Occupational Hygiene Assessments Occupational Health



Environmental Health Chemistry

Pilbara Minerals Level 2, 146 Colin Street WEST PERT WA 6005

Attention: Natalie Maguire

Dear Natalie

Respirable Crystalline Silica Content of a Composite Spodumene Concentrate

Executive Summary

The Globally Harmonised System of Classification and Labelling of Chemicals (GHS) has been introduced by the Work Health and Safety (WHS) Regulations in Australia as a means of classifying workplace hazardous chemicals and communicating their hazards through labelling and safety data sheets.

Crystalline silica has been classified as carcinogenic to humans (lung) by the International Agency for Research on Cancer (IRAC Group 1 carcinogen; GHS Category 1A; Specific Target Organ Systemic Toxicity (Repeated Exposure): Category 1). Crystalline silica is only carcinogenic if it is respirable (Respirable Crystalline Silica known as RCS) and reaches the deepest part of the lungs. If the concentration of RCS is <0.1% w/w in a product, then it does not have to be classified as carcinogenic and labelled as such under GHS. The Safety Data Sheet also does not have to state that the product is carcinogenic if the RCS is <0.1%w/w.

The RCS concentration can be measured using the SWeRF (Size Weighted Respirable Fraction) Method to determine if the RCS is >0.1%w/w.

The SWeRF Method uses actual sedimentation values, rather than calculated sedimentation values. The result for sedimentation analysis was:

- Bucket 7: RCS/SAMP2407/FINES RCS = 0.12%
- Bucket 8: RCS/SAMP2408/COARSE RCS =<0.001%
- Bucket 9: RCS/SAMP2409/BLEND RCS = 0.032%

It would be likely that the Fines would have a higher RCS than either the Blend or Coarse Samples. The Fines were marginally above the 0.1% threshold.

1. Background

Previously Glossop Consultancy had analysed samples for Pilbara Minerals and this is another round of samples.

Essie Elliott (Sales and Shipping Lead) first contacted us on the 5th June 2024 about conducting analysis of new samples. It took quite some time for the samples to be delivered by Centurion. The samples when delivered had to be sieved before sending to QUT for analysis. The sieving was done by Glossop Consultancy.

The method to be used to determine the RCS is known as the SWeRF (Size Weighted Respirable Fraction) Method. The Size Weighted Respirable Fraction (SWeRF) is that fraction of a material weighted by its probability to reach the alveoli as given in EN 481. A paper on the SWeRF Method has been published: *SWeRF*—A Method for Estimating the Relevant Fine Particle Fraction in Bulk Materials for Classification and Labelling Purposes by Ingeborg Pensis, Frank Luetzenkirchen and Bernd Fried. Ann. Occup. Hyp., 2013, 1–11.

The SWeRF Method allows two techniques to be used:

- Calculation
- Sedimentation

The Calculation technique relies on determining the amount of respirable dust in a sample from measurement of the Particle Size Distribution and then using a bulk analysis for quartz to determine the % of crystalline silica in the sample or product.

The sedimentation technique relies on the material to be tested to be mixed with a fluid and allowed to settle so coarse particles sink faster than fine particles. Using Stokes Law, the settling time can be calculated, and the respirable fraction is extracted and analysed. The Sedimentation technique is more robust than the Calculation technique because in mixtures of minerals there can be very different distribution of minerals in the different size fractions. Laurie Glossop has seen this many times, especially in mining concentrates. It is our Professional Opinion that the Sedimentation technique should be used to provide more certainty about RCS in products. Often the concentration of the RCS is significantly less than in the bulk material.

Another important point to understand is about the aerodynamic equivalent diameter (AED) of different density particles. As the density of a particle increases its aerodynamic equivalent diameter increases. The AED increases as the square root of the density. If you have a spodumene particle, it has a density of $3.2g/cm^3$ which means a 2µm size particle by laser sizing will have an AED of 3.6µm, and in sedimentation will behave as a 3.6µm size particle. The density of crystalline silica particles is $2.65g/cm^3$, and behaves lighter than spodumene minerals. There was significant amount of amorphous material which had an AED < 5µm and this was observed with the larger proportion compared to the bulk mineral sample.

The % respirable silica in the bulk sample was calculated by the using the % weight of the $<5\mu$ m fraction multiplied by the % silica in the $<5\mu$ m fraction.

Pilbara Minerals provided a representative composite samples to Glossop Consultancy of the above spodumene composite samples.

The Spodumene composite was analysed by the SWeRF Sedimentation Method presented in the Pensis paper referenced above.

2. Analysis of the Three Samples July 2024

Three buckets of product were supplied:

- 1. Bucket 7: RCS/SAMP2407/FINES
- 2. Bucket 8: RCS/SAMP2408/COARSE
- 3. Bucket 9: RCS/SAMP2409/BLEND

All the samples were initially sieved through an $850\mu m$ sieve and then a $75\mu m$ sieve.

The amount of <75µm material for Bucket 8: RCS/SAMP2408/COARSE was so low it was not sent for further analysis as it was massively under the level to be an issue for RCS.

Quantitative XRD analysis was performed on the samples sent to Queensland University of Technology (QUT).

The samples were initially calcined at low temperature to "burn-off" the fatty acid on the concentrate from flotation. The fatty acid interferes with the sedimentation.

These samples were initially separated into the respirable fraction by sedimentation using Stokes Law. The <75µm material was used for the sedimentation.

The sedimentation was performed in a volumetric cylinder with a height of the dispersed concentrate of 30cm. To obtain the respirable fraction the solids were taken from a depth of 5cm after a 40 minute sedimentation time. The solids were filtered and weighed. To obtain the total respirable fraction you need to multiply by 6 to obtain the total weight of the respirable fraction in the cylinder.

Sedimentation weights:

Table of < 5µm yield (mass used is after ashing)

X24268		
PO242501	Pilbara Minerals Blend	Pilbara Minerals Fines
Mass used (g)	7.174	10.282
Mass obtained, <5µm(g) 5cm	0.041	0.047
Mass obtained, <5µm(g)30cm	0.25	0.28
< 5µm Yield (%)	3.5	2.7

As can be seen the $<5\mu$ m (respirable fraction) was 3.5% for the Blend and 2.7% for the Fines of the $<75\mu$ m fraction.

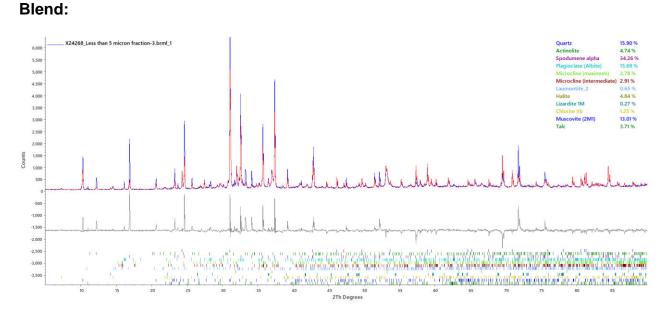
The XRD of the <5µm is shown below:

Table of absolute phase abundances (wt%, original sample)

X24268	3 Pilbara	4 Pilbara
PO242501	Minerals Blend	Minerals Fines
Quartz	3.0	9.1
Dolomite		
Siderite		
Apatite		
Goethite		
Olivine		
Amphibole	0.9	1.9
Spodumene (α)	6.5	11.8
Diagiaglass	3.0	10.0
Plagioclase K-Feldspar	5.0 1.1	3.1
Laumontite	0.1	5.1
Halite	0.9	1.1
Serpentine	0.1	0.4
Chlorite	0.2	3.1
Illite/mica	2.5	7.0
Smectite	2.0	710
Talc	0.7	
Amorphous	81.1	52.5

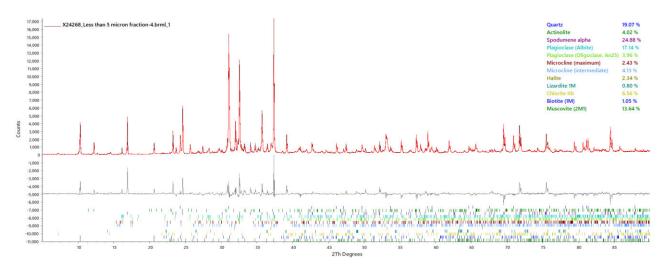
Please note the amorphous concentration is high in these samples showing significant grinding. Quartz was easily detected in the samples.

The XRD analysis is shown below:



The concentrations of minerals does not take into account the amorphous content. The Table above of minerals takes into account the amorphous concentration.

Fines



The concentrations of minerals does not take into account the amorphous content. The Table above of minerals takes into account the amorphous concentration.

RCS Concentration in the Bulk Samples

Bucket 8: RCS/SAMP2408/COARSE

The concentration of RCS in the COARSE Sample is <0.001%

Bucket 9: RCS/SAMP2409/BLEND

Bucket 9: RCS/SAMP2409/BLEND	Weight (g)	%
Weight Sample	1,012	100
Not passing 850µm	380	38
Passing 850µm	632	62
Not passing 75µm	318	31
Passing 75µm	314	31
Weight for Sedimentation (75µm)	7.2	
Weight <5µm	0.25	
Total weight <5µm	10.9	
Quartz % in Weight <5 µm		3.0
Weight RCS	0.33	
%RCS in sample		0.032

Bucket 7: RCS/SAMP2407/FINES

Bucket 7: RCS/SAMP2407/FINES	Weight (g)	%
Weight Sample	1,002	100
Not passing 850µm	8.7	0.86
Passing 850µm	993	99.1
Not passing 75µm	530	
Passing 75µm	471	47
Weight for Sedimentation (75µm)	10.28	
Weight <5µm	0.28	
Total weight <5µm	12.8	
Quartz % in Weight <5µm		9.1
Weight RCS	1.2	
%RCS in sample		0.12

3. Conclusion

The concentration of RCS in the samples were:

- Bucket 7: RCS/SAMP2407/FINES RCS = 0.12%
- Bucket 8: RCS/SAMP2408/COARSE RCS =<0.001%
- Bucket 9: RCS/SAMP2409/BLEND RCS = 0.032%

Only the Fines was just above the 0.1% criteria to be classified as carcinogenic.

As expected, the highest concentration of RCS was in the Fine sample and the lowest the Coarse and the Blend in the middle.

The uncertainty in the concentration is likely to be about 10%.

Yours sincerely

B.Sc Ph.D COH MAIOH FAIOH

3rd September 2024