Songklanakarin J. Sci. Technol.
32 (2), 189-195, Mar. - Apr. 2010

Songklanakarin Journal
of Science and Technology

http://www.sjst.psu.ac.th

Original Article

Processing of hornblende syenite for ceramics

Chairoj Rattanakawin[1], Suraphol Phuvichit[2], Yuenyong Panjasawatwong[3] and Siwadol Supapia[1]

[1] *Department of Mining and Petroleum Engineering, Faculty of Engineering,*

[3] *Department of Geological Sciences, Faculty of Science,*
Chiang Mai University, Muaeng, Chiang Mai, 50200 Thailand.

[2] *Department of Mining and Petroleum Engineering, Faculty of Engineering,*
Chulalongkorn University, Pathum Wan, Bangkok, 10330 Thailand.

Received 28 September 2007; Accepted 9 January 2009

Abstract

The purpose of this research is to preliminarily study the hornblende syenite processing. The study includes characterization, separation and evaluation. Characterization has been carried out using thin section, X-ray diffraction, X-ray fluorescence and electrokinetic measurement. A variety of techniques such as magnetic separation, froth flotation and combination of these techniques were used to separate feldspar from syenite. Evaluation of the separations has been done using data from yield of feldspar, X-ray fluorescence and cone firing test. The feldspar yield was used to evaluate the process efficiency. Besides chemical analysis, cone shrinkage, fired color and degree of vitrification were used to monitor the quality of the recovered feldspars. The feldspars were furthermore compared to the standard feldspar samples obtained from a ceramic manufacturer. Finally, the processed feldspars were graded for using in various kinds of ceramics.

Keywords: ceramics, feldspar, hornblende syenite, mineral processing

1. Introduction

Feldspar is one of the basis minerals used to prepare various types of ceramics, e.g. tiles, sanitary wares, table wares, etc. It can be used as a ceramic body and glaze in order to decrease firing temperature and to increase the degree of vitrification. Due to deficiency in potassium feldspar for ceramic industries in Thailand, some of the feldspar is imported from neighboring countries (Rattanakawin *et al.*, 2005, and 2006). To be self-sufficient on the supply of this ceramic raw material, other sources of alkaline minerals can be used. These minerals are mixed feldspar (K_2O+Na_2O > 12%), pottery stone and syenite. Syenites can be classified into various types according to their associated minerals. For example; hornblende syenite is a quartz-free igneous rock consisting predominantly of hornblende and feldspars.

Hornblende is a common constituent of syenites. The characteristics concerning its separation are its paramagnetic property and its response to flotation reagents, both amine (Manser, 1975) and sulfonate (Rattanakawin, 2006). Therefore, it is possible to separate hornblende from syenite by magnetic separation and/or froth flotation (Rau, 1985) in order to obtain feldspars. The purpose of this research is to preliminarily study the hornblende syenite processing including its characterization, separation and evaluation respectively.

2. Methods

2.1 Characterization

A syenitic rock was sampled from Ban Krok Sakae,

*Corresponding author.
Email address: chairoj@eng.cmu.ac.th

Amphoe Tatakeap, Chachoengsao (1484421N and 791589E, Sheet no.5335 IV of the Royal Thai Survey topographic map) as shown in Figure 1.

The sample was then characterized for its petrographic data and liberation size; mineralogical and chemical composition; and electrokinetic and ceramics properties. The petrographic study was made on three thin sections with the modal analysis of 800 counts on those sections. The liberation size was estimated by grain counting of each sieve size fraction of ground samples using ore microscope.

The mineralogical study was done by X-ray diffraction using D8-Advance BRUKER linked with Intel Pentium IV Processor. The measuring conditions are as follows: Cu K-alpha radiation at 40 kV and 40 mA; start and stop angles at 5 and 78 degrees; scanning speed of 0.2 sec./step with increment of 0.02; detection with scintillation counter. The -200 mesh syenitic sample was packed into a hole on plastic plate. After that the well-packed sample was x-rayed at the above-mentioned conditions. The intensity of detected signals was then plotted as a function of 2θ. Finally the intensity peaks were selected, searched and matched with those of the standard minerals compiled by the JCPDS using a computer program DIFFRAC PLUS.

The chemical composition of both raw and processed syenitic samples was analyzed using X-ray fluorescence with The ED 2000 OXFORD and the Oxford XpertEase Windows™. Primary X-ray was generated using Rhodium Target. High Voltage of 5 kV and 900 μA was set to measure Na, Mg, Al, Si, K at the Very Light Elements condition, whereas voltage of 12 kV and 600 μA was used to investigate Ca, Ti, and Fe at the Solids (S-V) condition. The reference and measuring samples were separately excited with primary X-ray for 100 sec. and the emitted secondary X-ray was detected with a lithium drifted silicon detector. Three certified reference feldspars; NCSDC 61102, SRM 99a and SRM 70a (Rattanakawin *et al.*, 2005) were used to create a standard calibration curve in which chemical analysis (% weight of oxides) of the syenitic samples was compared and evaluated. Loss on ignition was also included in the analysis by determining the weight loss of the sample fired at 1000°C for one hour.

The electrokinetic property of iron bearing minerals was measured using electrophoresis technique. The Zeta-Meter System 3.0+ was employed to measure zeta-potential of the diluted and well-dispersed hornblende at suspension pH ranging from 2-6. HCl and NaOH with concentrations of 0.1 and 1 mol/L, respectively, were used to adjust the suspension pH. The applied voltages were set to be 100, 200 or 300 Volts depending on observed velocity of the charged hornblende particles. Then the zeta potential can be calculated from the applied voltage and the velocity of the particle using Excel program.

Cone firing test was used to determine ceramics properties of raw and processed syenitic samples. The samples were coned and fired at 1280°C for 30 minutes. After that shrinkage, fired color and degree of vitrification of the cones were evaluated.

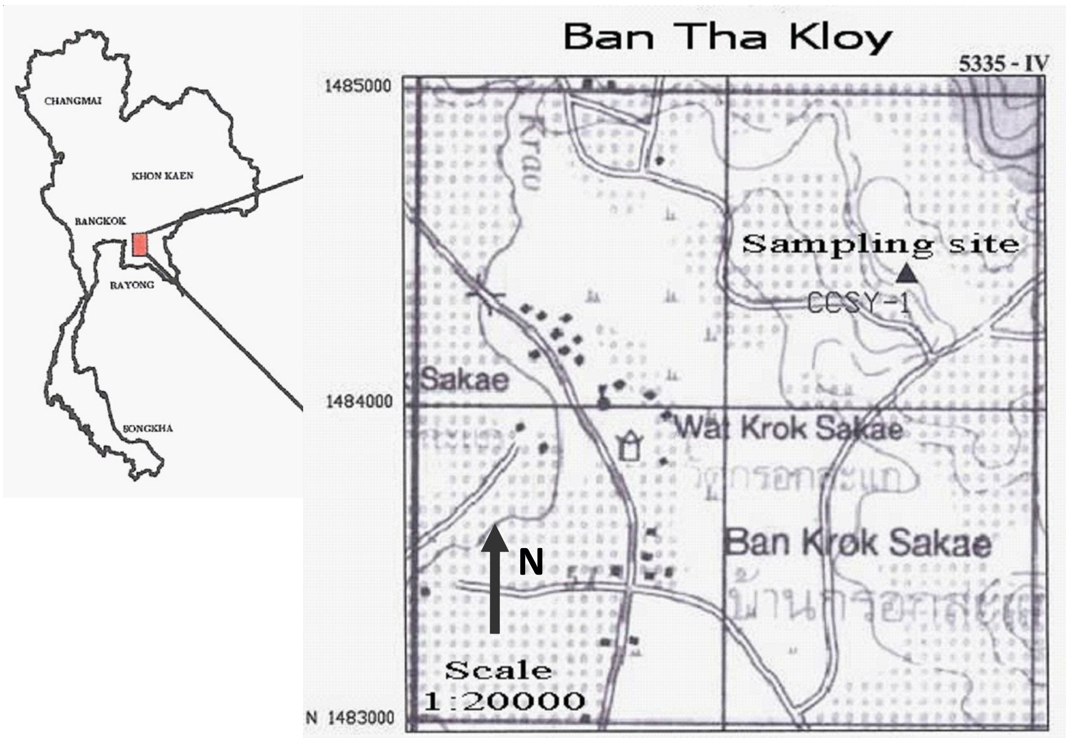


Figure 1. Topographic map showing location of syenitic rock sampling.

2.2 Separation

A variety of techniques such as magnetic separation, froth flotation and combination of these techniques were applied to separate feldspar from syenitic rock. Wet high intensity magnetic separator (WHIMS) of batch type (Boxmag Rapid, Type LHW with an array of stainless steel wedge-bars in the plate box) was used to separate paramagnetic gangues. The separating process was done by single passing of the ground feed (20% wt. solids pulp) at a flow rate of 10 L/min. under the applied field intensity of about 12,000 Oersted (or magnetic induction of about 16,800 Gauss). The magnetic separation was alternatively performed singly or co-operatively with flotation. The flotation procedure is as follows:

1. Ball milling 1 kg. of a syenitic rock at 60% wt. solids for 3 min. to the passing size of about 65 Tyler mesh.
2. De-sliming at about 200 mesh by rinsing the suspended particles.
3. Adjust the ground pulp to 30% wt. solids.
4. Conditioning the pulp in a laboratory flotation cell at 1000 rpm with sulfuric acid at a desired pH (standard condition at pH 3) and collectors (either amine or sulfonate) with various concentrations for 3 min.
5. Addition of frother (pine oil) about 50 g/ton rock.
6. Flotation of iron bearing minerals (mostly hornblende) in conjunction of the pine oil.
7. Discard of float product.
8. Filter and drying of sink product.
9. Removal of iron contaminants from grinding and/or the remaining of a syenitic rock itself in the sink product using a dry low intensity magnetic separator.

2.3 Evaluation

The finished sink products were weighed, sampled, analyzed by X-ray fluorescence, and cone-fired respectively. Evaluation of the separation was done using the yield of feldspar and its chemical composition, cone shrinkage, fired color, and degree of vitrification as criteria. The feldspars were furthermore compared with standard feldspar samples obtained from the raw material section of a ceramic manufacturer. Finally, the feldspars were graded for using in various kinds of ceramics.

3. Results and Discussion

3.1 Petrographic study of a syenitic rock

The rock sample is non-porphyritic and medium grained, having sizes largely in a range of 1-2 mm. The study reveals that the sample is compositionally syenite formed by K-felspathization rather than crystallization of syenitic magma.

From the modal analysis, the sample is constituted largely by K-feldspar (61%) with subordinate plagioclase (20%) and amphibole (13%). The associated minerals are quartz (3%), biotite (1%), Fe-Ti oxide (1%) and small amounts of apatite, zircon and sphene/leucoxene. Plagioclase is a primary mineral while K-feldspar, quartz, and biotite are secondary minerals. Amphibole and Fe-Ti oxide appear to have both primary and secondary origins.

K-feldspar crystals are all microcline with deformed twin lamellae and perthitic textures. In addition, the crystals commonly have many plagioclase inclusions (Figure 2) showing a severe alteration. The altered inclusions in a single K-feldspar have the same optic orientation signifying that the crystals have been formed by the alteration process called K-feldspathization. The K-feldspar crystals are slightly clouded with clay minerals, and partly replaced by fibrous amplibole and quartz.

Plagioclase crystals occur either as isolated grains or as inclusions in K-feldspar. They are severely altered to abundant clay minerals and sericite, and rare fibrous amphibole, biotite and calcite.

The amplibole has been observed as both prismatic and fibrous varieties (Figure 3). The prismatic variety is inter-

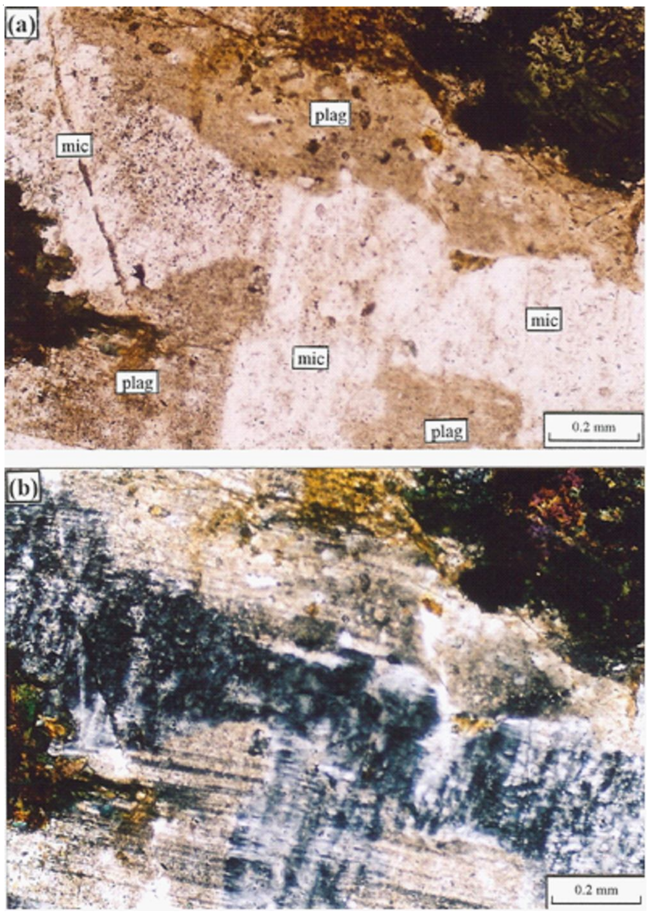


Figure 2. Photomicrographs of a syenitic sample showing plagioclase (plag) inclusions that have the same optic orientation, and a perthitic-textured microcline (mic) host in ordinary light (a), and between crossed polars (b) respectively.

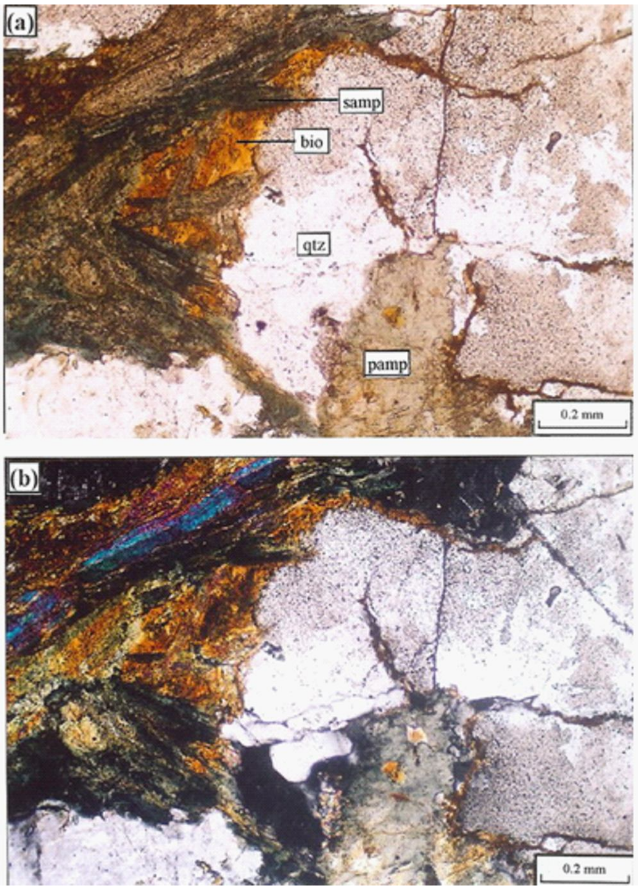


Figure 3. Photomicrographs of a syenitic sample showing primary amphibole (pamp), secondary amphibole (samp) biotite (bio) and quartz (qtz) in ordinary light (a), and between crossed polars (b) respectively.

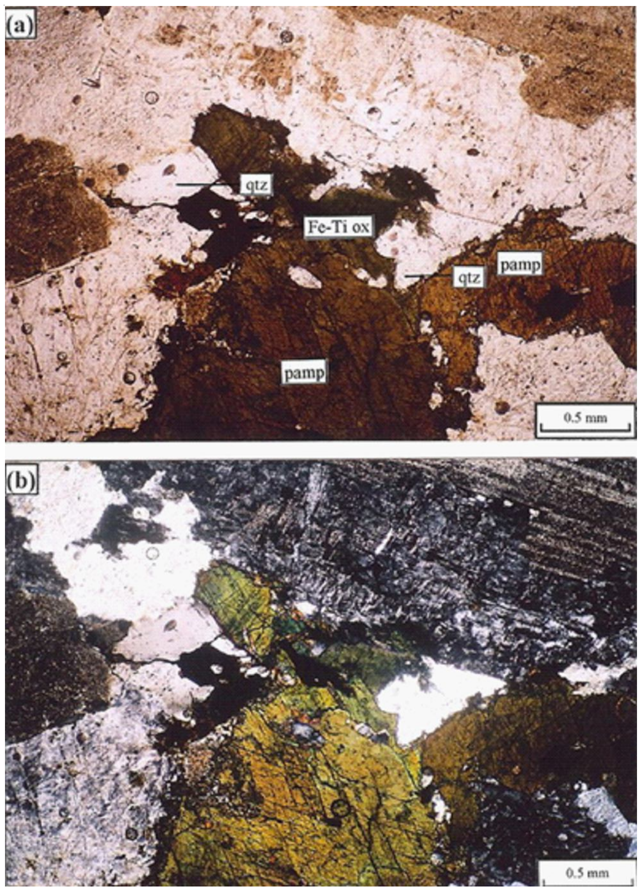


Figure 4. Photomicrographs of a syenitic sample showing primary amphibole (pamp), secondary quartz (qtz) and Fe-Ti oxide (Fe-Ti ox) in ordinary light (a), and between crossed polars (b) respectively.

preted to be a primary mineral, and is variably replaced by fibrous amplibole, quartz, biotite and/or Fe-Ti oxide in different proportions. The fibrous variety is definitely of a secondary nature.

Quartz occurs as isolated anhedral grains, a characteristic of secondary quartz, while biotite occurs as small flakes. Fe-Ti oxide has been recognized as small particles disseminated in a primary amphibole and as free particles (Figure 4). The oxide is partially replaced by hematite/iron hydroxide.

It appears from the grain counting of each sieve size fractions of ground sample (Table 1) that an appropriate liberation size is about -65 Tyler mesh. Because there is a large amount of locked feldspar-hornblende particles at sizes

Table 1. Size analysis and grain counting of ground syenitic rock; Feldspar (Feld.), Hornblende (Horn.), Locked feldspar and hornblende particle (F.+H.) and Quartz (Qtz.)

Size (mesh)	Cum. % wt. retained	Feld. (%)	Horn. (%)	F.+H. (%)	Qtz. (%)
+20	13.42	22.88	32.55	41.00	1.76
-20+28	38.91	23.90	27.23	46.19	1.77
-28+35	56.33	37.12	29.70	30.91	1.34
-35+48	67.40	41.52	41.56	15.11	0.89
-48+65	75.82	43.33	44.80	10.07	0.89
Pan	100.00				

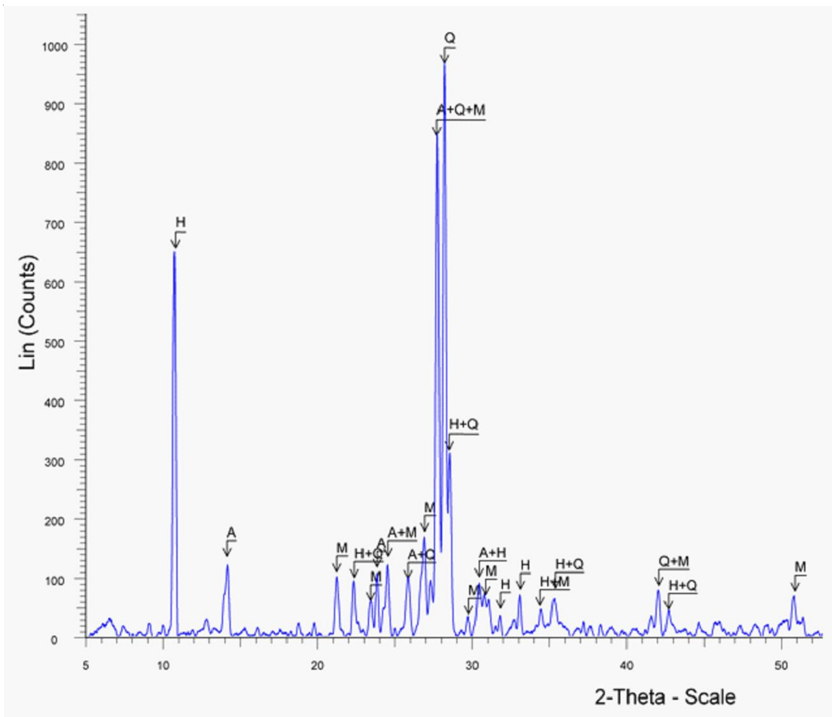


Figure 5. XRD trace of a syenitic rock; A = Andesine, H = Hornblende, M = Microcline, and Q = Quartz.

larger than this size. The -65 mesh particle should be suitable for separation either by magnetic separation or froth flotation effectively. Therefore the syenitic rock was specifically ground to meet this passing size prior to any separation.

3.2 Mineralogical study using X-ray diffraction

The XRD trace of a syenitic rock (Figure 5) shows that microcline ($KAlSi_3O_8$), andesine ($Na_{.499}Ca_{.491}Al_{1.488}Si_{2.506}O_8$), hornblende ($Na_{.9}K_{.4}Ca_{1.6}Mg_{2.8}Fe_{1.4}Ti_{.5}Al_{2.4}Si_6O_{23}(OH)$) and quartz are the major constituents. Both microcline and andesine are feldspar. The microcline is alkaline feldspar while the andesine is plagioclase having composition between albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$). Hornblende is one mineral of the amphiboles commonly found in this syenitic rock. As a result, this rock is characterized as a hornblende syenite.

3.3 Separation by WHIMS and/or flotation

The chemical composition; and cone shrinkage, unfired and fired color, degree of vitrification, and yield of processed feldspar were compared to those of raw and the standard feldspar samples (Rattanakawin *et al.*, 2005) obtained from a ceramic manufacturer. These are shown in Tables 2 and 3 respectively.

Comparing all monitoring criteria, especially % Fe_2O_3, of all products to those of the raw syenitic rock shows that all separation techniques can enhance the product qualities at certain extent. For example, %Fe_2O_3 decreases from 3.11 to 1.51 and about 0.5, respectively, when separated by WHIMS only, by WHIMS-flotation or by flotation with different conditions. It appears that flotation can reduce iron bearing minerals in the syenitic rock much better than using single magnetic separation. The flotation and WHIMS-flotation techniques give fairly the same result in terms of product qualities. However, operating cost of the WHIMS-flotation technique is expected to be lower than that of the flotation only due to less reagent consumption.

It is interesting to note that iron bearing minerals respond well to flotation with both amine and sulfonate. This

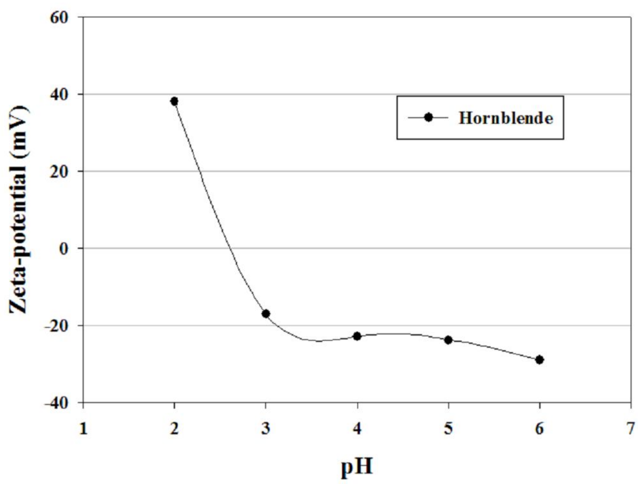


Figure 6. Zeta potential of hornblende as a function of pH.

phenomenon can be explained on the basis of electrokinetic property of hornblende and hydrolysis of cations, especially ferric ion, derived from those minerals. Figure 6 shows the plot of zeta potential of hornblende as a function of pH.

From the zeta potential-pH plot, the point of zero charge (PZC) of hornblende is about 2.60. Above the PZC, the surface is negatively charged so the amine ions can physically adsorb in this region and flotation occurs at pH 3. However, similar results can be observed when hornblende is floated with sulfonate at the same condition. This occurrence may be due to an activation of hornblende by ferric hydroxyl complex at pH 3. This is the same pH in which quartz was floated with sulfonate in the presence of ferric salt (Fuerstenau *et al.*, 1985). Although hornblende can be floated from the syenitic rock either by amine or sulfonate, it is preferable to float it with sulfonate industrially because sulfonate is much cheaper than amine. An alternative collector for hornblende flotation may be fatty acid such as oleic acid or its salts. This collector could be chemisorbed on hornblende particles via ferrous or ferric ions.

The inefficient separation of iron bearing minerals (ampliboles, biotite, Fe-Ti oxide, hematite or iron hydroxide) from feldspar may be due to their non-liberated sizes and alteration on their surfaces. In order to enhance the separation, syenitic rock must be ground to completely liberate these minerals as much as possible. However, more grinding expense is the cost of this operation. Also, more slime generation leads to high reagent consumption and low production. The alteration of primary amphibole to fibrous form is suspected to have changed its surface structure and chemistry. The modified surface may not respond well with the prescribed flotation reagents. In addition, the coating of hematite or iron hydroxide on processed feldspars typically leads to unfired brown color and eventually to the greyey white one after firing. Bleaching of the iron-coated feldspar is considered to be economically prohibited.

3.4 Evaluation of the separation

As shown in Tables 2 and 3, the processing of a hornblende syenite yields more feldspars than from a mixed Na-K feldspar or hand-sorted K-feldspar. However, the quality of the products is worse than that of the standard floated Na-K feldspar. Even the quality of the M-S-200 product is merely comparable to that of the hand-sorted K-feldspar. Indeed, this product could be used only for ceramic body in tiles regardless of whiteness. Therefore it is necessary to further upgrade this product if high quality ceramics are required.

4. Conclusions

Due to the finer size of iron bearing minerals, it is very difficult to separate these minerals from syenitic rock by magnetic separation, mechanical flotation and combination of these techniques effectively. An application of column flotation may be effective in separation of these fine particles in which selectivity is hard to achieve. However, yield and throughput of the processed feldspar are invariably decreased.

Acknowledgement

The first author would like to thank Mr. Charong Khamklai, Rajamangala University of Technology, Lanna Northern Campus for his thin section preparation; Dr.Apinon Nuntiya, Department of Industrial Chemistry, Chiang Mai University for his cone firing test; Mr. Utit Thongklueng, Department of Mining and Petroleum Engineering, Chulalongkorn University for his XRD and XRF analysis; and Mr. Benjapol Thacom, Office of Primary Industries and Mines Region 3 for his zeta potential measurement. Above all this paper is dedicated to Assoc. Prof. Thongchai Pungrassami, his first teacher in Geology at the Department of Mining and Material Engineering, Prince of Songkla University.

References

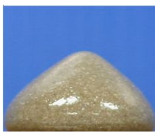
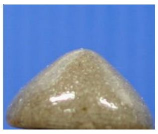
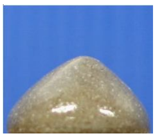
Fuerstenau, M.C. Miller, J.D. and Kuhn, M.C. 1985. Chemistry of Flotation, SME, New York, U.S.A., pp. 90-118.

Manser, R.M. 1975. Handbook of Silicate Flotation, DOB Services (Hitchin) Ltd., U.K., pp. 116-118.

Table 2. Chemical analysis of raw, processed and standard samples

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LOI	Remarks
CCSY-1	65.89	0.19	18.04	3.11	0.02	0.79	5.42	5.98	0.57	Raw syenitic rock
CCSY-1-M	66.21	0.07	16.72	1.51	0.00	1.02	6.78	7.65	0.50	non-mag. WHIMS
A-200	67.93	0.02	18.25	0.51	0.02	0.70	4.77	7.18	0.62	Amine 200g/t
S-200	68.96	0.02	17.39	0.49	0.01	0.74	5.04	6.81	0.54	Sulfonate 200g/t
M-S-200	67.45	0.02	18.56	0.48	0.02	0.63	4.48	7.90	0.46	WHIMS & Sulfonate 200g/t
FK-SK/7	66.55	0.06	19.30	0.56	0.17	1.07	3.55	7.96	0.77	Standard Hand-sorted K-feldspar
FK-AN/Body	68.47	0.01	17.84	0.10	0.03	1.37	5.81	5.94	0.44	Standard floated Na-K feldspar

Table 3. Cone shrinkage, unfired and fired color, degree of vitrification, and yield of processed feldspar comparing to those of raw and standard feldspar samples.

Sample	Fired Cone	% Shrinkage (on firing)	Unfired Color	Fired Color	Degree of Vitrification	Yield
CCSY-1(Raw)		66.44	Dark Grey	Black	Fused	-
CCSY-1-M		51.67	Brown	Darkbrown w/ Black spots	Moderate	77.12%
A-200		48.17	Brown	Greyey white	Moderate	63.09%
S-200		49.10	Brown	Greyey white	Moderate	63.64%
M-S-200		48.92	Brown	Greyey white	Moderate	57.27%
FK-SK/7(Standard)		46.92	Brown	Greyey white w/ Brown spots	Moderate	about 20%
FK-AN /Body(Standard)		47.67	Brown	White	Good	about 50%

Note: Amounts of slime and iron bearing minerals separated by flotation are approx. 12% and 25% by weight, respectively.

Rattanakawin, C. Phuvichit, S. Nuntiya, A. and Tonthai, T. 2005. Value-adding and processing of feldspar in northern region, Thailand. In Report of Investigation for Bureau of Primary Industries, Department of Primary Industries and Mines, Bangkok, Thailand.

Rattanakawin, C. Phuvichit, S. Nuntiya, A. and Tonthai, T. 2006. Value-adding and processing of feldspar in eastern region, Thailand. In Report of Investigation for Bureau of Primary Industries, Department of Primary Industries and Mines, Bangkok, Thailand.

Rattanakawin, C. 2006. Flotation (in Thai), Department of Mining and Petroleum Engineering, Chiang Mai University, Chiang Mai, Thailand, pp. 230-242.

Rau, E. 1985. Feldspar. In SME Mineral Processing Handbook, N.L. Weiss, editor. SME, New York, U.S.A., pp. 29-9-29-11.