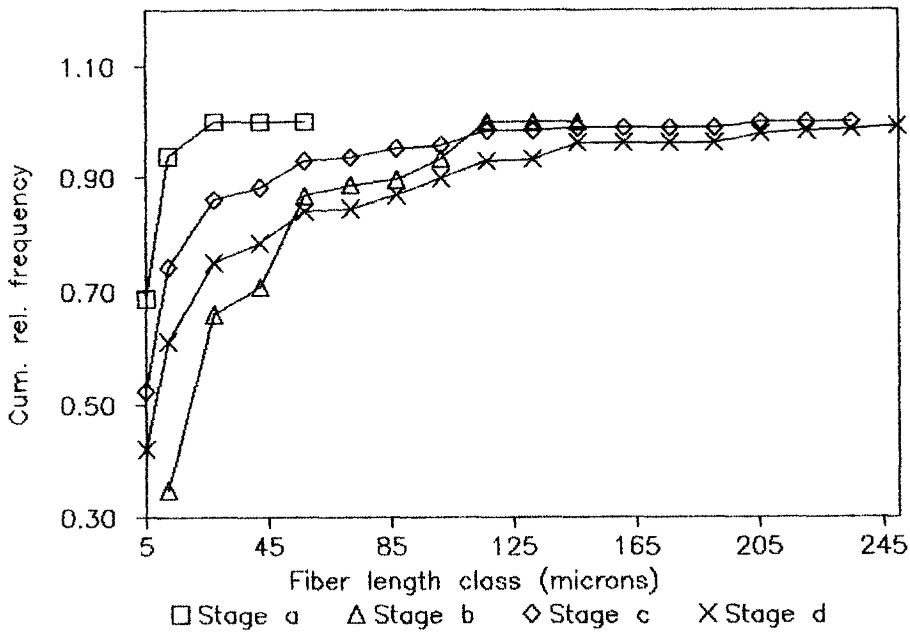

Figure 2. Cumulative relative length frequencies (Stages **a** to **d**)

since no broken pieces or cracked fibrous forms are found. At Stage **c**, some shorter fibers are again released because new blanket material is being used, but the cumulative frequencies of shorter fibers are lower than in Stage **a**, since longer fibers are released from first use blanket during the removal of joint fillings. The high attrition during removal of the old joint filling also contributes to the classes of shorter lengths. At Stage **d** shorter fibers are scarcer than in the previous case due to the absence of new blanket material.

Figure 3 summarizes the changes in fiber morphology occurring during the operations at the baking furnaces.

A pathway of morphological transformations of NARB material can be defined on the basis of observed morphological changes in air suspended fibers following various degrees of attrition and crystalization of the refractory blankets. According to this model, moderate attrition of new material releases relatively short, thick fibers, which can be assumed to be fragments of the very long original fibers composing the bulk of the blanket. Exposure to temperatures in the range 1100-1200 deg C, added to recrystalization of the material to cristobalite-mulite results in the production of non-permanent fibers. These are apparently fragile and

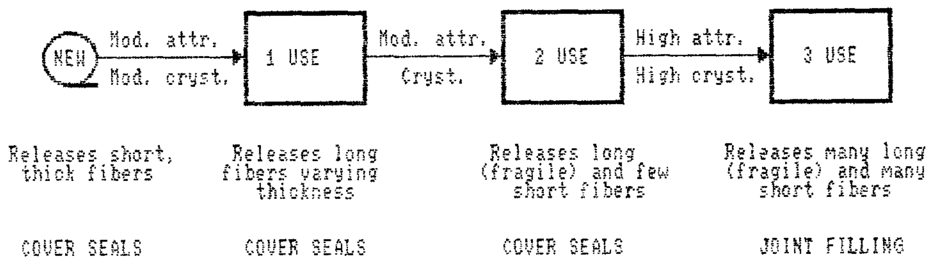

Figure 3. Summary of NARB characteristics at operation phases in the preparation of baking furnace chambers

through further manipulation and attrition can be eroded to non-fiber particulate. However, most of the "dust" generated when handling first or second use NARB consists actually in long thin fibers.

Acknowledgments. R. Weiss cooperated in obtaining the samples for this study. C. Foresio cooperated in obtaining the photographic material

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Received December 30, 1989; accepted March 28, 1990