# Production of White Barite from Barite Concentrates of Shaking Tables by Bleaching Process after Magnetic Methods

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## Abstract

*Market price of industrial minerals depends on the purity of products, and increases almost exponentially with the decrease in grade of coloring impurities. Therefore, this work was conducted to investigate the applicability of dry/wet high gradient magnetic separation (HGMS) and bleaching methods on the rejection rate of coloring impurities from barite ore. Experimental works were conducted on a processing plant concentrate. Both wet and dry magnetic separation processes failed in rejection of coloring impurities. Barite specifications especially for paint industry could not be satisfied due to the presence of coloring impurities in smearing form in the feed, not as free particle. But, improvement in product quality was found to be higher in wet process than that in dry one. Therefore, further cleaning of barite was applied on wet HGMS product by mineral acid ($H_2SO_4$, HCl) leaching. Acids significantly improved the quality of barite. However, bleached product quality did not meet the specifications by sulfuric acid leaching. On the other hand, saleable barite could be obtained by HCl bleaching at 15% HCl concentration for 15 minutes. Beneficiation tests stated that brightness index of barite could be increased from 68.05% to 90.12% by wet HGMS followed by HCL bleaching.*

*Keywords: barite, magnetic methods, bleaching, whiteness, concentrate*

**Introduction**

Beneficiation of barite ore by physical methods (gravity or flotation) is capable of producing high quality concentrates with 97% $BaSO_4$ grade or more (Deniz, 2000), which conforms to most stringent market specifications for the chemical and oil industries. However, such highly pure barite concentrate might not satisfy the product specifications especially for paint, paper and glass industries concerning the whiteness, brightness and yellowness indexes. Barite powder for paint production can be classified into three groups according to $BaSO_4$ grade, optical properties and specific gravity (Table 1). Market price of barite power depends on its purity: market price of purest barite power may be as high as there to five times that paid for concentrates for break lining, radiation-proof concrete and oil industries.

Considerable efforts have been given to remove the coloring impurities of industrial raw materials.

In particular, ferric species, which causes orange tint to the raw material, reduces market value of industrial minerals (Yan et al., 1978). Flotation and gravity methods are the commonly applied ones in the rejection of impurities, in which physical, chemical and physicochemical properties of minerals are exploited (Deniz, 2004; Groudev et al., 1978; Guimares et al., 1987). However, these methods have been seen to be less effective for iron removal than chemical bleaching, which may be due to the smearing of iron impurities on particle surface. Nowadays, high gradient magnetic separation (HGMS) and bleaching processes have gained importance in the beneficiation of industrial minerals. Fe-containing coloring impurities have reasonable magnetic susceptibility. Therefore, HGMS is one of the most successful beneficiation methods in the removal of coloring contaminants from industrial minerals (Chiesla, 2003).

Reductive dissolution of iron oxide minerals by inorganic and organic reagents has also been investigated by several researchers, in which basic mechanism involved are reported (Blesa and Maroto, 1986; Borghi et al., 1989; Chiarizia and Hortwiz, 1991; Dos Santos Afonso et al., 1990; Patermarakis and Paspaliaris, 1989; Stone and Morgan, 1987; Torres et al., 1990). Acidic reductive leaching is one of the best known and most widely employed chemical processes for beneficiating minerals of industrial interest. Conventional acidic bleaching is performed by means of reagents such as sodium hypochlorite, sulfur dioxide, and sodium dithionite for the preparation of highly pure industrial raw material for industrial application areas in the production of paint, ceramics, glassware, paper, etc. Other techniques are also available such as those based on conventional mineral acid ($H_2SO_4$ or HCl) leaching (Conley and Lloyd, 1970; Veglio´ et al., 1996).

This study was performed to increase the brightness index of gravity circuit product of a concentrator. Removal of coloring impurities was investigated by wet/dry magnetic separation and bleaching techniques.

Tab. 1. The optical properties and specific gravity of barite powder for paint industry

Tab. 1. Właściwości optyczne i gęstość proszku barytu dla pigmentów

| Quality | Specific gravity, $g/cm^3$ | $BaSO_4$, % | Brightness Index (R457), % | Whiteness Index (RY), % | Yellowness Index (YI), % |
|---|---|---|---|---|---|
| Extra | 4.5 | >97 | >90 | >94 | <5 |
| I | 4.4 | >94 | >88 | >92 | <6 |
| II | 4.4 | >92 | >84 | >90 | <7 |

Tab. 2. The chemical compositions of pre-concentrates of shaking table using in the experimental studies

Tab. 2. Skład chemiczny koncentratu po wstępnym wzbogacaniu na stole koncentracyjnym

| Oxides | $BaSO_4$ | $Fe_2O_3$ | MnO | $Al_2O_3$ | CaO | $SiO_2$ | MgO | $Na_2O$ | $K_2O$ | Loss |
|---|---|---|---|---|---|---|---|---|---|---|
| % | 91.56 | 2.89 | 3.92 | 0.89 | 0.13 | 0.72 | 0.08 | 0.33 | 0.31 | 0.29 |

Tab. 3.Analysis of barite pre-concentrate used in this work

Tab. 3. Wyniki analizy koncentratu barytu po wstępnym wzbogacaniu wykorzystanego do badań

| Brightness (R457), % | Whiteness (RY), % | Yellowness (YI), % | Specific gravity, $g/cm^3$ |
|---|---|---|---|
| 68.05 | 77.61 | 14.03 | 4.32 |

## Material and methods

### *Material*

Sample was taken from concentrate pond of shaking table circuit of Başer Mining Co. in Isparta, Turkey. Chemical composition of test sample was determined by X-ray fluorescence (XRF) technique (Table 2). The pre-concentrate was determined to be mainly composed of $BaSO_4$, $SiO_2$, CaO, $Fe_2O_3$, and MnO. Optical properties of sample were determined by Datacolor Elrepho SF450X photoelectric spectrophotometer (Figure 1a). Gravimetric analysis method was applied to determine specific gravity of sample by using Le Chatelier measuring bottles. Experimental setup for specific gravity measurement was given in Figure 1b. Characteristic properties of test sample were given in Table 3.

### *Method*

Boxmag Rapid HGMS magnetic separator (Figure 2a) was employed as wet magnetic separation, which enabled the adjustment of magnetic field intensity to required value. Sample was passed through the separator, and then, the separating box was rinsed gently. Feeding to the separator was made manually. Nonmagnetic barite product of wet separator was filtered, dried, weighted and analyzed.

Dry magnetic separation was performed by Carpco HGMS magnetic separator (Figure 2b).Adjustment of magnetic field intensity and feed rate was made automatically.

The bleaching tests were carried out in 1 litter glass beaker, in which mechanical stirring was applied at a stirring speed of 400 rpm. Reactor capacity was adjusted to 400 ml, containing 100 g sample. HCl and $H_2SO_4$ were used as leaching agents at ambient temperature (about 21°C). Effects of acid concentration and leaching time were investigated. After bleaching, solid was washed thoroughly to eliminate the remaining leach residues, HCl and $H_2SO_4$ , and then filtered and dried. The optical properties of bleached solid sample were determined by Elerepho Spectrophotometer. Each test was repeated three times and the values reported are a mean average.

## Results and discussion

### *Dry high gradient magnetic separation*

Dry magnetic separation tests were performed manipulating the magnetic field intensity at the pre-determined optimum conditions (drum speed: 25 rpm; loading capacity: 30 kg/h; gap: 27 mm). Effect of magnetic field intensity on the brightness index was given in Figure 3a. The results showed that coloring impurities could partially be removed. When magnetic field intensity was applied as 2 Tesla, optical properties of concentrate of wet magnetic separator were determined as 72.08%, 81.73% and 12.06% for brightness, whiteness and yellowness indexes, respectively. However, measured values did not meet the specifications of paint or paper industries. Then, dry process failed in removing the coloring impurities of barite pre-concentrate.

### *Wet high gradient magnetic separation*

Coloring manganese and iron oxide impurities of barite were also tried to be rejected by wet HGMS method. Feed pulp of barite pre-concentrate having 25% solid rate was used in the experimental works. Effect of magnetic field intensity was observed to be more predominant in wet separation of magnetic impurities than dry process (Figure 3). Cleaner nonmagnetic barite concentrate could be obtained by increasing field intensity. Cleanest barite concentrate could be ob-

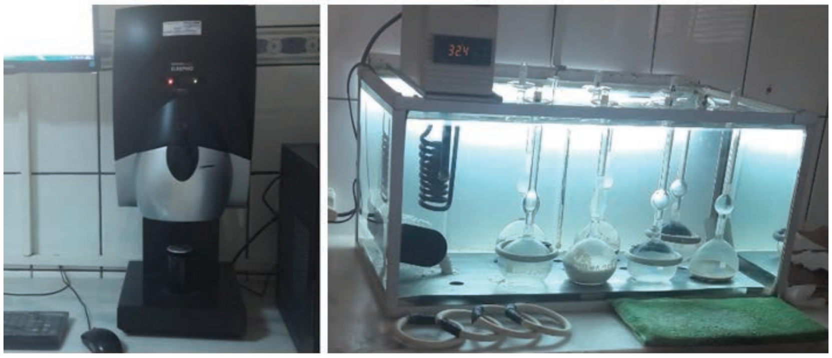

Fig. 1. a) Elerepho Spectrophotometer b) Le Chatelier glass specific gravity measurement setup

Rys. 1. a) Elerepho Spectrofotometr b) miernik gęstości Le Chatelier 'a

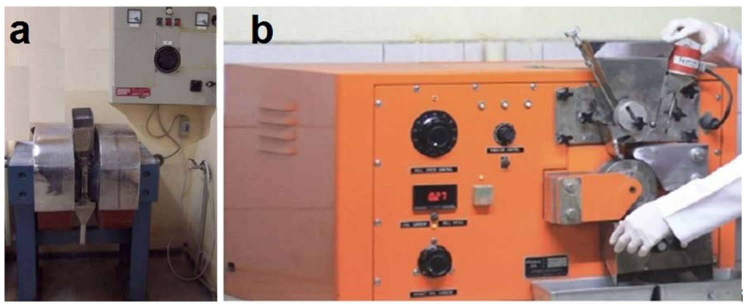


Fig. 2. a) Boxmag Rapid Laboratory HGMS b)Carpco Laboratory HGMS

Rys. 2. a) separatorm magnetyczny Boxmag Rapid Laboratory HGMS b) separator magnetyczny Carpco Laboratory HGMS

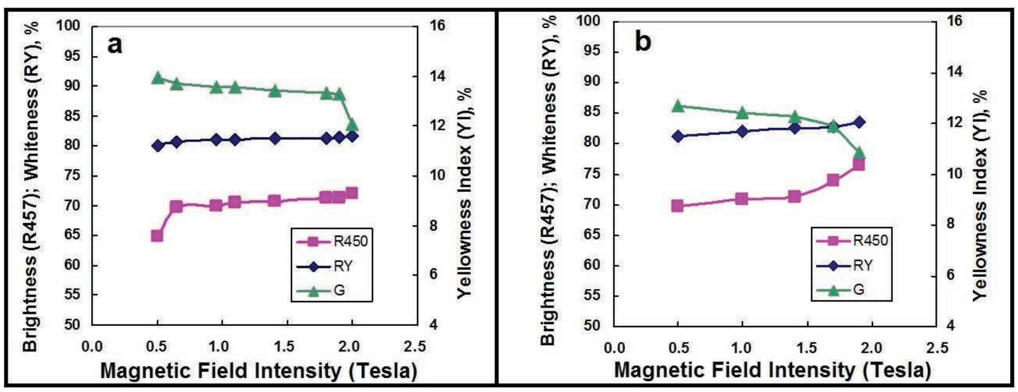


Fig. 3. Effect of magnetic field intensity on the optical properties of barite; a) dry HGMS b) wet HGMS

Rys. 3. Wpływ natężenia pola magnetycznego na właściwości optyczne barytu; a) wzbogacanie magne-tyczne na sucho HGMS b) wzbogacanie magnety-czne na mokro HGMS

tained by applying 1.9 Tesla in wet process, in which case a product was obtained with 76.45% brightness index, 83.43% whiteness index and 10.87% yellowness index. However, sufficiently high brightness index necessary for common end uses could not be satisfied. This result was attributed to the presence of magnetic impurities in barite sample as smeared form on the particles.

***Bleaching of barite***

The bleaching test was applied on wet HGMS concentrate. Experiments were carried out in a mechanically stirred 1 litter beaker at a solid rate of 25%. Effects of concentration (5%, 10%, 15% and 20%) and type (HCl and $H_2SO_4$) of acid bleaching, and leaching time (1, 5, 15, 30 minutes) on the bleaching of barite were investigated. During bleaching, coloring Fe-impurity was thought be removed from barite sample according to following reactions releasing highly soluble ferric-compounds.

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O \quad (1)$$

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \quad (2)$$

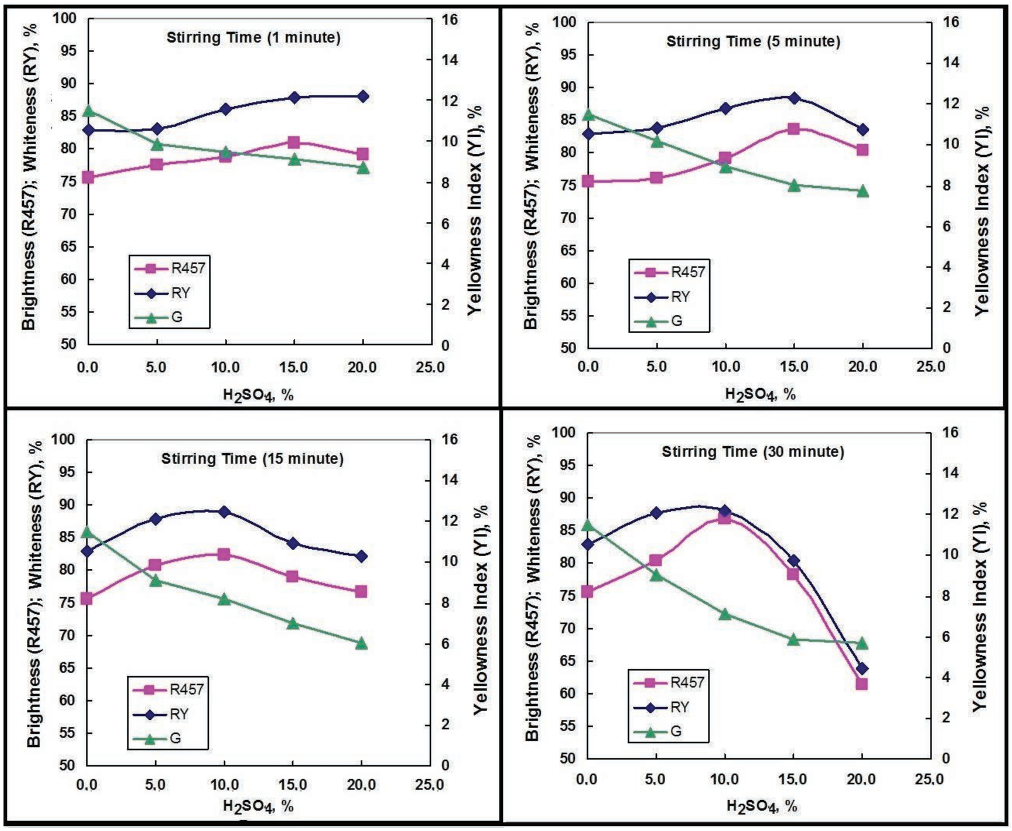


Fig. 4. Effects of sulfuric acid concentration and stirring time on the optical properties of barite

Rys. 4. Zależność stężenia kwasu siarkowego I mieszania na właściwości optyczne barytu

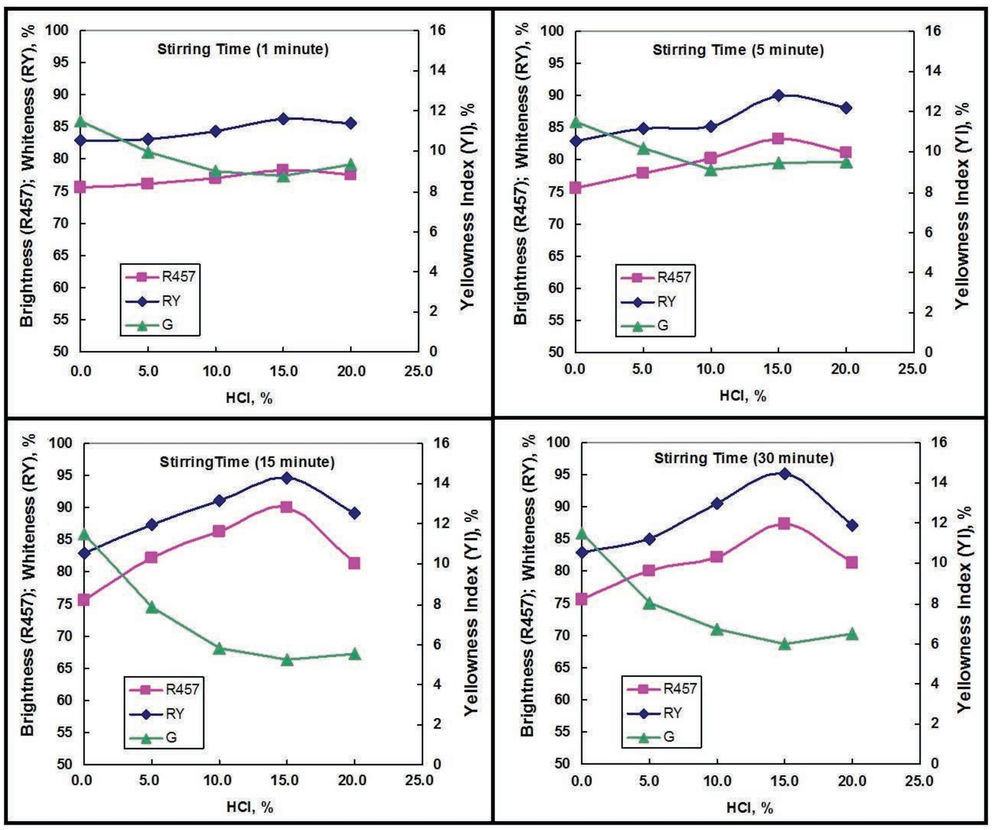


Figure 5. Effects of hydrochloride acid concentration and stirring time on the optical properties of barite

Rys. 5. Wpływ stężenia kwasu chlorowodorowego i czasu mieszania na właściwości optyczne barytu

Tab. 4. Analysis of barite concentrate prepared by wet HGMS followed by HCl bleaching

Tab. 4. Wyniki analizy koncentratu barytu po wzbogacaniu magnetycznym na mokro I ługowaniu HCl

| Brightness (R457), % | Whiteness (RY), % | Yellowness (G), % | $BaSO_4$, % | Specific gravity, g/cm$^3$ |
|---|---|---|---|---|
| 90.12 | 94.62 | 5.23 | 97.12 | 4.5 |

Figure 4 shows the effect of sulfuric acid on the optical properties (R457, RY and G) of bleached barite. It was seen that better bleaching results were obtained with extended leaching periods at 10% acid concentration. On the other hand, high acid concentration (15%) was observed to be necessary in case of shorter leaching times.

Sulfuric acid leaching tests showed that cleanest barite could be obtained at 10% acid concentration with extended leaching time. Optical analysis of bleached barite was found as 85.95%, 87.6% and 6.75% for brightness index (R457), whiteness index (RY) and yellowness index (YI), respectively. Significant improvement in the rejection of coloring impurities was achieved by sulfuric acid leaching as compared with the results of magnetic separation tests. However, saleable product could not be obtained.

HCl bleaching results of barite sample were given in Figure 5. High quality barite was obtained by HCl leaching process especially by extending the leaching period as compared with $H_2SO_4$ leaching. Acid concentration was found to be important leaching variable. Maximum rejection of coloring impurities was achieved with the HCl concentration of 15%. Optical properties of bleached barite deteriorated at higher concentrations. Leaching time was also observed to be effective on product quality. Coloring impurities could not be rejected sufficiently in the shorter leaching times. Maximum brightness and yellowness indexes were obtained by applying bleaching in 15% HCl leaching medium for 15 minutes. Slight improvement in the whiteness index of bleached barite was obtained when leaching was applied for 30 minutes. But, brightness and yellowness index values deteriorated in case of extended leaching periods. Beneficiation tests stated that brightness index of barite could be increased from 68.05% to 90.12% by wet HGMS followed by HCL bleaching (Table 4).

**Conclusions**

This study was performed to remove coloring impurities of a processing plant concentrate by wet/dry HGMS and bleaching methods. Although better results were taken from wet magnetic separation process, magnetic coloring impurities could not sufficiently be removed for a saleable product both by wet and dry processes. This finding was attributed to the presence of coloring impurities as smeared form on barite particles, not as free particles. Therefore, bleaching was applied on the concentrate of wet HGMS process. Significant improvement in product quality was observed by sulfuric acid leaching at 10% acid concentration applying leaching for 30 minutes leaching. However, coloring impurities could not sufficiently be removed for a saleable product. On the other hand, bleaching by hydrochloric acid gave appreciable results: saleable barite was observed to be obtained by applying bleaching at 15% HCl concentration for 15 minutes. Beneficiation tests stated that brightness index of barite could be increased from 68.05% to 90.12% by wet HGMS followed by HCL bleaching.

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## *Wybielania koncentratów barytu po wzbogacaniu grawitacyjnym i magnetycznym*

*Cena rynkowa wzbogaconych minerałów zależy od czystości produktów i wzrasta niemal wykładniczo wraz ze spadkiem stopnia zabarwienia zanieczyszczeniami. Celem przedstawionych badań było zbadanie możliwości zastosowania separacji magnetycznej prowadzonej na sucho i na mokro w separatorze wysoko gradientowym (HGMS) i metodach wybielania na szybkość usuwania zanieczyszczeń barwiących z rudy barytowej. Prace eksperymentalne zostały przeprowadzone na koncentracie z zakładu przetwórczego. Procesy separacji magnetycznej na mokro i na sucho nie doprowadziły do usunięcia zanieczyszczeń barwiących. Wymagania stawiane barytowi, w szczególności dla przemysłu farbiarskiego, nie mogły zostać zaspokojone ze względu na obecność zanieczyszczeń barwiących w matrycy minerałów a nie w postaci wolnych ziaren. Stwierdzono, że poprawa jakości produktu jest wyższa w przypadku procesu separacji magnetycznej na mokro. W związku z tym dalsze oczyszczanie barytu prowadzono na koncentracie z separacji magnetycznej HGMS na mokro przez wymywanie kwasem mineralnym ($H_2SO_4$, HCl). Kwasy znacząco poprawiły jakość barytu. Ługowanie $H_2SO_4$ było nieefektywne, nadający się do sprzedaży baryt można uzyskać przez bielenie HCl przy stężeniu 15% HCl przez 15 minut. Testy weryfikujące wykazały, że wskaźnik jasności barytu można zwiększyć z 68,05% do 90,12% przez wzbogacanie magnetyczne na mokro w separatorze HGMS, a następnie wybielanie w HCl.*

*Słowa kluczowe: baryt, metody magnetyczne, bielenie, biel, koncentrat*