

CHEMICAL ACTIVATED GRINDING OF CEMENT RAW MATERIALS AND SHALE BY ACIDIC COAL MINE WATER

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ABSTRACT: Compliance with environmental norms of cement raw materials grinding or clinker grinding, feasible production systems and low cost production facilities are needed in today's modern technology, also enable the high capacity production. However, raw materials and chemical nature of them requires a variety of adaptation methods. For this purpose, universities and industry needing to work together to provide the basic information required in pilot scale. This study examined the cement raw materials, types of Şırnak limestones, Şırnak marly limestone and marly shale and coal shale. The representative samples were taken from local areas of Şırnak. 24% high Hardgrove Grinding Index were determined at the chemical activated grinding of samples producing yield. For this purpose, chemical treated and further ground for Şırnak limestone, Şırnak marly shale and coal shale were discussed.

1. INTRODUCTION

For grinding raw materials in a grinding mill plant, the chemical treatment method is governing much effective in energy consumption of mills. Power needs will decrease with chemically fractured material. In the standards, the tests of mainly Bond and Hardgrove Index are commonly used as an industrial standard providing distinct energy requirements in all industrial applications. A chemically activated grinding process can save energy in grinding of hard materials, such as cement clinker, granulated slag, limestone, and quartz. This process subjects to the aggregate materials to high internal fracturing weakness between the macro and micro fissures and crack faces. Although this comminution technique closely resembles natural alteration, the degree of alteration by chemical breakage in chemical activation achieved within the chemical pots is carried out, even after only a single pass. Howard & Datta determined that chemical comminution having many advantages, this method using ammonia, providing ash liberation in coal grinding with chemical breakage

[Howard and Datta, 1976, Howard et al., 1977].

A Bond Work Index test is a standard test for determining the Ball Mill Work Index of a sample of ore. It was developed by Fred Bond in 1952 and modified in 1961 [Bond, 1952]. In the fundamental design of grinding circuits in the plants, the Bond method is widely used for each material in particularly scale-up mills, evaluating power needs and in the estimation of performance. Its use as an industrial standard is very common, providing satisfactory results in all industrial applications.

The Hardgrove work index can be used only for determining the grinding power for coal and soft rocks but also to classify the difference in hardness of different coals and coal shale. Every coal material has a characteristic Hardgrove index at standard level. The power required to break the high ash coal fine is higher due to the high content of harder shale material [Sengupta, 2002; Özbayoğlu et al., 2008].

The Hardgrove index is widely used to estimate the power required to grind chemically treated fractured coal materials. Because of the short determination of this index, fracturing intensity has investigated the effect of mechanical parameters on grinding, and the relationship between them.

The strength values obtained by the micro-cracks, fractures, tensile stress cracks and pores created by chemical treatment are the common geological parameters for the materials such as the rocks [Tavares and King, 2002; Tavares et al., 2005; Refahi et al., 2007]. The parameters regarding rocks give the failure values to the geotechnical engineers. Chemical fracturing and following comminution on the purpose is to break rock to given sizes. It has improved the assesment of tests interrelated between the failure energy and the final size reduction and surface area.

It is significantly mentioned that alteration of cement raw materials, such as limestone, marl, tuff or shale rocks, interrelation between compressive strength and propagating fissures. Chemical alteration by ammonia or chemical solutions changed the ground characteristics of coal [Howard and Datta, 1976; Howard et al., 1977]. These improvements in the chemical technique are especially useful for coal grinding in pulverized coal burning industries.

The unaxial compressive failure load of the cement raw materials interrelated with the grinding so that the relationship can be defined among the Bond Work and Hardgrove Index values and compressive strength of chemically fractured coal characteristics will emphasize the great importance. The aim of this study is to investigate the behavior of limestone, marly limestone and shale

under different chemical conditioning methods. Chemical activation bath is using 0.1N ammonia, 0.1M sulfuric acid and waste acidic coal mine water to establish a relation among strength and HGI properties and Bond Grindability, Bond Work Index.

1.1. The Standard Bond Grindability Test

The most widely known measure of grindability is Bond Work Index which was defined as the resistance of the material to grinding and quantified the specific work input (kWh/t) required to reduce the material from theoretically infinite size to 80% passing 0.106 mm. The work index is subject to variations due to variations in the inherent properties of minerals and rocks, variations in the grinding environment and variations in the mechanism of energy transfer from the grinding equipment to its charge.

The standard Bond grindability test is a closed-cycle dry grinding and screening process, which is carried out until steady state condition is obtained. This test has been described as follows [Unland et al., 2005; Tavares, 2007; Toroman and Uçurum, 2012; Gökçe et al., 2012].

In the design of grinding circuits in a mineral processing plant, the Bond method is widely used for a particular material in dimensioning mills, determining power needs and in the evaluation of performance. Its use as an industrial standard is very common, providing satisfactory results in all industrial applications. Despite having many advantages, this method has some drawbacks, such as being tedious and time consuming, and also requiring a special mill. Due to these difficulties, a number of easier and faster methods have been developed to determine the Bond

work index [Tavares, 1998; Austin, 2004; Li et al., 2005].

The general characteristic of all these methods is the need for either a Bond mill. A non-standard method for determining the Bond work index was presented using an experimental relationship between the Bond work index and the mechanical and strength properties of the material [Bergstorm, 1985].

1.2. Hardgrove Index Method

The HGI tests on parent coals and their binary and ternary blends were carried out using the standard Hardgrove method. For a comparative study, four standard reference coals were also used. Gross representative samples, weighing 5 kg, were collected by engineers for each coal seam with 50 increments taken following the ASTM D 409-08 procedure [ASTM, 2006]. A representative sample was obtained using the coning and quartering technique.

For the determination of the HGI values, each gross sample was crushed to 4,75mm (4 mesh) in an impact crusher. The crushed sample was split into smaller lots of 250 g, using a standard method of sampling. Samples each weighing 250 g was dried in an air-drying oven at 80°C for three hours until a constant weight loss was observed. Each air-dried sample of 4.75mm in size was placed on a 1.18mm (No. 16) sieve nested with a 0,600 mm (No. 30) sieve. The 1.18mm (No. 16) fraction was ground in a laboratory grinding mill until the whole material passed through the 1.18mm (No. 16) sieve, followed by sieving through the 0,600 mm sieve (No. 30). Sieving of each sample was performed by a mechanical sieving machine for five minutes. The sieving procedure was followed by the sieving method (ASTM, 2006). The 0,600 mm (No. 30) fraction

was discarded and the 0,600 mm fraction was saved for determination by the Hardgrove Grindability Indices by an HGI machine.

2. MATERIAL&METHODS

In this study, Point load index I_c and uniaxial strength were initially measured for the the limestone and shale samples. Standard Bond grindability tests were carried out and work indices (W_i) were calculated. The chemical analysis of limestone and shale samples is given in (Table 1).

Table 1: Chemical composition of Limestone, Marly limestone and shale samples used in experiments.

Material	CaO	SiO ₂	Na ₂ O	Fe ₂ O ₃	MgO	K ₂ O	LOI
Limestone	48.28	2.5	0.4	3.6	2.0	0.6	40.2
Marly Limestone	34	19.6	1.4	6.7	4.5	2.5	21.7
Marly shale	12	44.8	4.7	9.4	5.6	3.2	7.5
Coal shale	5.42	54.8	1.1	7.1	2.15	2.1	21.5

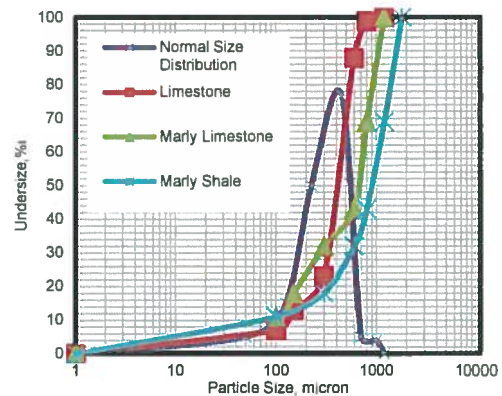


Figure 1: Particle Size Distribution and Normal Size Distribution of HGI Limestone and Shale samples.

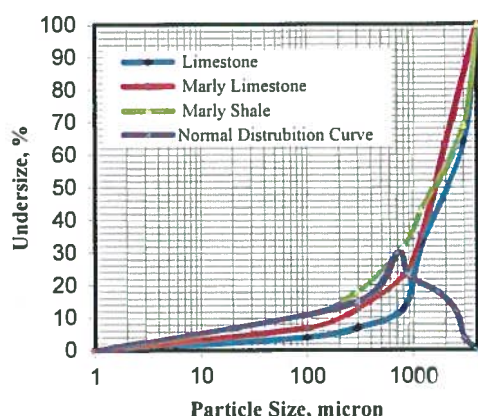


Figure 2: Particle Size Distribution and Normal Size Distribution of Bond Test Limestone and Shale Samples.

The samples are crushed in a laboratory scale jaw crusher, and then the standard Bond grindability test is performed. The Bond work index values (W_i) are calculated from the equation below.

The standard Bond grindability test is a closed-cycle dry grinding in a standard ball mill (30.5x30.5 cm) and screening process, which is carried out until steady state condition is obtained. This test was described as in the standard. The feed samples had the particle size distribution as illustrated in (Figure 1 and 2).

Original 5 kg coal samples and coal shale samples are put in 70 °C warm chemical solutions of 0,1N ammonia and 0,1M Sulfuric acid and acidic mine water in 3 days period, respectively. Further those chemically activated samples were tested for HGI and Bond grindability.

3. RESULTS AND DISCUSSION

The material is packed to 700 cc volume using a vibrating table. This is the volumetric weight of the material to be used for grinding tests. For the first grinding cycle, the mill is started with an arbitrarily chosen number of mill revolutions. At the end of each grinding cycle, the entire product is discharged from the mill and is screened on a test

sieve (P_i). Standard choice for P_i is 106 micron. The oversize fraction is returned to the mill for the second run together with fresh feed to make up the original weight corresponding to 700 cc. The weight of product per unit of mill revolution, called the ore grindability of the cycle, is then calculated and used to estimate the number of revolutions required for the second run to be equivalent to a circulating load of 250%. The process is continued until a constant value of the grindability achieved, which is the equilibrium condition. This equilibrium condition may be reached in 6 to 12 grinding cycles. After reaching equilibrium, the grindabilities for the last three cycles are being averaged. The average value was taken as the standard Bond grindability (G_B).

The products of the total final three cycles are combined to form the equilibrium rest product. Sieve analysis is carried out on the material and the results are plotted in order to find the 80% passing size of the product (P_i).

$$W_i = 1.1 * \frac{44.5}{P_i^{0.23} * G_B^{0.82} * \left[\left(\frac{10}{\sqrt{P_{80}}} \right) - \left(\frac{10}{\sqrt{F_{80}}} \right) \right]} \quad (1)$$

where W_i is the work index (kwh/t); P_i , screen size at which the test is performed (106 μ m); G_B , Bond standard ball mill grindability, net weight of ball mill product passing sieve size P_i produced per mill revolution (g/rev); P_{80} , sieve opening which 80% of the product passes (μ m); F_{80} , sieve opening which 80% of the feed passes (μ m). The Grindability of samples was determined from HGI and Bond test and the average values with minimum and maximum values for each sample type are given in (Table 2).

Table 2: Grindability properties of using rocks

Rock Name	G (g/rv)	Wi (Kwh/t)	HGI	Density
Limestone	3.23	7.0	46	2.62
Marly Limestone	2.53	6.6	34	2.61
Marly	2.62	6.7	42	2.51
Coal shale	3.79	7.9	57	2.41

In experimental studies, The Bond grindability of Şırnak limestone, marly limestone and shale is the most difficult than other samples. The biggest reasons of low Bond grindability, the porosity of sample was low is based on the solid rock texture.

Although the rocks of Şırnak asphaltite and coal shale were the same type, there are no differences comminution characteristics. The reason of this condition, their porosity has similar as the structure of coal.

The strength of samples was determined from compressive load test and the average values with minimum and maximum values for each sample type are given in (Table 3).

Table 3: Compressive strength of Limestone and Shale Samples.

	I _s Point load Strength, kg/cm ²	σ _c Uniaxial Compressive Strength, kg/cm ²
Limestone	18.90-25.00	128.70
Marly Limestone	19.80-26.00	186.30
Marly Shale	15.00-22.00	94.80
Coal Shale	12.00-16.00	61.50

The effect of period of chemical activation on grinding was tested. The graphs were observed as illustrated in (Figure 3). Two days treatment was sufficient for developing grindability manner of the coal samples. HGI values increased at about 24 % at two days

period. The relationship among Bond Grindability and HGI values were similar in chemical treated limestone and shale samples. The most important reason of the relationship was the same as in the breakage under chemical shattered samples and porous structure is more effective rather than solution in the grinding mill.

The chemical treated samples were ground in Bond and Hardgrove equipment and the results are illustrated in (Figure 4). As seen in Figure 4 0,1 N ammonia solution increased finer particle size fraction of minus 0,2 mm at about 13%. Bond breakage rate at 212 micron was higher for Şırnak asphaltite reaching 3%/min.

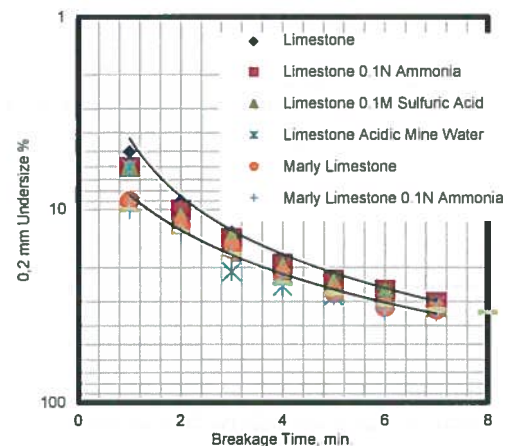


Figure 3: Bond breakage with Chemically Treated Limestone Samples in 3 days.

From the chemical activated test results, Hardgrove grinding Index is determined and the results were shown in (Figure 5). Hardgrove index values increased to 105 values for Şırnak Coal Shale. For Marly Limestone reached to 65 value of HGI from 42.

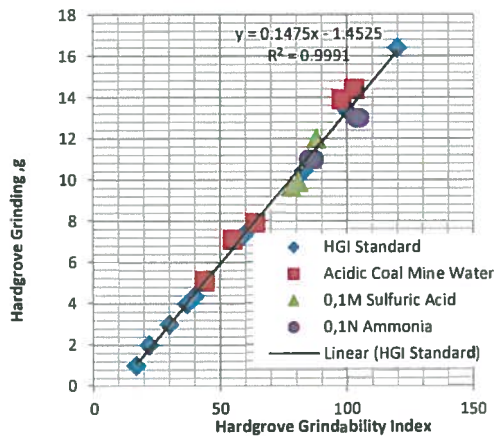


Figure 4: Bond breakage with chemically treated limestone and shale samples in 3 days.

4. CONCLUSIONS

In this study, a method which reduces and eliminates inefficiency and problems during the determination of work index and Bond's grindability is described. The effect of physico- mechanical parameters of the materials on grindability and its relation with grindability are investigated. It is possible to determine physico-mechanical parameters. Statical methods contain difficult test procedures and problems as encountered at Bond's grindability process. However, tests are simple, easy and show minor problems in dynamic methods. A good correlation is obtained between Bond grindability and work index with the values determined from the Hardgrove Index method as a result of the tests done.

The best correlation was found between Bond (Grindability and work index) and HGI. Moreover, HGI give better results than static methods because coal grinding is also a compression process. The HGI method has many advantages, because of its ease of use and the relatively short time required compared to Bond methods. The depth of particle bed is a key variable in determining the fragmentation of coals and shale by high

velocity impact. This may not be the case with static loading.

Two different methods of characterizing breakage manner of coal are investigated for the purpose of predicting performance in the comminution. Bond method was performed as standard tests and assume that the common test best reflecting the dominant behavior of coals.

HGI method was important in coal breakage and mechanical properties for shale.

The most important result of this study is the correlation between Bond, HGI and compressive strength for chemical activated grindability. In future studies, the correlation will be clearly established by taking the porosity into consideration, and increasing the number of samples.

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