PRESENCE OF ASBESTIFORM MINERALS IN LIGHTWEIGHT CONCRETES. THEIR ENVIRONMENTAL IMPACT

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Abstract

Lightweight concrete has a lower unit weight than conventional concrete and a high thermal insulation capacity. It is manufactured with either natural or artificial lightweight aggregates. Vermiculite, one of the natural lightweight aggregates used, is a micaceous material that when heated increases its original volume due to an exfoliation process, so its incorporation in concrete or mortar imparts very low density. These natural materials usually contain impurities such as asbestiform minerals that can be released during the expansion process, causing a harmful environmental effect. Commercial asbestos-containing materials are currently banned due to the asbestos-related lung diseases they cause.

In the province of Córdoba, Argentina, there are vermiculite mines where impurities such as asbestos group minerals have been identified. Studies using stereomicroscope, petrographic microscope, XRD, SEM, DTA and chemical analyses were conducted to characterize the different types of asbestos present and determine their particle size to assess whether they could be harmful to human health. Mica group minerals, abundant quartz and amphiboles were identified. The latter occur as isolated green crystals and their average length is 900 µm. Tremolite was determined by XRD.

The aim of the present work is to reveal the presence of these minerals and warn about their use and disposal at the end of the useful service life of the work.

1. INTRODUCTION

Lightweight concrete has a lower unit weight than conventional concrete, which is of the order of 2350 kg/m^3, and high thermal insulation capacity. It is classified as non-load-bearing or insulating lightweight concrete, and as structural lightweight concrete. This classification is based on the unit weight and the type of aggregate used [1].

Lightweight concrete has been used since ancient times. In the 1st century BC, the Romans used concrete made with pumice as aggregate to build the dome of the Pantheon in Rome. However, the use of lightweight concrete became widespread when lightweight aggregates were manufactured on an industrial scale. Currently, in Argentina their use is very limited, with lightweight aggregates being almost exclusively used in non-load-bearing concretes or in precast elements (beams, slabs, etc.) [1].

This type of concrete may be made using lightweight aggregates (fine and coarse) of natural or artificial origin, or additives that create a significant volume of voids in the material mass (cellular concrete). Pre-expanded vermiculite is one of the natural aggregates that may be used; it is a micaceous material that when subjected to heating at between 700 and 1300º C expands to 30–35 times its initial volume. This exfoliation process is caused by water vapour release as a result of a heating effect and therefore, the bulk volume weight of vermiculite is only 60–130 kg/m^3 and its incorporation in concrete or mortar imparts very low density. Vermiculite-based lightweight concretes may have apparent specific weights between 350 and 1200 kg/m^3. From the standpoint of its human health effect, previous studies have shown that vermiculite does not cause harmful effects when it is used as aggregate [2].

However, it is often mentioned that impurities (quartz, carbonates, amphiboles, asbestiform minerals, etc.) may be present and released into the air as a result of the expansion process and inhaled by people related to the industrialization process. The health effect of asbestos group minerals is closely linked to their morphology [3]. Asbestos is a commercial term that includes minerals of the serpentine (chrysotile) and amphibole (crocidolite, amosite, anthophyllite, actinolite and tremolite) groups. Asbestos minerals occur in a fibrous habit, are flexible, resistant to fire, to chemical and biological degradation and have good tensile and flexural strength. Due to these characteristics, their fibres have a harmful health effect since they can enter the airways and accumulate in the lungs, causing cancer or asbestosis [4]. For this reason, the production, importation, commercialization and use of amphibole and chrysotile fibres, and the products containing them have been banned by the Argentine Ministry of Health since 2000.

In the province of Córdoba, Argentina, there are many currently inactive vermiculite mines, namely *Los Guanacos*, *Penachos Blancos* and *La Saltona*, which have similar mineralogy, with quartz, iron oxide and amphibole impurities. Some of the materials from these deposits analysed in previous work contain asbestiform minerals [5, 6]. If they are used as lightweight concrete aggregates, they should be subjected to a previous mineralogical study to verify whether they contain asbestos.

The aim of the present work is to warn about the presence of asbestiform minerals in vermiculite, identified in previous work, in order to take the necessary precautions when they are used in lightweight concretes and in their final disposal at the end of the work useful life.

2. MATERIALS AND METHODS

Vermiculites from the province of Córdoba (Argentina), used as lightweight aggregates in the construction industry, were studied and found to contain asbestos [5], [6]. The deposits are located in the *Sierras Chicas de Córdoba* in the Department of Calamuchita, in the region comprised between Molinari and la Falda, 5 km east of the Valle Hermoso town.

The petrographic studies were conducted using a stereomicroscope, an Olympus, trinocular polarizing microscope and a JEOL JSM 35 CP scanning electron microscope equipped with an EDAX probe for qualitative elemental microanalysis (from B to U) on gold-metallised samples. Samples were analysed by X-ray diffraction using a Rigaku D-Max III-C diffractometer with Cu (Kα), λ=1.54059 Å radiation and a graphite monochromator operated at 35 kV and 15 mA between 3 and 60° 2θ.

3. RESULTS

3.1 Polarized light microscopy on thin sections

Vermiculite is composed of large brownish-grey crystals with marked pleochroism and straight extinction. Based on its optical characteristics (close to parallel extinction, perfect exfoliation in one direction and a small 2V (-) angle, it belongs to the phyllosilicate group. Due to its great expansion capacity when submitted to a temperature above 800ºC, it was identified as vermiculite. Chalcedony veins and abundant anhedral saccharoidal quartz crystals with undulatory extinction are commonly observed in the intercrystalline spaces. Talc has crystallised as fibrous aggregates in the contact between the micaceous minerals specially associated with vermiculite. In some zones, iron oxides have precipitated as an alteration product of mica. Opaque minerals were identified as hematite and birefringent minerals as iron oxyhydroxides.

In some samples, fibrous minerals of the amphibole group (Figure 1a), tremolite-actinolite series, were found inside and between vermiculite sheets. The fibres vary from 6 μm to 30 μm in length and from 0.8 and 3.5 μm in width. They exhibit an acicular habit, are very fragile and have a hackly fracture. Their modal content is below 10%.

In other samples, amphibole crystals have greater development, especially in the contact with vermiculite. They are from colourless to pale green, with slight pleochroism. Dark green crystals of a similar crystal habit are also present (Figure 1b). This change in colour is closely linked to the compositional variation of the series and to iron oxidation/mobilization. In some zones they occur as long, tabular, prismatic crystals without preferential orientation with mottled textures and in others, as subparallel fibrous aggregates with vein- or comb-like textures. Basal sections are distinguished by exfoliation development in two directions, forming 56° and 124° angles (Figure 1c), while long sections show parallel exfoliation traces. They display moderate to strong birefringence, and the extinction of long sections varies between 10 and 20°. Fibre sizes vary from a few microns to 800 μm in length, and their average width is 15 μm. In these samples, the modal content of amphiboles is greater than 10%. In its elongation direction the structure shows fibres attached in parallel. In some cases, the contact between micaceous and amphibolic minerals is clear and in others transitional, with vermiculite including prismatic crystals altering their boundaries.

Fractures are mainly filled with carbonatic minerals, such as calcite, and in some zones there are colourless fibrous minerals with straight extinction that due to their optical properties were identified as sepiolite.

The host rock containing vermiculite is a serpentinite. Vermiculite occurs in large attached crystals forming centimetric packages with progressive steatization processes, especially in the peripheral zones, and chlorites are arranged in a lepidoblastic texture. Chromite relicts are scarce. Fibrous mineral veins, which formed inside the vermiculite sheets, were examined with the optical microscope on thin sections. They exhibit hackly fracture, great crystal development and are slightly coloured with straight extinction and moderate birefringence (≈ 0.02). Based on their optical properties, they were identified as anthophyllite (Figure 1d).

This amphibole group mineral together with tremolite and actinolite are included in the asbestos group as the most harmful to health.

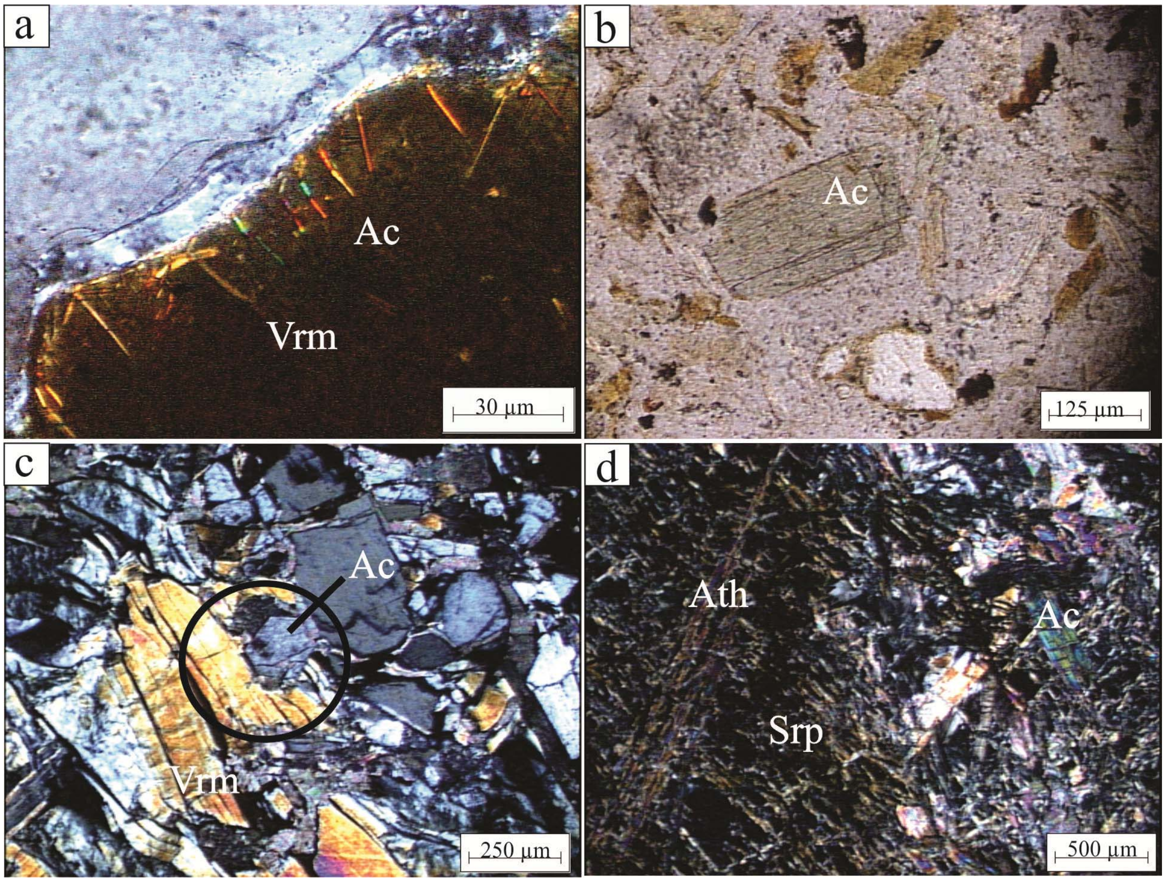

Figure 1: a) Amphiboles inside vermiculite sheets (under crossed nicols). b) Coloured amphibole, with pleochroism (under parallel light). c) Basal crystal in the two cleavage directions typical of these minerals. d) Anthophyllite with acicular morphology inside the serpentinite, and tremolite-actinolite with prismatic morphology. Ac: actinolite-tremolite, Vrm: vermiculite, Srp: serpentine, Ath: anthophyllite.

3.2 X-ray diffraction

Numerous samples from the deposits studied were examined. The diffraction pattern obtained from the host rock of one of them is shown in Figure 2a. A micaceous mineral, attributed to vermiculite, with the highest peak intensities at 14.2 and 4.57 Å, comparable to ICDD card No. 16-613 [7], was clearly identified. Reflections of talc, quartz and sepiolite were also recognised. The latter mineral showed its maximum peak intensities at 12.8 and 4.41 Å (ICDD 29-1492). The amphibole group minerals, tremolite-ferroactinolite series, showed their highest peak intensities at 8.29, 3.12 and 2.70 Å. In order to concentrate the amphibolic minerals found inside vermiculite, the sample was ground to pass a No. 400 sieve, removing the lighter material in a dense medium. The decanted material was irradiated in the same conditions as the natural sample (from 3 to 60º; 2θ Cu Kα). The diffraction pattern of Figure 2b shows that the reflections of the 110 and 310 planes intensified, confirming the presence of tremolite-ferroactinolite. The maximum peak intensities appeared at 3.11, 8.37, 3.36 and 2.70 Å, which are comparable to ICDD card No. 41-1366 [8].

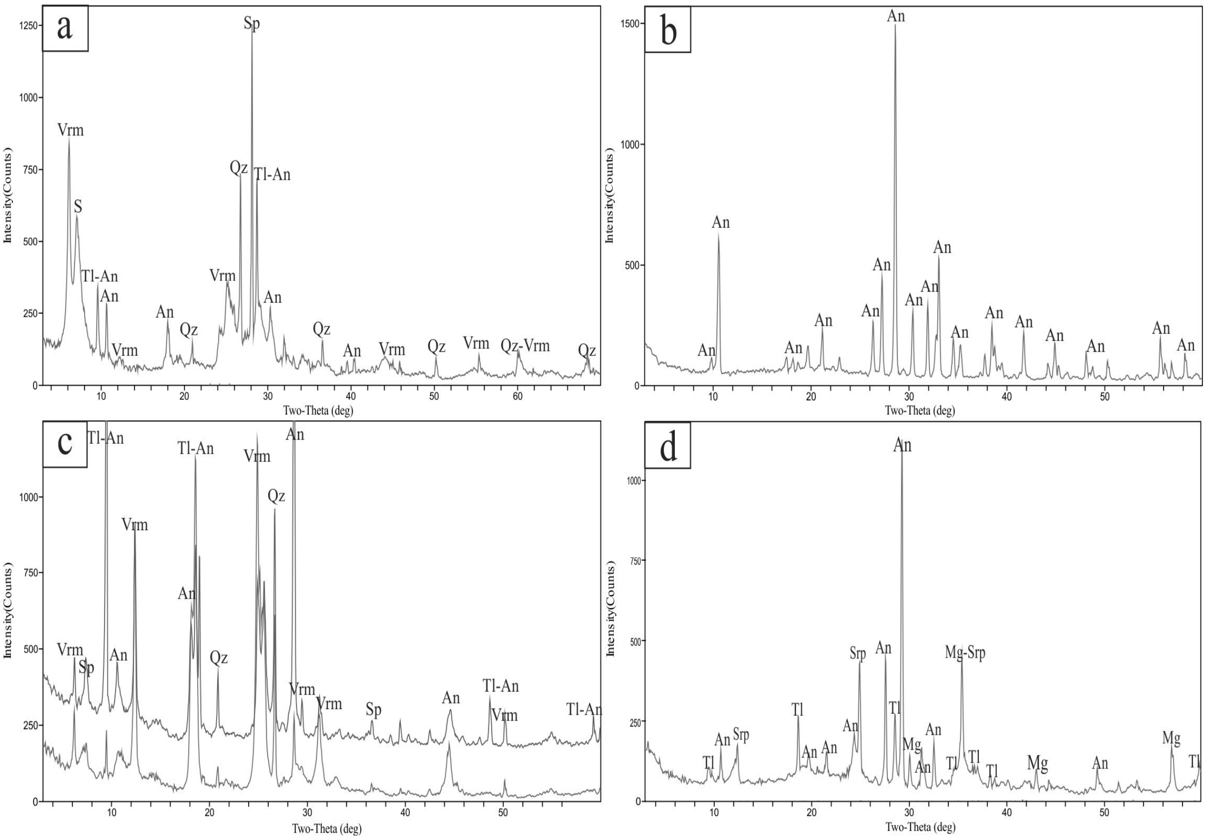

Figure 2: a) Diffraction pattern of bulk samples. b) Amphibole concentrate. c) Comparison of two mining works of the same deposit. d) Fibrous mineral veins in vermiculites. (Vrm: vermiculite, Srp: serpentine, Qz: quartz, Tl: talc, An: amphibole, Sp: sepiolite).

The diffraction patterns of two different zones of the mining works are compared in Figure 2c. There are no appreciable variations in peak intensity, so their per cent relations may be considered similar. A micaceous mineral, attributed to vermiculite, with its maximum peak intensity at 14.2 and 4.57 Å, was identified. Reflections assigned to talc were detected. Subordinate amounts of quartz, sepiolite and amphiboles were identified.

A micaceous material was identified in the natural material extracted from another deposit; it was attributed to phlogopite with its maximum reflections at 9.96 and 3.34 Å, comparable to ICDD card No. 10-495 [7], containing subordinate vermiculite. The peak intensity indicates very good crystallinity. No amphiboles were identified in any of the samples.

Furthermore, a diffraction pattern of the fibrous mineral in veins inside vermiculite revealed the presence of anthophyllite (ICDD 42-544; ICDD, 1993) with scarce antigorite, magnetite and talc (Figure 2d).

3.3 Scanning electron microscopy (SEM)

The lamellar, sheet-like habit typical of this type of mineral and the increase in volume after heating were observed by SEM (Figure 3a). Amphibole crystals of fibrous habit (length-to-width ratio greater than 3) with prismatic morphology and truncated basal ends were identified within the micaceous mass. These fibres developed from exfoliation fractures and do not show sharp or splintery ends. Amphiboles were found only in vermiculite sheets rather than isolated or disperse (Figure 3b). They vary from 50 to 100 µm in length and from 5 to 15 µm in width. The EDS analysis revealed Si, Al, O, Mg, Fe and K elements typical of vermiculite.

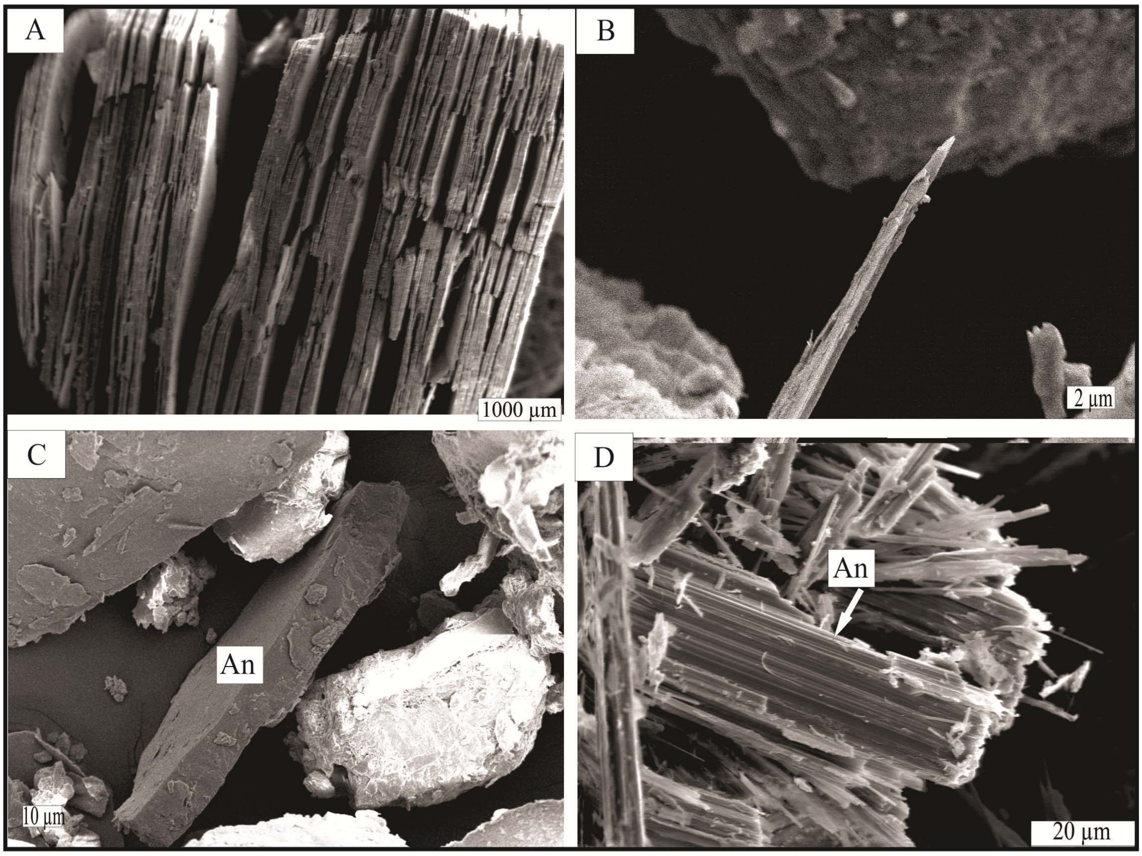

Figure 3: a) Exfoliated vermiculite, b) Amphibole fibres, c) Amphiboles with prismatic morphology, d) Anthophyllite fibres with acicular morphology.

In some cases, the fibres of veins, even those cross cutting the vermiculite, do not exhibit acicular morphology, where elongated tabular and prismatic forms prevail (Figure 3c).

The habit is the key characteristic to determine their health effect. Crystals with prismatic morphology, as in this case, would cause no harmful effects. However, studies on these materials have shown that their splitting and crumbling may cause breakage and asbestiform acicular forms [9].

In other zones, the fibres arranged in veins exhibit fibrous acicular morphology, with great crystal development forming randomly arranged bundles. The length-to-width ratio of the largest fibres is greater than 100, their ends are needle-like and they crumble into smaller fibres maintaining their physical properties. The EDS analysis identified Mg, Si and C, the latter being proportionally increased by the presence of calcite. Figure 3d shows part of a vein with fibrous amphibole crystals within a rock mass, with asbestiform morphology. Crumbling and crystal development can be seen. These samples contain natural vermiculite (uncalcined) forming dense and compact packages with an irregular and rough surface, with calcium carbonate being present. In other zones vermiculite is deformed and open, with no amphiboles.

3.4 Chemical analyses

The chemical composition of the different minerals identified in the studied deposits and a comparison with similar minerals from different parts of the world are included in Table 1 [10]. Phlogopite $KMg_3Si_3AlO_{10}(F,OH)_2$ from Franklin, New Jersey, United States; synthetic fluorphlogopite from Burgess, Ontario, Monte Braccio, Italy; Madagascar; New Zealand; Yakutia, Russia; Howes Hill, Australia; South Africa; Monte Somma, Italy; San Juan, Colorado, USA, and India. Vermiculite $(Mg,Fe,Al)_3(Si,Al)_4O_{10}(OH)_2.4H_2O$ from India; North Carolina, Maryland, Pennsylvania, USA; Bavaria; Kenya; and Finland. Tremolite-actinolite $Ca(Mg,Fe)_5Si_8O_{22}(OH)_2$ from USA and Wales, and talc $Mg_3Si_4O_{10}(OH)_2$ from Italy and Norway.

Table 1: Chemical analyses of vermiculite, tremolite, actinolite, phlogopite and talc from different parts of the world [10]. X= mean value and S= standard deviation.

%	Vermiculite		Tremolite		Actinolite		Phlogopite		Talc	
	X	S	X	S	X	S	X	S	X	S
SiO_2	34.66	1.25	57.93	1.93	55.17	-	39.71	2.07	61.86	1.67
Al_2O_3	15.14	2.19	0.83	0.81	2.69	-	15.56	4.34	0.82	0.80
Fe_2O_3	5.60	2.58	0.09	0.01	11.07	-	5.20	4.51	1.58	0.23
MgO	22.14	2.67	24.50	0.12	16.21	-	22.25	5.16	30.85	0.02
CaO	0.19	0.21	12.14	0.16	12.08	-	0.26	0.37	0.20	0.28
Na_2O	0.09	0.15	1.76	0.44	0.82	-	0.74	0.99	-	-
K_2O	0.02	0.03	0.65	0.05	-	-	1.41	1.46	-	-
LOI	10.73	1.08	0.98	0.68	-	-	2.64	1.37	4.97	0.07

These results indicate that the only minerals containing calcium are amphiboles (asbestos group mineral). Taking into account the mean values of SiO_2 and CaO in vermiculites and if they are compared with the results of the chemical analyses from the mines studied, it follows that there is a considerable increase of these oxides that would be related to the amount of amphibole impurities, except for a sample where calcite ($CaCO_3$) was identified but in a very low proportion.

4. DISCUSSION

Expanded vermiculite has been successfully used in the manufacture of lightweight products and especially in cementitious matrices for a long time, but it may contain minerals that are potentially harmful to human health such as magnesium silicates with asbestiform habit. Their fibres are very stable in the environment, decrease in size but maintain a very aggressive morphology when they become part of the atmospheric dust.

By the different analytical methods applied, amphiboles were identified to be present inside vermiculites from the province of Córdoba (Argentina) both in isolated fragments and arranged in veins. The mere presence of these minerals is a warning to enhance the environmental control of the ores extracted, focusing mainly on the atmospheric particulate material. Previous studies on ores mined under similar conditions revealed that exposure to them may cause health problems [11].

The mineralogical analysis of asbestos is a key issue to evaluate its health hazard by determining its morphology, fibre size and behaviour during natural degradation and industrial processes. Not all forms of asbestos are equally carcinogen or harmful to health, amphibole fibres being the most harmful [11]. Due to their optical properties, morphology and crystal structure, anthophyllite and tremolite-actinolite are the most hazardous.

One of the greatest environmental disasters in US history related to the presence of amphiboles in vermiculites occurred in the vermiculite mine in Libby, Montana, which was the largest vermiculite mine in the world. In a town with only thousands of inhabitants, 200 residents died from illnesses directly related to asbestos exposure. At world level, vermiculite is used as a lightweight aggregate in concrete, acoustic insulation, fire-resistant walls, boards and panels [12]. Many of these products included vermiculite from Libby, which at the time was not known to contain the fibrous amphiboles that are so harmful to health.

Vermiculite exfoliation, expansion to 30–35 times its initial volume and the weakness of its structure favour the release of impurities such as amphibole fibres into the air. Although studies on these minerals have been published in Argentina, only some of them deal with asbestos contamination [5, 6]. Lightweight vermiculite concretes require a detailed analysis and those containing asbestos impurities should be discarded. That is, lightweight concretes manufactured with vermiculite from the deposits studied in this paper should be analysed in detail before being used in cementitious matrices.

5. CONCLUSIONS

- The different minerals present in vermiculite were identified by XRD, polarised light microscopy, SEM, EDS and chemical analyses. Based on their optical characteristics, morphology, particle size and other properties they may be classified as asbestiform amphiboles.
- In many cases, the amphibole content of the materials studied is not greater than 10%. However, its mere presence is a warning to enhance environmental controls.
- The expansion process vermiculite is subjected to in order to manufacture lightweight products may release amphibole particles into the air.
- When evaluating the use of vermiculite to manufacture lightweight concretes, it is suggested that precautions be taken to ensure the quality of the material and avoid environmental problems that are difficult to solve.
- An evaluation for the presence of vermiculites in lightweight concretes to be removed is equally important in order to take precautions during their mobilization, transport and final disposal.

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