Supporting information of

Dissolution and nano and micro particlates generation behavior of Be ores in synthetic lung fluid (SLF) using FlFFF-ICP-MS

The different incidences of CBD cases found by a particular Be processing company (Wambath et al, 2008)

At facility A, a beryllium mine and ore processing mill, one person had ever been detected with CBD out of 360 persons who have worked there. At facility B, a beryllium oxide ceramics manufacturing facility with a similar population exposure profile for beryllium (figure S1), the rate was 17/709, a difference that was statistically significant (Deubner 2001). Furthermore, the person with CBD at facility A had worked 10 years in facility C, a large complex beryllium materials manufacturing facility with much higher air levels (figure S1) and a rate of CBD comparable to facility B, leaving the exposure source for this case of CBD ambiguous. For further comparison, a fourth facility (D), a copper-beryllium alloy strip rolling and wire drawing mill with a much lower air level profile, has also detected one case of clinical CBD and also surveillance CBD.

Details of the material accessible in the Be processing facilities described above:

Particle exposure in the mine and mill occurs during the processes of preparation of two ores, imported beryl (aluminum beryllium silicate) and locally mined bertrandite (beryllium silicate), extraction of beryllium with acid, and of the precipitation of beryllium hydroxide. The bertrandite ore body at the open pit mine is exposed by contractor removal of overburden. Workers scoop up the soft volcanic ash ore with a bulldozer and front end loader and move it to piles. Contractors load from the piles into trailers, tow the trailers to the mill and discharge the ore. At the mill following crushing of large rocks, the ore is ball milled to a powder and leached with hot sulfuric acid. Therefore exposure occurs to beryllium ore dust produced by moving and pulverization without chemical alteration. The beryl process is more complex, the rocky ore being hand sorted to remove extraneous materials, and then loaded in an arc furnace,

where it is melted and then poured into water to form a glassy frit. The frit is ground and heat treated prior to being leached with hot sulfuric acid. Workers are therefore potentially exposed to beryl and bertrandite ore dust during sorting and moving, and to modified ore as frit and heat treated frit.

Simulated lung fluid

Synthetic lung fluid (SLF) consists of Gamble's solution (table S2) adjusted with (0.1 normal sulfuric acid) to a pH of 7.2 to represent extra cellular fluid or to pH 4.5 to represent macrophage lysosome fluid.

Tables and Figures

Table S1: Composition of simulated lung fluid (SLF) (Gamble's solution) in mM

Species	Concentration (mM)
Na^+	150.7
Ca^+	0.197
NH_4^+	10
H_2CNH_2H (glycine)	5.99
H_2CO (formaldehyde) methanol solution	67
Cl^-	126.4
SO_4^{2-}	0.5
HCO_3^-	27
HPO_4^{2-}, $H_2PO_4^-$	1.2
$COH(CH_2)_2(COO)_3^{3-}$ (citrate)	0.2
Bubbled with pure CO_2 for 15 minutes	

Table S2. CC-ICP-MS operation conditions

parameters	Q_{inject}	t_{inject}	t_{trans}	t_{elut}	Q_{tip}	Q_{focus}	Q_{cross}	$Q_{detector}$	Q_{slot}
In day 0 to day 64									
Focus Step									
Units	ml/min	min	min	min	ml/min	ml/min	ml/min	ml/min	ml/min
	0.1	5	1	N/A	0.1	3.9	1	0.4	2.6
Elution Step									
stage 1	N/A	N/A	N/A	7	4	N/A	1	0.4	2.6
stage 2				5	3.7		0.7	0.4	2.6
stage 3				5	3.7		0.7	0.4	2.6
Rinse Step									
	N/A	N/A	N/A	5	3	0	0	0.4	2.6
On day 149									
Focus Step									
units	ml/min	min	min	min	ml/min	ml/min	ml/min	ml/min	ml/min
	0.15	8	1	N/A	0.15	2.05	1.2	0.4	0.6
Elution Step									
stage 1	N/A	N/A	N/A	45	2.2-1.3	N/A	1.2-0.3	0.4	0.6
stage 2				3	1.3-0		0.3-0	0.4	0.6
Rinse Step									
	N/A	N/A	N/A	5	1	0	0	0.4	0.6

Table S3: Summaries of FFF operation conditions for different size range

OPERATION CONDITIONS	
RF power (W)	1550
Plasma gas flowrate (L/min)	15
Hydrogen flowrate (mL/min)	2.5
Helium flowrate (mL/min)	2.5
Carrier flowrate (L/min)	0.8
Make-up gas (L/min)	0.2
Auxiliary gas (L/min)	0.9
Sample flowrate (mL/min)	0.3
Acquisition time per isotope (sec)	0.05
Repetition	3
Total acquisition time for 19 isotopes (sec)	2.85
Total running time (sec)	1500 - 1860
Tuning solution: ^{133}Cs mean (cps) wth H_2 in collision cell % RSD	 34,000 < 3%
Sample nebulizer tubing: Material Internal diameter (mm)	 Tygon 1.02
AF4 carrier tubing: Material Internal diameter (mm)	 Peek 0.25

Table S4 The Al mass balance analysis results

samples	pH	concentrations, mg/L					R_{ICP-MS} = no CF FFF / Bulk ICP-MS
		Day 128	Day 149 (FFF-ICP-MS)				
		Bulk ICP-MS	CF FFF	< 3 kDa	no CF FFF	R_{FFF} = CF / no CF - 3KDa	
Al							
BeO	**7.2**	0.083	0.003	<0.004	0.002	> 153	2.832
Be(OH)2		<0.02	0.004	<0.004	0.009	N/A	N/A
FRIT		0.835	0.029	0.011	0.044	87.14	5.222
BERT		1.332	0.101	0.021	0.195	57.88	14.631
BERYL		1.167	0.041	0.027	0.066	106.85	5.642
SiO2		<0.02	0.011	N/A	0.032	> 34.37	N/A
BeO	**4.5**	<0.02	0.005	<0.004	0.001	N/A	N/A
$Be(OH)_2$		<0.02	0.002	<0.004	N/A	N/A	N/A
FRIT		5.567	0.405	0.050	0.500	90.15	8.985
BERT		1.214	0.031	0.021	0.053	96.30	4.406
BERYL		1.707	0.091	0.025	0.505	18.93	29.610
SiO2		0.140	0.060	N/A	0.092	> 65.2	65.860

N/A represents either the values are not available, such as Al concentrations in suspensions samples; or not accessible, such as in R_{FFF} / R_{ICP-MS} sample suspensions.

Table S5 The Si mass balance analysis results

samples	pH	concentrations, mg/L					R_{ICP-MS} = no CF FFF / Bulk ICP-MS
		Day 128	Day 149 (FFF-ICP-MS)				
		Bulk ICP-MS	CF FFF	< 3 kDa	no CF FFF	R_{FFF} = CF / no CF - 3KDa	
Si							
BeO	**7.2**	< 1.5	0.133	<0.04	0.150	> 88.4	N/A
Be(OH)2		< 1.5	0.145	<0.04	0.238	> 164.3	N/A
FRIT		7.268	0.209	0.119	0.381	79.634	5.249
BERT		4.745	0.171	0.107	0.368	65.536	7.749
BERYL		4.185	0.147	0.120	0.162	352	3.859
SiO2		36.816	0.317	N/A	0.012	> 2641.67	0.032
BeO	**4.5**	< 1.5	0.156	<0.04	0.032	> 487.5	N/A
$Be(OH)_2$		< 1.5	0.103	<0.04	N/A	N/A	N/A
FRIT		34.188	0.722	0.411	0.951	133.764	2.783
BERT		4.065	0.259	0.082	0.229	176.204	5.624
BERYL		2.462	0.053	0.105	0.163	90.732	6.626
SiO2		5.449	0.281	N/A	0.382	> 73.56	7.003

N/A represents either the values are not available, such as Si concentrations in suspensions samples; or not accessible, such as in R_{FFF} / R_{ICP-MS} sample suspensions.

Figure captions

Figure S1: Population exposure for four facilities, mean exposure values by percentile of population exposed at that level or lower

Figure S2: Recovery test of Be, Al and Si in Amicon Ultra 3-4

Figure S3: Concentrations of Al < 450 nm fraction in various ore-SLF suspensions at two pH values: 4.5 (top) and 7.2 (bottom). Samples were collected on day 0, 2, 8, 16, 32, 64 and 128 and measured with bulk ICP-MS. The missing date points represent Al concentration were below the detection limit of ICP-MS. Data are from measurements for duplicate samples.

Figure S4: Concentrations of Si < 450 nm fraction in various ore-SLF suspensions at two pH values: 4.5 (top) and 7.2 (bottom). Samples were collected on day 0, 2, 8, 16, 32, 64 and 128 and measured with bulk ICP-MS. The missing date points represent Al concentration were below the detection limit of ICP-MS. Data are from measurements for duplicate samples.

Figure S1

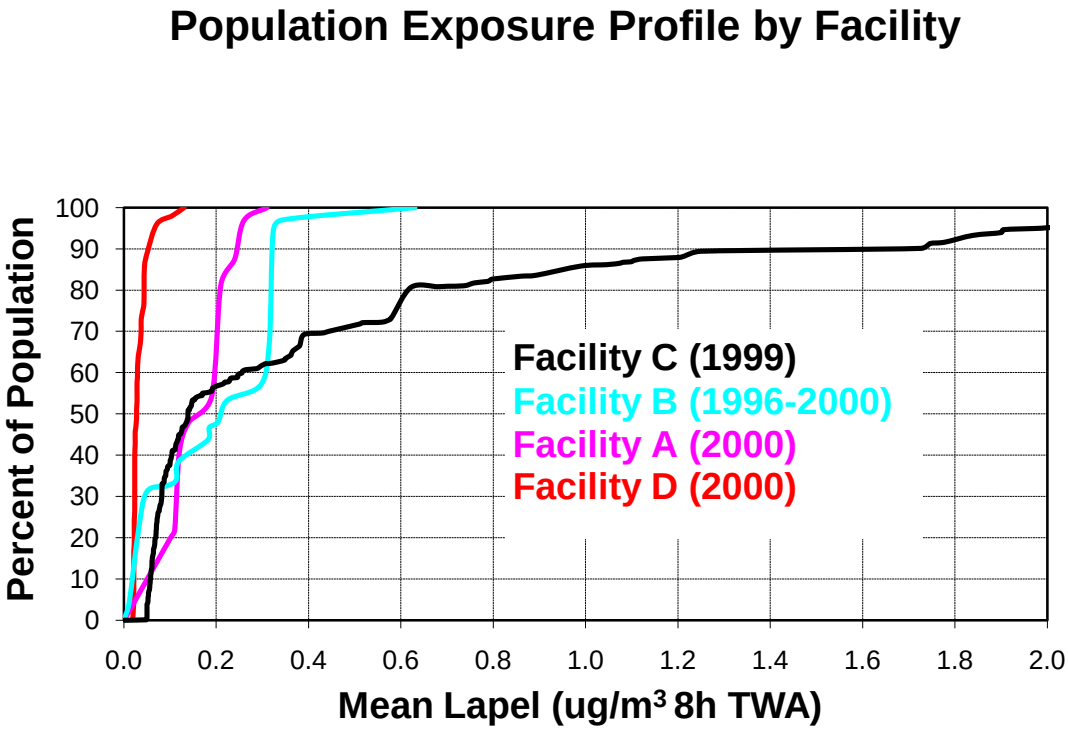

Population Exposure Profile by Facility
Percent of Population
100
90
80
70
60
50
40
30
20
10
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Mean Lapel (ug/m3 8h TWA)
Facility C (1999)
Facility B (1996-2000)
Facility A (2000)
Facility D (2000)

Figure S2

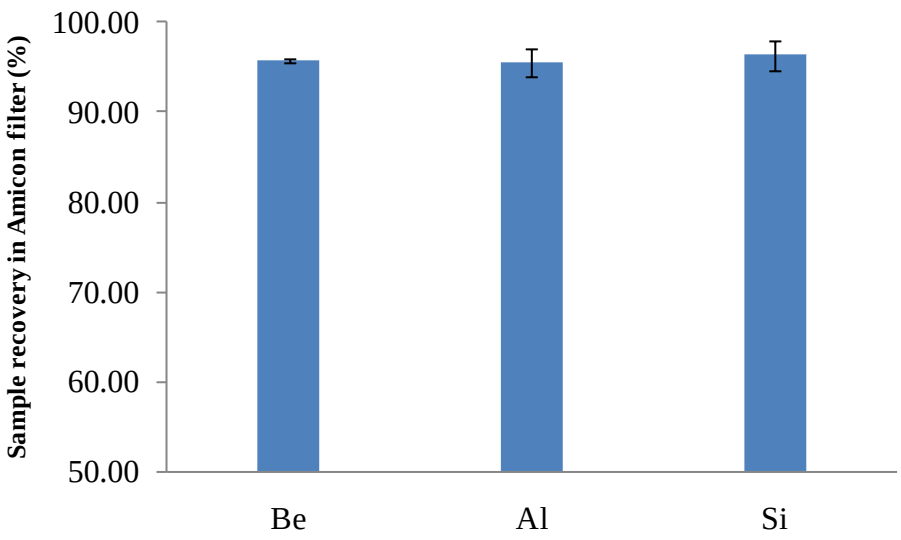

Sample recovery in Amicon filter (%)
100.00
90.00
80.00
70.00
60.00
50.00
Be
Al
Si

Figure S3

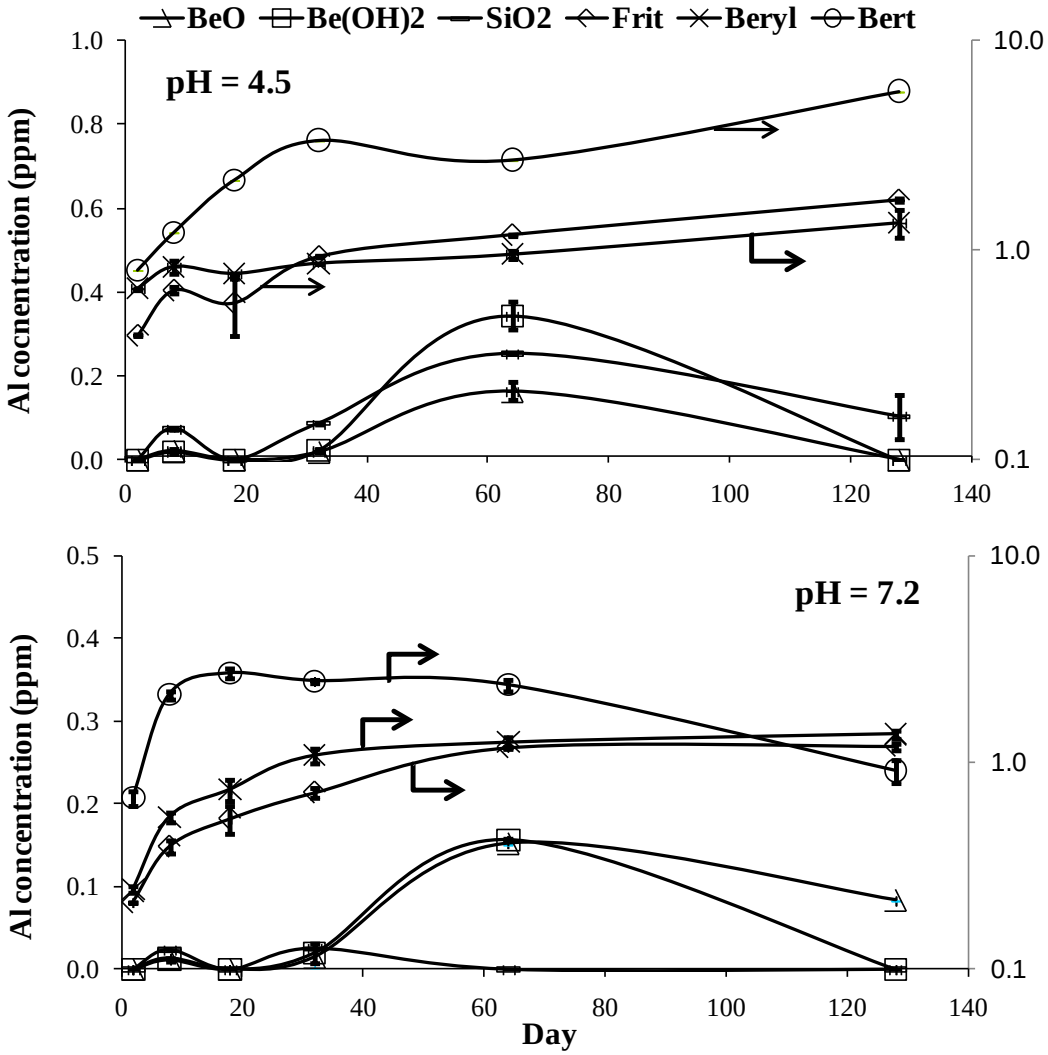
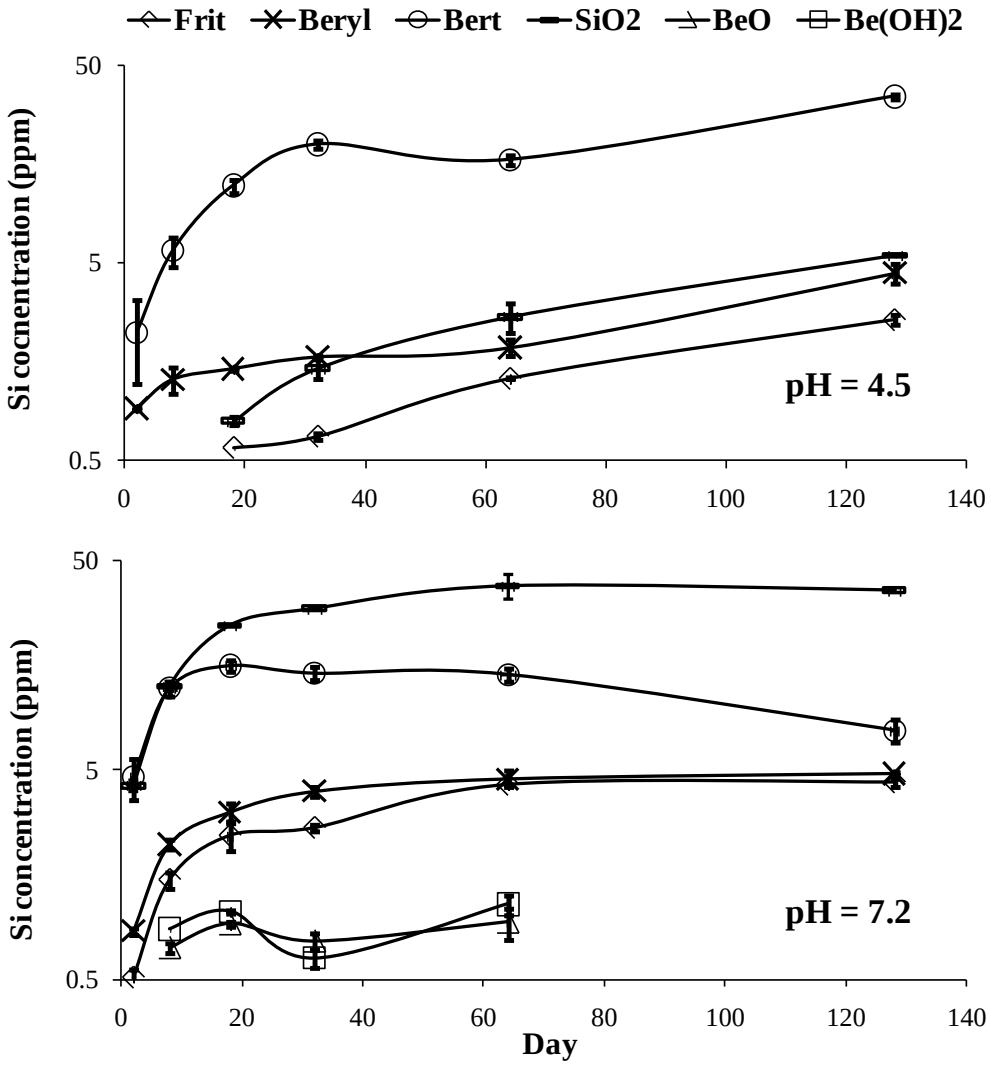

BeO
Be(OH)2
SiO2
Frit
Beryl
Bert
pH = 4.5
pH = 7.2
Al cocnentration (ppm)
Al concentration (ppm)
Day

Figure S4


Frit
Beryl
Bert
SiO2
BeO
Be(OH)2
Si cocnentration (ppm)
50
5
0.5
pH = 4.5
0
20
40
60
80
100
120
140
Si concentration (ppm)
pH = 7.2
Day