

# Material Characterization Tests prior to Colemanite Flotation

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**ABSTRACT:** Sample preparation is one of the most important stages prior to application of any particular concentration method in mineral processing. The acquisition of representative samples from a mineral deposit plays a crucial role and affects all subsequent preparation and concentration tests. The test samples used in this study were supplied from the Ed-Holding's Emet Colemanite Mine in Türkiye. Prior to flotation testing, some preliminary work was carried out on the raw colemanite ore samples. This work studies the material characterization tests to find out what the samples actually contained as principal and gangue minerals and in which particular particle size range. Sample preparation was followed by identification techniques such as X-ray diffraction analysis, complete chemical analysis, particle size distribution tests and solubility tests.

## 1. INTRODUCTION

The main purpose of this work was to investigate the recovery of colemanite from ore samples supplied by Eti-Holding from the Emet deposits of Türkiye, by using froth flotation. Literature on borate flotation reveal that to date there has been no exact procedure devised for this process, although the existence of some laboratory studies, commercial patents and confidential applications on plant scale in the USA has been reported by a number of investigators over many years. (Özkan, 1994, 1999a, 1999b, 2000, Özkan et al, 1997, Özkan and Lyday, 1995)

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## 2. MATERIAL AND METHODS

### 2.1. *Source of the Material*

To find out where the test samples forwarded by Eti-Holding were taken, the author went to the Eti-Holding Emet Colemanite Mine in Türkiye as a preliminary field study as part of this project. As a result, a geological section of the place where the samples were taken was constructed and investigated by taking hand samples and photographs. One fact that should be considered is that the samples that were provided were taken from the Bottom Section of the Hisarcik open pit mine by Eti-Holding authorities, unfortunately with great care being taken to obtain colemanite crystals separately from the gangue minerals.

### 2.2. *Sample Preparation*

Sample preparation is one of the most important stages prior to application of any particular concentration method in mineral processing. The acquisition of representative samples from a mineral deposit plays a crucial role and affects all subsequent preparation and concentration tests. (Anon, 1989, MacDonald et al, 1985, Wills, 1992)

In this study, therefore, great care was taken in the sample preparation stages due to the facts mentioned above. Approximately 30 kg of colemanite ore sample, sized at minus 200 mm, was first crushed to minus 40 mm with a primary jaw crusher, then quartered twice. One-fourth of the sample was saved for records, the rest was crushed to minus 8 mm through a secondary jaw crusher. Crushed samples were passed through a tertiary roll crusher in order to obtain convenient particle sizes for grinding tests, for which a laboratory rod mill was used to grind samples into different particle sizes over different time periods.

All grinding tests were carried out in a rod mill whose operating parameters were kept constant as given below:

Inner Diameter of Mill	: 157 mm
Length of Mill	: 314 mm
L / D Ratio	: 2 / 1
Diameter of Rods	: 24 mm
Length of Rods	: 266 mm
Number of Rods	: 10
Weight of Rods	: 10,532 g
Speed of Mill	: 100 RPM (90 % of critical speed)
Weight of Sample used:	approx*. 1 000 g

### 2.3. X-ray Diffraction Analysis

In order to identify the crystal structures of the raw colemanite samples, representative samples were prepared according to the flow sheet for complete sample preparation given in Figure 2, at a particle size of minus 0.106 mm.

In this study X-ray diffraction techniques were used to determine the crystal structure of representative colemanite samples. The general plan was first to determine the d-spacing values for each diffraction peak on the X-ray diffraction patterns and then to plot these on a rule. This rule was compared with a graph of reference samples.

To find a position on the graph where curves corresponded to points on the rule a position was found where data fit the monoclinic system. With the rule positioned where the points on the rule matched the curves on the graph, the monoclinic indices were recorded for each point on the scale. Finally, the relative intensities of the diffraction peaks were calculated and a table giving the d-spacing values, relative intensity and indices for each peak were constructed. X-ray diffraction data and graphs were obtained by using the Picker High Precision Powder Diffractometer and are shown in Figure 3 with a comparison of the peaks of the

reference and present samples. The operating information of the instrument was as follows, 55 Kv, 44 mA, fine focus copper tube, incident beam monochromator (germanium 11 rplanes), copper K-alpha radiation wavelength ( $\lambda$ : 1.5405981 Å),  $2\theta$ : 0 %, 0.05 degree receiving slit, scintillation detector of Philips type PW 1964/60, diffractometer radius of 18/Pi inches and 2 degree Soller slits in diffracted beam. The scanning rate was 0.020° per step scan in 4 seconds.

The reference samples cited in the PDF (Powder Diffraction File) number 33,267 of the ICDD (International Centre for Diffraction Data) were from Ryan, Death Valley, Inyo County of California in the USA and are exhibited at the Mineralogy-Geology Museum of Delft University, Netherlands. These samples were described as transparent and colourless and likely to exhibit preferred orientation. Opaque grey samples from other localities gave an identical diffraction pattern.

### 2.4. Complete Chemical Analysis

After determining that the present samples were almost entirely crystalline colemanite, it was necessary to determine what these samples contained as major elemental components. A crushed sample was ground to minus 0.106 mm with a rod mill in order to obtain the required particle size for complete chemical analysis. The amount of ground sample was reduced to 100 g with a spinning-riffler, avoiding any contamination, and this representative colemanite ore sample was subjected to a complete chemical analysis for which as well as wet chemical analysis methods, such as gravimetric for sulphates, titration for CaO, B<sub>2</sub>O<sub>3</sub> and sulphides, and absorption for carbonates, some instrumental analysis methods such as A.A.S. (Atomic Absorption Spectrometry for SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, MnO<sub>2</sub>, SrO and As<sub>2</sub>O<sub>3</sub>, and A.E.S. (Atomic Emission Spectrometry) for Na<sub>2</sub>O and K<sub>2</sub>O were employed. Complete chemical analysis results are shown in Table 1.

The complete chemical analysis results confirmed X-ray diffraction analysis results and showed that the sample was essentially pure colemanite, although the theoretical B<sub>2</sub>O<sub>3</sub> % content of pure mineral is 50.8 % B<sub>2</sub>O<sub>3</sub> and the analysis reported 46.9 % B<sub>2</sub>O<sub>3</sub>. In this form, the ore would not require any upgrading to obtain a saleable product. The chemical analysis results also showed relatively low silica, sulphur and alkali metals, but high arsenic and strontium contents.

Table 1. Complete Chemical Analysis Results of Representative Colemanite Samples

Components	Weight %	Method Used	Precision $\pm$ %
B <sub>2</sub> O <sub>3</sub>	46.90	Volumetric	0.20
CaO	20.50	Volumetric	0.20
LOI* or H <sub>2</sub> O	22.51	Mass	0.10
SiO <sub>2</sub>	3.77	A.A.S.	1.50
As <sub>2</sub> O <sub>3</sub>	2.00	A.A.S.	0.70
SrO	1.55	A.A.S.	0.70
MgO	1.18	A.A.S.	1.00
Al <sub>2</sub> O <sub>3</sub>	0.86	A.A.S.	1.50
CO <sub>3</sub>	< 0.50	Absorption	2.00
Fe <sub>2</sub> O <sub>3</sub>	0.31	A.A.S.	0.70
TiO <sub>2</sub>	0.21	A.A.S.	1.00
SO <sub>4</sub>	0.25	Gravimetric	0.50
K <sub>2</sub> O	0.19	A.E.S.	0.70
Na <sub>2</sub> O	0.06	A.E.S.	0.70
SO <sub>3</sub>	0.02	Volumetric	3.00
MnO?	<0.01	A.A.S.	0.70

\*Loss On Ignition (at max. 800 °C)

In order to check the data on the boron content of the samples, borate chemical analyses were carried out by conventional wet chemical analysis methods on several representative colemanite ore samples. After several duplicate tests, the B<sub>2</sub>O<sub>3</sub> % content was determined as between 38 and 42 % B<sub>2</sub>O<sub>3</sub> and these data confirmed that further investigation of the sample collection methods was needed.

The field study at the mineral deposit in Türkiye revealed that the samples forwarded by Eti-Holding were colemanite crystals collected separately from gangue minerals from the Bottom Section of Hırsarıçık Open Pit Mine at Emet Colemanite Deposits of Türkiye.

At the beginning it had been intended to study the upgrading of truly representative colemanite samples from the mine, but the sampling error necessitated a change in strategy. It was decided to carry out flotation optimisation tests using the relatively pure colemanite as a reference material.

#### 2.5. Particle Size Distribution Tests

In mineral processing, finding out the trend of mineral particles in terms of their size distributions after crushing or grinding tests is a necessity prior to application of any concentration method. In order to determine any trend, several different techniques can be used as analysis tests. In this study, Gates-Gaudin-Schuhmann Plots were used to characterise the particle size distributions. The crushed ore

sample from the roll crusher stage of the standard procedure was sampled and reduced by the coning and quartering method to give a sample of approximately 100 grams, and tested by using sieves with six different sizes of aperture. The rod mill was then chosen as a convenient grinding device for further size reduction in order to avoid production of very fine particles that might cause slime coating problems during subsequent batch flotation tests. The crushed samples were ground separately for five different time periods, and same set of sieves was used to carry out particle size distribution tests. The results of these analyses together with results for the crushed ore tests, are given in Figure 1 in order to compare with each other.

In order to achieve convenient particle size reduction for the liberation particle size of colemanite samples from the Emet mine, 15 minutes grinding time with rod mill was determined as convenient as the cumulative weight rate of 75 % under size fraction of 0.210 mm.

In order to determine B<sub>2</sub>O<sub>3</sub> % contents of each particle size fraction after the optimum grinding time period, particle size fractions of samples after 15 minutes grinding were analysed using conventional wet chemical analysis methods for borates, (Vogel, 1987). In order to determine the desliming particle size, whole sample using a series of sieves of different apertures and the results are given in Table 2

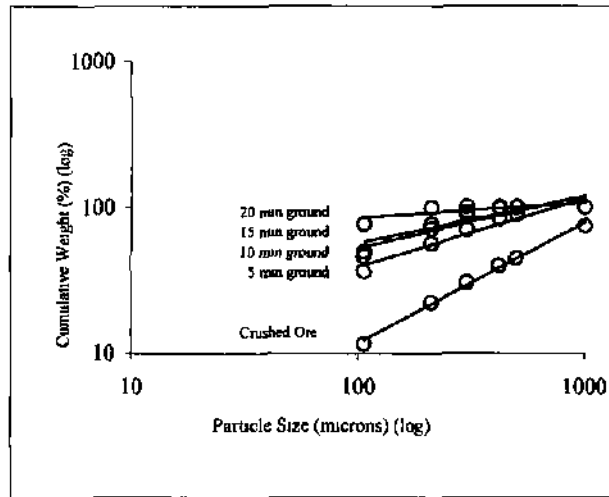


Figure 1. Gates-Gaudin-Schuhman Plots of the Test Sample

Table 2: Particle Size and B<sub>2</sub>O<sub>3</sub> % Distribution Analysis Results of Sample after 15 min Grinding

Fractions (d) mm	Weight %	Grade B <sub>2</sub> O <sub>3</sub> %	B <sub>2</sub> O <sub>3</sub> % Dist.	Cumulative Under Size			Normal Dist.
				W%	B <sub>2</sub> O <sub>3</sub> %	Dist %	
- 1.000 + 0.500	0.31	48.14	0.34	100.00	43.68	100.00	0.62
- 0.500 + 0.420	1.19	48.05	1.31	99.69	43.67	99.66	14.88
-0.420 + 0.300	6.44	47.49	7.00	98.50	43.62	98.35	53.67
-0.300 + 0.210	16.48	46.99	17.73	92.06	43.34	91.35	183.11
-0.210 + 0.106	26.35	46.62	28.12	75.58	42.55	73.62	253.37
-0.106 + 0.090	2.55	48.71	2.84	49.23	40.37	45.50	159.38
- 0.090 + 0.075	4.50	48.53	5-00	46.68	39.92	42.66	300.00
- 0.075 + 0.063	5.00	48.37	5-54	42.18	39.00	37.66	416.67
- 0.063 + 0.053	2.82	48.00	3.09	37.18	37.74	32.12	282.00
-0.053+0.045	3.32	47.72	3-63	34.36	36.90	29.03	415.00
- 0.045 + 0.020	15.32	46.64	16.36	31.04	35.74	25.40	612.80
- 0.020	15.72	25.12	9.04	15.72	25.12	9.04	786.00
TOTAL	100.00	43.68	100.00	-	-	-	-

The minus 0.106 mm fraction was closely sized to determine the fines' distribution in order to select a lower size limit for test material to minimise problems due to slimes.

Initially, desliming was carried out at 0.045 mm, however the weight percentage of the minus 0.045 mm fraction was large (30 %). This would result in unacceptably large B<sub>2</sub>O<sub>3</sub> losses in a commercial processing operation.

It was therefore decided to deslime the material at 0.020 mm to minimise losses prior to flotation. For

the purpose a DIN standard 0.020 mm sieve was used in wet sieving operation.

## 2.6. Solubility Tests

Practical solubility tests were carried out in a flotation cell which the subsequent batch flotation tests were to be conducted. Although solubility of pure colemanite crystals has been studied previously by several researchers, the determination of practical solubility was needed for this particular colemanite

ore sample in order to compare previous solubility data with current results. (Alkan et al, 1991, Çolak et al, 1993, Karagolge et al, 1992, Kocakerim et al, 1993, Kocakerim and Alkan, 1988, Yazar, 1971)

Practical solubility tests can be used to estimate material losses during batch flotation tests in terms of the residence time of the sample in the flotation cell. Although solubility depends upon not only time, but also temperature, air pressure, impeller speed of mixer, acidity of solvent and chemical composition of sample as kinetic parameters, in this study, since some of the sub-conditions were kept constant, it was decided that solubility tests could be carried out based upon residence time of sample, particle size of samples, solid/liquid ratio and impeller speed in the flotation cell.

When the tests were carried out to determine the effect of residence time on solubility, the other operating parameters were fixed at the values to be used in the batch flotation tests, i.e. impeller speed of 1,350 rpm, flotation particle size range of -0.210 + 0.020 mm, solid/liquid ratio of 20 %. When the tests were carried out to study the effect of solid/liquid ratio, the other parameters were fixed at 10 minutes residence time with similar conditions for impeller speed and particle size distribution as in previous tests. Further tests were carried out on closely sized fractions, + 0.500, - 0.500 + 0.355, - 0.355 + 0.210, - 0.210 + 0.020 and - 0.020 mm with other operating parameters at previous values. The effects of impeller speed of flotation machine were studied with 10 minutes residence time, 20 % solid/liquid ratio and - 0.210 + 0.020 mm feed size distribution range.

The solubility test results are given as four separate graphs in Figure 2 for comparison of each test parameter. As can be seen from these graphs, the solubility value shows similar trends for residence time and impeller speed but different trends in terms of solid/liquid ratio of the slurry and particle size fractions of the sample.

When residence time is increased, there is a steady rise in solubility at the beginning from 5 min to 20 min and afterwards there is a minimal increase up to the maximum time of 90 min, showing that a solubility value of  $1.05 \pm 0.05$  g/l is typical after 20 min residence time. A similar trend can be seen from the graph of impeller speed against solubility. In this graph, there is a gradual increase in solubility from impeller speeds of 500 to 1500 rpm, and afterwards a solubility value of  $1.05 \pm 0.05$  g/l is established.

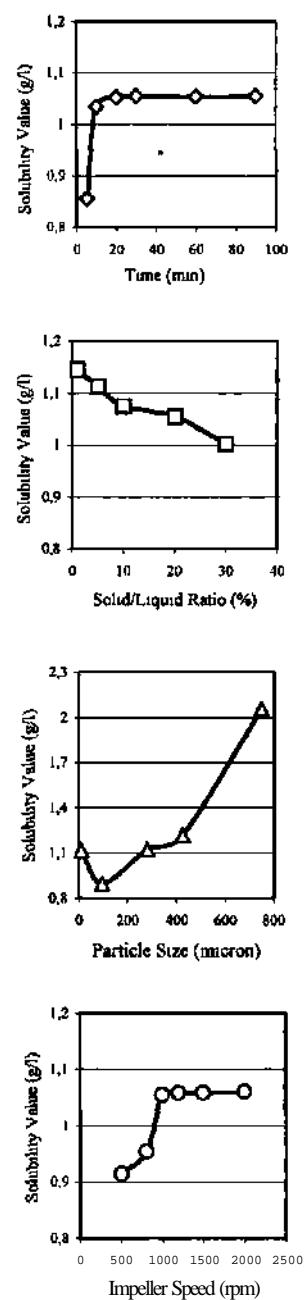


Figure 2. Solubility Graphs of the Samples in terms of Some Physical Parameters

From the graph of solid/liquid ratio of slurry against solubility there is a slight decline in solubility value, when the solid/liquid ratio is increased from 1 to 30 %. Since a solid/liquid ratio of 20 % was chosen for subsequent batch flotation tests, the solubility would be similar to the previous tests, i.e.  $1.05 \pm 0.05$  g/l.

When particle size fractions of colemanite ore sample are considered as parameters, a sharp decrease in solubility value could be seen till minus 0.020 mm fraction, when size fractions become finer. It is obvious that, the finest colemanite particles show much more solubility value than coarse size fractions. When optimal flotation feed size is considered at minus 0.210 mm plus 0.020 mm, the solubility value could be ignored as  $1.05 \pm 0.05$  g/l as can be seen from the graph of solubility value against particle size fractions.

### 3. DISCUSSION AND CONCLUSIONS

All of the material characterisation tests have revealed that, colemanite ore sample from the Emet deposits of Türkiye has got its own specific characteristics in terms of mineralogical and chemical content which directly or indirectly affect the mineral processing tests due to crushability, grindability and liberation degree prior to application of a particular concentration method. It should be noted that the above characteristics are the most important criteria in terms of mineral processing.

From the results of material characterisation tests it could be seen that this ore contains almost pure colemanite crystals, much more freely than it was previously thought due to the place where the samples were taken in the deposit, therefore all tests have been influenced by the fact that the Hisarcık bottom section of Emet colemanite deposits mainly consists of almost pure colemanite mineral, although some arsenic sulphides and clay minerals were observed during the sample preparation tests. There is an interesting contradiction at this point that despite the higher arsenic oxide content, shown by complete chemical analysis, it was observed that arsenic sulphide minerals having a red or an orange colour are present in the ore samples, although X-ray diffraction analysis did not show any contamination in terms of the presence of arsenic sulphide minerals.

Interpretation of the identification tests clearly shows that, the target mineral which will be recovered during the subsequent flotation, could be

either colemanite or other observed gangue minerals, i.e. orange and red coloured arsenic sulphides or brownish black clay minerals which could be seen in the fine size fractions, especially during the sieve analysis and desliming stage.

At laboratory scale, 15 minutes grinding with a rod mill was found to be the optimum grinding period in order to provide the liberation particle size of minus 0.210 mm, which is also to be checked with the subsequent flotation tests by using optimal fixed conditions according to different particle size fractions.

It should be noted that material characterisation tests could only provide brief information unless followed by an application of a particular concentration method. For this reason, during the batch flotation tests, the criteria above were considered thoroughly due to their effect on the efficiency of the process. However, size reduction alone can sometimes be considered as a concentration technique especially for certain industrial minerals with clay impurities which could cause further problems such as slime coatings. In this case, material characterisation tests will play a crucial role in terms of recovery of the target mineral. Therefore, the particle size distribution tests for fine material of minus 0.106 mm were carefully carried out in order to determine the content of target mineral.

Consequently, it was found that the boron content of the fine material sharply decreased at minus 0.020 mm, and this fraction was therefore considered as slimes. Thus, all concentration tests will be affected by the slimes content which will decrease the final recovery due to desliming losses. This unavoidable effect will be minimised by a controlled-grinding procedure which can be achieved by altering the grinding parameters such as time, amount of sample and characteristics of grinding media.

Flotation tests after thorough material characterization analyses showed that the sample should be carefully deslimed at minus 0.020 mm. When selective single stage direct colemanite flotation procedure, e.g. use of natural pH value, a specific petroleum sulphonate at 1, 500 g/t and alcohol type frother at 50 g/l was applied onto the current samples with a desliming stage at 0.020 mm particle size, the colemanite concentrate grade was 48 B<sub>2</sub>O<sub>3</sub> % with a recovery of almost 90 % B<sub>2</sub>O<sub>3</sub> against a feed of 36 B<sub>2</sub>O<sub>3</sub> %. If this desliming stage is not applied, then the concentrate grade and

recovery values sharply decrease to 40 B<sub>2</sub>O<sub>3</sub> % and 35 % B<sub>2</sub>O<sub>3</sub>, respectively

Solubility seems to be not effective during flotation experiments, due to buffer pH value (about 9) of pure coiemamte However, some B<sub>2</sub>O<sub>3</sub> losses are unavoidable during flotation because of the solubility of coiemamte at 1 g/l

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