A PHYSICO-CHEMICAL STUDY OF DUST SAMPLES FROM THE DERELICT AND OWNERLESS ASBESTOS MINE DUMPS IN MPUMALANGA PROVINCE, REPUBLIC OF SOUTH AFRICA

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ABSTRACT

Asbestos is generally defined as a group of naturally occurring fibrous, silicate mineral that is abundant on the crust of the Earth. Despite the cessation of asbestos mining due to associated health effects in the Republic of South Africa in 2001, there is still a concern about possible environmental exposure to asbestos fibres. This paper reports the dust fall rates for a period of six months from January 2017 to June 2017 using the American Standard Test Method, ASTM D1739 of 1970 at five sampling sites that are within the local communities that are close to the derelict and ownerless asbestos mine dumps in Mpumalanga Province. This method is the recommended method of collection and analysis of dust fall rate in South Africa. After filtration, dust fall rates were determined gravimetrically. Filter papers containing dust fall samples were further analyzed using the Scanning Electron Microscope - Energy Dispersive X- ray (SEM – EDX), X-Ray Diffraction and Fluorescence (XRD and XRF) techniques. The amount of the serpentine asbestos group vs amphibole asbestos group obtained were 23 and 3%m/m at site A, 5 and 2%m/m at site B, 15 and 0%m/m at site C, 36 and 7%m/m at site D, as well as 7 and 0%m/m at site E. Other minerals detected in random order include feldspar, kaolinite, quartz, mica and talc. The non-silicate minerals detected were illimenite, metallic and organic and different types of amphibole: actinolite, barosite, ferri-magnesiotaramitel, grunerite, tremolite, winchite and feldspar; albite, andesine, anorithite, bytownite, labradorite, microcline, oligoclase, anidine, and sanidene. Most particles dust with shapes that include granular, sponge like, spiral, semi rectangular and semi triangular. The length to width ratios of the serpentine asbestos group ranged from 2:1 to 6:1, while the amphibole ratios were about 3:1 to 5:1. The continued presence of asbestos group minerals in inhalable fractions of airborne dust material is worrying and should be mitigated accordingly. Keywords: dust fall, asbestos, minerals, physico-chemical, and characterization, SEM, XRD.

1 INTRODUCTION

Asbestos mining around the world has caused environmental and human health concerns [1]. Asbestos is generally defined as a group of naturally occurring fibrous, silicate minerals that is abundant on the crust of the Earth [2], [3]. Asbestos mineral is known as a "miracle mineral" needle like in shape [4]. In the past, little was known about its health and environment effects [5]. Since the banning of asbetsos mining in South Africa in 2002 and in other countries the effects are still visible and continue to impact the health and environment negatively [6]. Asbestos mine dumps in Mpumalanga Province are not rehabilitated and dust particles/fibres could easily be lifted and transported by wind, and then settle in sensitive areas like nearby local communities. Asbestos materials were used for gaskets, floor titles, friction materials, cement building materials, lifts and machinery, etc. [7]. The purpose of this research is to study the geochemical, mineralogical and morphological characteristics of the microscopic dust particles/fibres from the filtered airborne dust and surface dust samples.



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2 EXPERIMENTAL DESIGN

2.1 Sampling points, geology and sampling points

The study area is situated in Mpumalanga Province and the asbestos mine dumps are located near communities around Mbombela (formerly Nelspruit), Malelane and Badplaas. All the five sites in Mpumalanga Province are not fully rehabilitated and are only partially covered with natural vegetation. Mbombela is the capital city of the Mpumalanga Province and is in the eastern part of the province. The province is known to have pine trees, escarpment and mountainous areas. Mpumalanga Province contains Tjakastad, Komatipoort Group and Transvaal SuperGroup. The common rocks found in the province are sandstones, shale, murchison, greenstone belt and intrusive granite. Komatities often display spectacular textures of skeletal crystals (known as spinifex textures) which branch out like fern leaves. The textures and the chemical makeup of the rocks can be deduced from Komatities lavas crystallized exceptionally rapidly from very hot and probably water-rich molten magma [8].

2.2 Sample collection methods

Dust fall dust sample were collected using a dust bucket, half deionized water, 2 m stand and mounted on the ground to support the equipment. The dust bucket units are exposed onsite for a period of 30 days.

Surface dust samples were collected using a brush, dust pan, sieved on site with 1.8 mm pore size stainless steel sieve to remove large particles and put into a labelled zipper plastic for storage.



Figure 1: A map showing geology and location of asbestos mines in Mpumalanga Province [9].



Figure 2: Dust fall and surface dust sample collect.

2.3 Samples preparations and analyses methods

In the laboratory, dust fall samples in buckets are filtered and the dust fall rates are measured by the gravimetric methods. The filtered dust fall samples on filter paper are mounted on specialized filter holders and used for both XRD and SEM investigations. Where possible, dust was extracted from the filters and analyzed by XRD as powder specimens. For SEM/EDS study, powders specimens are prepared as grain mounts. All specimens for SEM/EDS are coated with carbon to provide a conductive surface for optimum imaging and X-ray microanalysis. SEM/EDS analysis was done at ~800-1000 times magnification depending on particle size and distribution with the brightness/contrast settings adjusted to highlight the minerals of interest. The results are presented in form of backscattered electron (BE) images for each sample [10]. The XRF is used to quantify the geochemical composition, while SEM-EDS is used to determine the physical or morphological features of the dust particles or fibres. All the specimens for SEM - EDS are coated with carbon to provide a conductive surface for optimum imaging. The XRF analysis major element analysis the milled sample (<75 μ fraction) was roasted at 1000°C for at least 3.0 g hours to oxidise Fe²⁺ and S and to determine the loss of ignition (L.O.I.). Glass disks were prepared by fusing 1.0 g roasted sample and 10 g flux consisting of 49.5% Li₂B₄O₇, 49.5% LiBO₂ and 0.50% LiI at 1150°C. Quality control/Quality assurance was done by using an in-house amphibolite reference material (sample 12/76). Also 1.0 in every 10 samples is duplicated during sample preparation. For trace element analysis 12g milled sample and 3.0 g Lico wax was mixed and pressed into a powder briquette by a hydraulic press with the applied pressure at 25 ton. The glass disks and wax pellets was analysed by a PANalytical wavelength dispersive Axios Xray fluorescence spectrometer equipped with a 4 kW Rh tube [11].

3 RESULTS AND DISCUSSIONS

3.1 Meteorological data

The meteorological data comprising of monthly averaged temperature, humidity, and rainfall and wind velocity for Nelspruit were obtained from South African Weather Service [12]. Data were collected from Nelspruit station (S 25° 50 '3'', E 30° 91' 10") site A,B,C are



Season	Period	Temperature (°C)		Humidity	Rainfall	Wind
		Maximum	Minimum	(%)	(mm)	speed (m/s)
Summer	Jan-17	26.8	18.3	75.8	198.6	1.2
	Feb-17	26.6	18.8	79.1	144.2	1.1
	Mar-17	28.5	19.1	77.7	152.2	2.5
Autumn	Apr-17	-	-	-	-	-
	May-17	-	-	-	-	-
Winter	June-17	-	-	-	-	-

Table 1: Average meteorology parameters for Nelspruit for Mpumalanga Province [13].

situated in Nelspruit and site D situated between Mozambique and Swaziland boarder gates and site E is situated between Badplaas and Carolina. The meteorological parameters were arranged according to the three (3) seasons i.e. January and February 2017 (Summer season), March, April and May 2017 (Autumn season) and June 2017 (Winter season).

The province is known to experience heavy rainfall and the highest average temperature is 28.5° C in March 2017 with regard to the dust fall rates for Sites A and C there were low and below 600 mg/m²/day and humidity was the highest with 79.1% in February 2017 and rainfall 152.2 mm, but the highest rainfall occurred in January 2017 with 198.6 mm. The average wind speed ranged from 1.1 to 2.5 m/s which is below the threshold of 5 m/s. In March 2017 autumn season also the settleable dust were also below residential limit which it accepted that during winter season the settleable dust rates should be high and also in autumn season but with regard to the results it is low.

The month of January 2017 is characterised strong winds from the NE and moderate winds from the NW. Therefore, winter season is characterised by strong to moderately strong winds particularly from N to ES and ESE. The monthly average wind roses for April 2017 (winter season) at the Nelspruit weather station, also next to the location of sampling sites A, B, C, D and E. About 2% of the total time (24 hours), the wind blows from West (W) at 8.0 m/s, 5% and 15% of the time, the wind blows predominantly from the West-South it blew from the S at 3% to 5% and 5.0 to 8.0 m/s respectively. In the ESE direction, the winds blow 5 and 15% of 24 hours at 5% to 10% to 5 and 3.0 to 5.0 m/s respectively. Strong winds also blew from W and WSW. Winds are calm at 1.2% of the time. The month of June 2017 is characterised strong winds from the NE and moderate winds from the NW. Therefore, winter season is characterised by strong to moderately strong winds particularly from S to SE and ESE [15].

3.1.1 Dust fall rates results

The dust fall rates results are below the residential limit of $600 \text{ mg/m}^2/\text{day}$. The results are inconsistent and the low dust fall rates which might be due to heavy rain which spilled over some of the dust samples which were previously captured. From January to April 2017 there was a decrease the wet season. Site C is the lowest dust fall with 3 mg/m²/day in March 2017 which is in autumn season from March to May 2017. The influence of the meteorological patterns play a role in decreasing the retain of dust fall in the dust bucket collector during wet season and less wind blowing





Figure 3: Meteorological data for Nelspruit from January to June 2017 [14].

Sampling points	Jan-17	Feb-17	Mar-17	Apr-17	May-17	Jun-17
Site A	51	18	142	14	95.3	26
Site B	20	26	27	27	141.8	39
Site C	14	9	3	8	53.6	92
Site D	25	109	143	137	46.2	26
Site E	138	29	146	-	51	19

Table 2: Dust fall rates results from January to June 2017.

3.2 Geochemical results

The geochemical results confirms the presence of oxides of silicate minerals SiO_2 (silicon oxide), Al_2O_3 (aluminum oxide), Fe_2O_3 (iron II oxide) and MnO (magnesium oxide). Sillicon Oxide ranged from 37.22 wt% at Site A to 72.85 wt% at Site B. Aluminum oxide from 6.83 wt% at Site A to 18.93 wt% at Site E. Iron oxide ranged from 3.38 wt% at Site B to 12.74 wt% at Site E. Magnesium oxide ranged from 0.15 wt% at Site E to 32.64 wt% at Site A. The lowest values detected were CaO, Na₂O, K₂O, TiO₂, P₂O₅ and Cr₂O₃.

3.3 Mineralogical results

Quartz (SiO₂) is the dominant mineral detected at all the sites 0% m/m to 85% m/m and is a silicate mineral. Serpentine asbestos mineral detected at Site C with 83% m/m and Site D with 38% m/m. Cellulose $(C_6H_{10}O_5)_n$ is detected at all the sites ranged from 43% m/m to 100% m/m. Cellulose is an organic compound and is from plant-based material. According to a study by [16] surface dust collected and analysed for XRD and the results detected amphibole, quartz, antigorite, chrysotile(from serpentine asbestos mineral group), chlorite, pyroxene, olivine and titanite. A study conducted by [17] reports bulk dust samples collected including rocks , soil, car tire and clothing were analysed for XRD and the results confirm the presences of albite, serpentine, amphibole, quartz, calcite, chlorite, biotite and actinolite. Another study by [18] reported that different dust samples collected and analysed using XRD detected chrysotile (serpentine asbestos mineral) and calcite

3.4 Morphological results

A SEM-EDS was used to identify the minerals that are associated with most microscopic particles or fibres that were detected on all the dust fall samples collected on filter papers. Fig. 4 shows one of the images that were captured during the SEM-EDS analyses of dust fall samples collected from site in Mpumalanga province. A wide range of mineral particles or fibres of different sizes and shapes were identified and it includes the largest feldspar particle which is located on the top center of the sample image. A summary of mineral count from samples collected from sites in Mpumalanga provinces are presented in Fig. 5 and Table 3 below.





Figure 4: Geochemical results.



Figure 5: Mineralogy results.

Ouartz Organio Amphibol Ouartz Amphibole Kaolinite Organic Organ nic Quart Amphibol Organic uart mphibole Site A Org eldspar Ouartz Brushite Feldspar Amphibole Ouartz Ouart₂ bole Duartz Serpentine Quartz Amphibol 250 µm Feldspar Quartz Feldspar Amphibole Feldspar Quartz Feldspar 1.00 uartz Juartz Mica DIN N uartz Feldspar Quartz Feldspar Ð, uartz Ouartz Feldsnar As-oxide Feldspar Site B Mica e-oxide eldspar Feldspar e-oxide Quartz Feldspar Quartz Amphibole 25 Feldspar Feldspar Quartz Quartz eldspar Privin 0 - 8 Feldspar Feldspar Kaolinit Kaolinite erpentine Metal Feldspar uartz eldspar fica)uartz 🚺 Feldspar Organi Quartz Quartz Quartz 🛛 e 100 µm

Figure 6: Part 1 – SEM-EDS results.



Figure 7: Part 2 – SEM-EDS results.

Metallic		2		1	
Ilmenite				1	
Talc		2	5		
Calcite/Calcite mixed	1				
Kaolinite	4	3	3		10
вэiМ	2	5		1	
Fe-oxide	ю	3	8	12	5
Quartz	32	33	30	15	24
Organic	13	5	15	3	2
Feldspar – Sanidene		5	3	1	2
Feldspar – Oligoclase	5	6		1	
Feldspar – Microcline	4	3	3	2	2
Feldspar – Labradorite	2			1	2
Feldspar – Bytownite		3			
Feldspar – Anorthite	ю	2	3	2	
Feldspar – Andesine	1	2		2	5
Feldspar – Albite	1	3	5	2	15
Feldspar	4	6	8	9	12
Amphibole – Winchite	1			2	
Amphibole – Tremolite			3	2	
Amphibole – Magnesiotaramite				1	
Amphibole – Grunerite	1				
Amphibole – Ferri- Amphibole – Ferri-				1	
Amphibole – Baroisite		2			
Amphibole – Actinolite				1	
Serpentine	3	2		7	
əlodinqmA	23	5	15	36	12
Sampling Sites	Site A	Site B	Site C	Site D	Site E

Table 3: Mineral count data.



Fig. 5 and Table 3 confirms the presence of serpentine and amphibole asbetsos mineral group. The amount of the serpentine vs amphibole asbestos group obtained were 23 and 3%m/m at site A, 5 and 2%m/m at site B, 15 and 0%m/m at site C, 36 and 7%m/m at site D, as well as 7 and 0%m/m at site E. Other minerals detected in random order include feldspar, kaolinite, quartz, mica, talc. The non-silicate minerals detected were limenite, metallic and organic and other different types of amphibole: actinolite, barosite, ferri-magnesiotaramitel, grunerite, tremolite, winchite and feldspar; albite, andesine, anorithite, bytownite, labradorite, microcline, oligoclase and sanidene. Most particles exist as aggregates or lumps with shapes that include cylindrical, irregular, semi rectangular and semi triangular. The length to width ratios of the serpentine asbestos group ranged from 2:1 to 6:1, while the amphibole ratios were about 3:1 to 5:1. A study by [19] dust fall sample collected and analysed for SEM-EDS confirms the presence chrysotile from serpentine mineral group and amphibole mineral group. Other silicate minerals quartz, plagioclase, kaolinite, feldspar and mica. According, [20] study surface and trapped dust samples were collected and analysed foe SEM-EDS confirms the presence serpentine and amphibole mineral group and other silicate minerals confirm quartz, feldspar, talc, mica, organic fibre and non-silicate minerals were calcite, clinochlore and mixed dust. Also a study by [21] dust fall samples were collected and analysed for SEM-EDS analysis confirms the presence of amphibole mineral group and other silicate minerals such as quartz, mica, plagioclase and non-silicate kaolinite, feldspar and chlorite.

4 CONCLUSIONS

All the dust rates are below the residential limit of 600 mg/m²/day and the meteorological parameters have influence on the dust fall rates especially during dry and wet seasons. The geology of the Mpumalanga Province confirms the detected asbestos mineral group minerals from results serpentine and amphibole asbestos mineral and they occurs in the rock seams/crack of banded iron formation and magnesium rick with occurrences from ultramafic rocks from metamorphic formation [22]. Geochemical, mineralogical and morphological results confirm the presence of silicate minerals serpentine and amphibole asbestos mineral groups. Asbestos mine dumps in Mpumalanga Province are not rehabilitated which requires urgent and permanent mitigation solutions to prevent liabilities from the local communities. The presence of theses asbestos minerals through inhalable fractions of particle dust/fibres materials is cause of concern.

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