Supported Information A

Estimation of Work Index for By-Product Red Gypsum Sample

The standard laboratory procedures for estimating work index (Wi) can be divided into two categories, including tests on individual particles of rock and bulk rock material. A number of tests are required to get an idea of the rock strength. In this study, the standard of "Bond Pendulum test" was applied to estimate the work index of by-product red gypsum. In this test the energy required to crush a dry by-product red gypsum particle by the impact of two swinging hammers was determined. The standard method adopted by Bond is described as follows.

Two equal hammers, 13.6 kg each, about 0.7 m in length and the striking face 50×50 mm were suspended from two wheel rims. The hammers were raised to a known height and when released strike simultaneously was blown on opposite sides of a dry test piece. The test piece was supported with its smallest dimension between the hammers. The hammers were initially raised to make an angle of 10° with the vertical then released. After the impact, the test piece was examined for fracture and the number of pieces broken was recorded. If the piece was not completely broken, the hammers were raised a further 5° and the process repeated till the piece was completely shattered. The heights of the hammers were recorded each time. Based on this standard, at least 10 samples should be used per test. However, 20 samples of by-product red gypsum were utilized, which this number is preferred in this standard.

The impact crushing strength (I) was calculated after each operation from the expression:

$$I = \frac{2 \times Mass\ of\ one\ hammer \times Final\ height\ of\ hammer\ (kg * m)}{d\ (mm)}$$

Where:

d = thickness of sample (mm)

The value of I was averaged over the 10 to 20 tests. The impact crushing strength of samples was used to calculate the Bond' crushing work index using the expression:

$$W_i(kWh/t) = \frac{C \times I}{Relative\ density\ of\ sample}$$

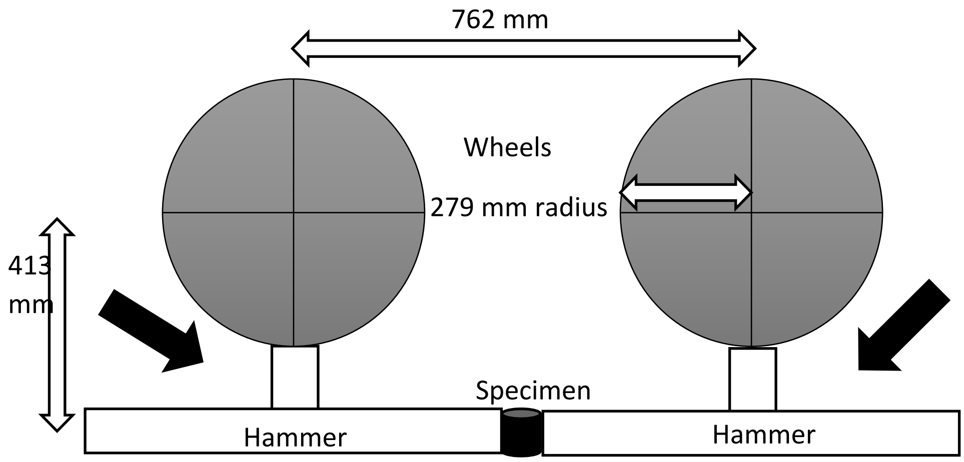
Where:

C is a constant which converts the impact crushing strength, numerically and dimensionally to the work index. C equals to 2.59 in the original Bond equation.

Calculations:

$$I = \frac{2 \times 13.6(kg) \times 1\ (m)}{3\ (mm)} = 9.066$$

$$W_i\left(\frac{kWh}{t}\right) = \frac{2.59 \times 9.066}{2.18} = 10.77$$



SIA: Bond's impact test to estimate work index of by-product red gypsum samples

Supported Information B

XRD Pattern

Pattern: PDF 00-006-0046 Radiation: 1.54060 Quality: User modified

Formula	Ca S O4 ·2 H2 O
Name	Calcium Sulfate Hydrate
Name (mineral)	Gypsum
Name (common)	

Lattice:	Monoclinic
S.G.:	I2/a (15)
Mol. weight =	172.17
Volume [CD] =	493.75
Dx =	
Dm =	
I/Icor =	-1.000

a =	5.68000
b =	15.18000
c =	6.51000
a/b =	0.37418
c/b =	0.42885
alpha =	
beta =	118.400
gamma =	
Z =	4

Deleted Or Rejected By: Deleted by 00-033-0311
Unit Cell Data Source: Powder Diffraction

Primary Reference
Publication: Private Communication
Authors: Gillery, F., The PA State Univ., Univ. Park, PA, USA.

Radiation:	CuKα1
Wavelength:	1.54060
SS/FOM:	10.6 (0.048,59)
Filter:	Not specified
d-spacing:	

d	2θ	I	h	k	l
7.59000	11.650	6117	0	2	0
4.27709	20.751	3058	-1	2	1
3.79182	23.442	1223	0	3	1
3.16415	28.180	245	-1	1	2
3.06081	29.152	3364	-1	4	1
2.86326	31.213	1529	0	0	2
2.78887	32.068	367	-2	1	1
2.67897	33.421	1713	0	2	2
2.58871	34.622	245	-2	0	2
2.53000	35.452	61	0	6	0
2.49820	35.919	367	2	0	0
2.45012	36.648	245	-2	2	2
2.40262	37.399	245	1	4	1
2.21385	40.723	367	-1	5	2
2.13855	42.225	122	-2	4	2
2.07557	43.570	612	-1	2	3
2.07291	43.629	489	-2	5	1
1.98928	45.564	245	1	7	0
1.95531	46.401	122	2	1	1
1.89750	47.902	979	0	8	0
1.87580	48.492	612	-1	4	3
1.86548	48.777	245	-3	1	2
1.83718	49.579	122	2	3	1
1.80938	50.393	612	-2	6	2
1.80003	50.673	245	-3	2	1
1.77763	51.358	612	2	6	0
1.70575	53.692	122	-2	5	3
1.68285	54.482	122	-3	2	3
1.66503	55.114	245	-3	4	1
1.64178	55.963	122	-1	6	3
1.61894	56.823	367	1	8	1
1.59819	57.630	61	-3	5	2
1.58248	58.257	122	-1	1	4
1.53040	60.441	122	-2	8	2
1.52215	60.804	122	1	2	3
1.49561	62.000	61	-1	9	2

Supported Information C

Calculation of the CO_2 Uptake for Mineral Carbonation Process of By-Product Red Gypsum

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(pCO_{2\,in} - pCO_{2\,out})_i * \Delta t * Q}{R * T * M}$$

$pCO_{2\,out}$: mean value of pCO_2 in the outflow (partial pressure of CO_2 up to 30%)

Δt: time interval (1 min)

Q: flow rate (5 L/min)

Flow meter rates are reported in standard liters per minute (slpm), which is the number of liters per minute under standard conditions of temperature and pressure.

R: gas constant (8.32 J/mol*K)

T: temperature (60 °C equals to 333.15 K)

M: mass of by-product red gypsum (10 g).

(1) Temperature

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(7) \times 1 \times 5}{8.32 \times 298.15 \times 10} = \frac{35}{24806.08}$$

CO_2 uptake = 1.41(mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(15) \times 1 \times 5}{8.32 \times 323.15 \times 10} = \frac{75}{26886.08}$$

CO_2 uptake = 2.78 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(15.8) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{79}{27718.08}$$

CO_2 uptake = 2.85 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(10.4) \times 1 \times 5}{8.32 \times 348.15 \times 10} = \frac{52}{28966.08}$$

CO_2 uptake = 1.79 (mmol/g)

(2) Liquid to solid ratio

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(15.8) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{79}{27718.08}$$

CO_2 uptake = 2.85 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(13.9) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{69.5}{27718.08}$$

CO_2 uptake = 2.50 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(9.8) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{49}{27718.08}$$

CO_2 uptake = 1.76 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(11.9) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{59.5}{27718.08}$$

CO_2 uptake = 2.14 (mmol/g)

(3) Stirring rate

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(8.9) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{44.5}{27718.08}$$

CO_2 uptake = 1.6 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(11.9 - 20\%) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{59.5}{27718.08}$$

CO_2 uptake = 2.14 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(14.35) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{71.75}{27718.08}$$

CO_2 uptake = 2.58 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(15.8) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{79}{27718.08}$$

CO_2 uptake = 2.85 (mmol/g)

(4) Particle size

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(15.8) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{79}{27718.08}$$

CO_2 uptake = 2.85 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(11.18) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{55.90}{27718.08}$$

CO_2 uptake = 2.01 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(7) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{35}{27718.08}$$

CO_2 uptake = 1.26 (mmol/g)

$$CO_2uptake\ (mmol/g) = \sum_i^n \frac{(4.8) \times 1 \times 5}{8.32 \times 333.15 \times 10} = \frac{24}{27718.08}$$

CO_2 uptake = 0.86 (mmol/g)

Supported Information D

Calculation of the Amount of Output and Input needed for Mineral Carbonation Process of By-Product Red Gypsum

In this research, the cost calculation of carbonation process is performed based on reference year in 2013. The energy used in the process of binding one tonne CO_2 in red gypsum represents a kilowatt hour of power per unit tonne CO_2 (kWh/tCO_2) stored. Additionally, the US Dollar ($) is considered as reference currency. The price of electricity per 1 kWh is 0.13 US$ (equal to 0.43 RM) based on the Ministry of Energy, Green Technology, and Water in Malaysia.

The cost of red gypsum mining is negligible. Three assumptions were made based on the experimental results to simplify the work. First, it was assumed that one t CO_2 is sequestrated. Second, one t CO_2 sequestration was performed based on the amount of red gypsum required. Third, the optimum liquid to solid ratio was considered to calculate the related cost.

Assumptions:

1 g = 1 ml: if specific weight equal to 1 g/cm^3 (or 1 wt.% = 1 ml)

1 t of CO_2 = 1.977 L

CO_2 uptake = 15.8% → 7.99 g

Distilled water needed for dissolution and carbonation experiment:

H_2SO_4 dilution → 92.95 ml
+ =
144.450 ml
NH_3 solution → 51.50 ml

Products:

(1) Product 1 (TiO_2): 0.0692 t per one t by-product red gypsum
(2) Product 2 (Fe_2O_3): 0.280 t per one t by-product red gypsum
(3) Product 3 ($CaCO_3$): 0.633 t per one t by-product red gypsum
(4) NH_4HSO_4: 0.125 t per one t by-product red gypsum

SID1: The calculation of output and input materials needed for mineral carbonation process of by-product red gypsum

Input		
Chemical and Material	Specific weight (g/cm^3)	The amount needed (kg)
CO_2 (gaseous phase)	1.977 (at 1 atm and 0 °C)	1000
Red gypsum	2.18	1251
H_2SO_4 (35%)	1.84	2720
NH_4OH (NH_3 solution 50%)	0.88	4620
Distilled water	1	14445
Output		
TiO_2	4.23	86.570
Fe_2O_3	5.24	350.280
$CaCO_3$	2.71	792.130
$(NH_4)HSO_4$	1.77	-7067.796 [a]

[a] Some chemicals are produced in the carbonation process, which are shown in the negative values.

Total costs = (transportation + energy consumption + chemicals and materials) –products income
Total costs = (11+1.47+208.44) – 158.60 = 62.31 US$

SID2: Mass balance of the input and output routes in the carbonation process of by-product red gypsum.

Input (t)	
Necessary chemicals	**The optimum L/S 10 ml/g**
CO_2	1
Red gypsum	1.251
H_2SO_4	2.720
NH_4OH	4.620
Distilled water	14.445

Output (t)	
Product 1	0.086
Product 2	0.350
$CaCO_3$	0.792
$(NH_4)HSO_4$	-7.067 [a]

[a] Some chemicals are produced in the carbonation process, which are shown in the negative values.

SID3: The amount of energy consumption for both input and output routes in mineral carbonation process of by-product red gypsum

Procedures	Energy consumption (kWh/t)
	L/S = 10 ml/g
Mining	-
Crushing	0.643
Filtration	0.25
Work index	10.77
Total	11.663

SID4: The amount and cost of chemical needed in mineral carbonation process for sequestration 1 t CO_2

Chemical	Amount needed (t)	Cost per t (US$)	Cost (US$)
Red gypsum	1.251	00.00	00.00
H_2SO_4	2.72	33.00	89.76
NH_3 solution	4.620	21.00	97.02
Distilled water	14.445	1.50	21.66
Total	-	-	208.44

L/S = 10 ml/g
t: tonne

SID5: The amount of sold products obtained from sequestration 1 t CO_2

Products	Amount achieved (t)	Sell per t industrial grade (US$)	Income (US$)
Product 1 (rich in TiO_2)	0.086	115.00	9.89
Product 2 (rich in Fe)	0.350	32.00	11.2
Product 3 ($CaCO_3$)	0.792	13.00	10.29
Remained solution [$(NH_4)HSO_4$]	7.067796	18	127.22
Total	-	-	158.60

L/S = 10 ml/g
t: tonne

SID6: The total cost of energy consumed for 1 t CO_2 sequestration

Step	Energy consumption (kWh/t)	Price of electricity per 1 kWh (US$)	Cost (US$)
Crushing	0.643	0.13	0.08
Filtration + Precipitation	0.25 10.77	0.13 0.13	0.03 1.40
Total	11.663	-	1.51

SID7: The total cost of energy consumed for 1 t CO_2 avoided

Step	Energy consumption (kWh/t)	Price of electricity per 1 kWh (US$)	Cost (US$)
Crushing	0.643	0.13	0.08
Filtration	0.25	0.13	0.03
+			
Precipitation	10.77	0.13	1.40
Heat	11	0.13	1.43
Power	24	0.13	3.12
Total	11.663	-	5.98

Total dissolved inorganic carbon (TDIC) was determined as carbon in a gas sample taken from gas-tight cylinder and in a sample after mineral carbonation process. The amount of TDIC (mmol) was calculated by applying Henry's law considering the known volumes of headspace and solution:

$$TDIC = ppm\left(K_H + \frac{V_G}{R.T.V_W}\right)$$

K_H: henry constant ($10^{-1.41}$ mol/l.atm at 25 °C)
V_G: gas volume of headspace (l)
V_W: volume of solution (l)

Additionally, based on the amount of procedure variables such as reaction temperature, liquid to solid ratio, and stirring rate; CO_2 uptake by red gypsum suspension were experimentally determined. The mass transfer of CO_2 into solid carbonate was calculated as the difference between the amount of CO_2 uptake and TDIC.