

Production of mechanically activated rock flour fertilizer by high intensive ultrafine grinding

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Abstract

This paper provides a first assessment of the use of mechanical activation to enhance the availability (i.e., leachability) of potassium from K-feldspar containing materials for soil improvement and agricultural purposes. A planetary mono mill was used to achieve high intensive dry grinding of both a K-feldspar concentrate and a nepheline syenite concentrate that served as a reference material. The K-feldspar concentrate was also milled in a pilot-scale HiCOM 15 nutating mill. The mill products were characterised with respect to their size distributions, specific surface areas and their relative degree of structural disordering as calculated from X-ray diffraction analysis. The enhanced solubility of the products in terms of potassium was determined directly through a three-step cascade leaching test. The results show that high intensive dry grinding could be used to increase the release of potassium from K-feldspar containing materials by more than an order of magnitude. When subjected to planetary milling, less than 10 min of milling was required to make the K-feldspar mineral more reactive than the intrinsically more soluble nepheline. The enhanced reactivity of the mill products is predominantly a function of their specific surface areas, but a significant part of the observed increase in reactivity must be attributed to structural disordering. The use of water as a grinding aid makes it possible to produce very reactive structurally disordered products with high specific surface areas.

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1. Introduction

Several investigators have studied the potential use of rock flour and mineral waste materials as a source of potassium for agricultural purposes (Heim, 2001; Harley and Gilkes, 2000; Gautneb and Bakken, 1995). Compared to synthetic fertilizers, alternatives consisting of crushed or ground mineral products exhibit a much slower release of potassium. Consequently, only relatively fast reacting minerals like biotite or nepheline have been found interesting. However, the practical abundance of these minerals is limited. Although biotite is a common constituent in rock flour and waste materials of granitic or syenitic origin,

the relative concentration of the mineral in these products is low, thus necessitating the spreading of considerable volumes. Nepheline on the other hand can only be found in special products. Hence, in practical terms, the abundance of these two minerals is much lower than that of the considerably more weathering resistant potassium feldspars which are commonly found as the predominant minerals in waste materials from mining and aggregate productions.

The release of potassium from potassium-rich silicates is a surface reaction. Mechanical activation of these minerals through intensive grinding could produce more reactive surfaces and result in a higher rate of release, but could require a considerable amount of energy (Kleiv and Sandvik, 2005). However, if based on local waste materials, the concept could prove to be economically feasible as both transportation costs and costs relating to waste disposal

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would be minimized. In more remote areas where transportation costs would be significant, activated rock flour from a favourably situated quarry or mine could quite possibly represent a real alternative for the local agriculture. As the rate of potassium release from potassium-rich silicates increases rapidly with decreasing pH, the concept would be particularly interesting in areas with acidic soils.

The main purpose of this study is to determine the effect of mechanical activation on the availability (i.e., leachability) of potassium in K-feldspar, using nepheline syenite as a reference material. Consequently, the experimental setup was designed to evaluate the difference between the original mineral concentrates and the corresponding activated products. Although the bulk of the experiments were conducted in lab-scale by use of a planetary mill, pilot-scale milling with a HiCOM nutating mill was also performed in order to provide a first assessment of the energy requirement of the proposed concept. All the activated materials were produced through dry milling in order to maximise the effect of mechanical activation. Dry milling would also simplify the future implementation of the concept and contribute to lower production and handling costs.

Following milling, the activated products were subjected to a simple leaching test in which both distilled water and a 0.01 M HNO₃ solution (i.e., approximately pH 2) was used as a leachant. The excessive strength of the acidic solution is not representative of acidic soils, but was chosen in order to accelerate the potassium release rates so that significant results could be obtained within the time frame of the experiments. Hence, the scope of this study has been to assess the relative reactivity of the different products as a function of their production parameters rather than to obtain realistic potassium release values for the weathering of such products in real systems.

2. Materials and methods

2.1. The original mineral concentrates

Two different potassium rich concentrates were used in this study; a K-feldspar concentrate (K600) and a nepheline syenite concentrate (Altafloat 500). Both the concentrates were supplied by the Norwegian mining company North Cape Minerals AS and were used as received without any further treatment. The concentrates consisted of classified material finer than 500–600 μm and contained very little dust.

The overall chemical composition of the original concentrates with respect to major elements was determined using the X-ray fluorescence (XRF) technique using a Philips PW 1480 X-ray spectrometer. The original concentrates were also subjected to an X-ray powder diffraction analysis (XRD), using a Philips PW1710 diffractometer with a PW 1830 generator, scanning from 2° to 60° with monochromatised CuK_α radiation. As part of the analytical procedure, the pulverised samples required for the XRF and XRD analysis were produced by milling samples of the respective concentrates for 30 s using a Siebtechnik

Table 1
Mineralogical and chemical composition of the original mineral concentrates

K-feldspar conc.		Nepheline syenite conc.	
Phase	Conc. (%)	Phase	Conc. (%)
<i>Mineralogical composition</i>			
K-feldspar	70	Na, Ca-feldspar	60
Na, Ca-feldspar	25	Nepheline	35
Quartz	<5	Calcite	<5
Oxide	Conc. (%)	Oxide	Conc. (%)
<i>Chemical composition</i>			
SiO ₂	65.70	SiO ₂	55.61
Al ₂ O ₃	18.81	Al ₂ O ₃	24.77
K ₂ O	11.33	K ₂ O	8.29
Na ₂ O	3.02	Na ₂ O	8.07
CaO	0.36	CaO	1.36
Fe ₂ O ₃	0.40	Fe ₂ O ₃	0.28
MgO	0.04	MgO	0.09
P ₂ O ₅	0.03	P ₂ O ₅	0.10
TiO ₂	0.01	TiO ₂	0.11
MnO	–	MnO	0.01
Sum	99.70	Sum	98.68
LOI ^a	0.14	LOI ^a	0.94

^a Loss on ignition.

agate disk mill. The results from the XRF and the interpretation of the XRD analysis are shown in Table 1.

2.2. Mechanical activation – planetary mill

Mechanical activation of the original K-feldspar and nepheline syenite concentrates was achieved using a Fritsch Pulverisette 6 planetary mono mill (batch mill) by dry milling of 20.0 g of each respective material in a 250 ml stainless steel mill chamber for various lengths of time. The milling was conducted at 500 rpm using twenty Ø20 mm stainless steel grinding balls with a total weight of 645 g.

The milling or activation time spanned from 2 min to 60 min. The temperature of the activated products in the mill chamber was measured immediately after production using an IR-sensor. The temperature rose rapidly during milling, typically reaching some 70–75 °C after 30 min. To prevent excessively high temperatures from occurring, no batch was subjected to more than 30 min of continuous milling. Consequently, a total activation time of 60 min was achieved by milling the materials in two stages separated by a 30 min cooling interval.

After milling the activated products were carefully retrieved using a brush and a spatula. Great care was taken to minimise the risk of cross contamination between batches. Between each batch milling operation the mill chamber and grinding balls were rinsed by milling 40 g of coarse quartz sand for 30 s at 500 rpm before the individual components were brushed clean, wiped with alcohol and allowed to dry.

After the first results had been obtained, two additional K-feldspar batches were run. These two batches were

produced according to the procedure outlined above, but with 1.00 ml of distilled water added to the mill chamber immediately prior to milling.

The materials produced by milling using the planetary mill (PM) are referred to as PM-activated K-feldspar and PM-activated nepheline syenite. A list of the different batches produced is given in Table 2.

2.3. Mechanical activation – HiCOM mill

Mechanical activation of the original K-feldspar concentrate was also achieved using a HiCOM 15 nutating batch mill by dry milling of 1000 g or 2000 g of feed material for various lengths of time. The milling was conducted at 750 rpm or 900 rpm using 12.0 kg of either a fine or a coarse stainless steel grinding ball mixture. The fine mixture consisted of 10 kg Ø5 mm balls and 2 kg Ø20 mm balls, whereas the coarse mixture was composed entirely of Ø20 mm balls. For each batch produced in the HiCOM mill 1–3 subsamples were retrieved as a function of milling time by pausing the mill and emptying the chamber at given intervals. Following the separation of grinding balls and milled product using a grate, a 200 g sample was obtained by spot sampling before the grinding balls and the remaining product were returned to the mill. The same

separation and sampling procedure was used at the end of each batch milling operation before the mill chamber and the grinding ball mixture were rinsed by milling 2000 g of the original K-feldspar concentrate for 30 s at 900 rpm.

The materials produced by milling in the HiCOM mill (HC) are referred to as HC-activated K-feldspar.

The milling or activation time spanned from 5 min to 19 min and was limited by the automatic shutdown of the mill when the temperature in the mill chamber reached 80 °C. Both the chamber temperature and the instantaneous power consumption were automatically measured during milling. A list of the different batches produced is given in Table 2.

2.4. Characterisation of mill products

Size distributions of the activated products were obtained from Fraunhofer diffraction analysis using a Coulter LS 230 Particle Size Analyser, whereas specific surface area was determined using the N₂-adsorption technique (i.e., the BET equation (Brunauer et al., 1938)) and a Flow Sorb II 2300 volumetric gas adsorption analyser.

Selected samples of both the original and activated K-feldspar were also subjected to an XRD analysis in order to evaluate the extent of structural disordering. The XRD

Table 2
Overview of produced batches showing production variables and material characteristics

Batch	Feed	Mill ^a	<i>t_M</i> (min)	Other settings ^b	<i>S_A</i> (m ² /g)	Size distribution (µm)			<i>F</i>
						<i>d</i> ₁₀	<i>d</i> ₅₀	<i>d</i> ₉₀	
N0	Original Neph. syenite conc.	–	–	–	0.69				
N1	20.0 g Neph. syenite conc.	PM	10	Standard	6.88	1.18	13.2	77.4	
N2	20.0 g Neph. syenite conc.	PM	60	Standard	5.63	1.22	13.5	76.2	
F0	Original K-feldspar conc.	–	–	–	0.51				1.00
F1	20.0 g K-feldspar conc.	PM	2	Standard	4.27	1.44	8.90	45.5	0.88
F2	20.0 g K-feldspar conc.	PM	5	Standard	7.93				
F3	20.0 g K-feldspar conc.	PM	10	Standard	10.47	1.20	11.6	71.0	0.70
F4	20.0 g K-feldspar conc.	PM	30	Standard	9.65	1.39	14.7	87.7	0.53
F5	20.0 g K-feldspar conc.	PM	60	Standard	7.89	1.43	14.1	84.3	
F1 deagg	F1 suspended in dist. water, centrifuged, decanted and dried				4.05				
F3 deagg	F3 suspended in dist. water, centrifuged, decanted and dried				9.51				
F4 deagg	F4 suspended in dist. water, centrifuged, decanted and dried				8.87				
F5 deagg	F5 suspended in dist. water, centrifuged, decanted and dried				6.90				
F6-5	2000 g K-feldspar conc.	HC	5	900 rpm/FGBM	1.84				0.95
F6-10	2000 g K-feldspar conc.	HC	10	900 rpm/FGBM	3.13				0.91
F6-15	2000 g K-feldspar conc.	HC	15	900 rpm/FGBM	4.40				0.89
F7-10	2000 g K-feldspar conc.	HC	10	750 rpm/FGBM	2.17				0.95
F7-19	2000 g K-feldspar conc.	HC	19	750 rpm/FGBM	3.31				0.89
F8-5	1000 g K-feldspar conc.	HC	5	900 rpm/FGBM					
F8-10	1000 g K-feldspar conc.	HC	10	900 rpm/FGBM	6.38				0.86
F8-13	1000 g K-feldspar conc.	HC	13	900 rpm/FGBM					
F9-10	1000 g K-feldspar conc.	HC	10	750 rpm/FGBM					
F9-13	1000 g K-feldspar conc.	HC	13	750 rpm/FGBM					
F10-10	1000 g K-feldspar conc.	HC	10	750 rpm/CGBM					
F10-15	1000 g K-feldspar conc.	HC	15	750 rpm/CGBM	8.55				0.83
F11-8	1000 g K-feldspar conc.	HC	8	900 rpm/CGBM					
F12	20.0 g K-feldspar conc.	PM	10	+1 ml dist. water	14.61				0.89
F13	20.0 g K-feldspar conc.	PM	60	+1 ml dist. water	13.98				0.59

^a PM = planetary mill, HC = HiCOM mill.

^b CGBM = coarse grinding ball mixture, FGBM = fine grinding ball mixture.

analyses were performed using the instrument, procedures and settings previously outlined. The relative degree of structural disorder was expressed by calculating the following ratio (Pazak, 1966; Baláž, 2000):

$$F = \frac{(\text{ILB})_i}{(\text{ILB})_0} \quad (1)$$

where $(\text{ILB})_i$ is the integral width of a given diffraction peak from material i and $(\text{ILB})_0$ is the corresponding value for the reference sample (i.e., the original K-feldspar concentrate). The F -values reported in this study are the arithmetic mean of the individual F -values for the peaks at $2\theta = 21.0^\circ$ {201} and $2\theta = 41.8^\circ$ {060}. Due to the complexity of the diffractogram and the extensive overlapping of diffraction peaks, no attempts were made to perform similar calculations for the nepheline syenite materials.

2.5. Deagglomeration test

In order to check whether the specific surface areas of the dry activated products were representative for the real specific surface areas in aqueous suspensions, 4.00 g samples of selected PM-activated K-feldspar products were suspended in 100 ml of distilled water. After 5 min of conditioning, the suspensions were centrifuged at approximately 1200g for 5 min before the supernatant was gently decanted. The remaining solid phase was dried for 48 h at 60 °C before the specific surface area was measured.

2.6. Leaching experiments

The leaching experiment was performed as a batch cascade test in which the solid material was subjected to three successive leaching steps. The test was conducted using a number of 125 ml polyethylene bottles by exposing individual 1.00 g samples of the different products to 100 ml of a solution consisting of either distilled water or 0.01 M HNO_3 . During each leaching step, the resulting suspensions were conditioned by orbital agitation at 25 ± 0.1 °C, using a thermostatic agitator.

Following the first leaching step, each suspension was centrifuged at approximately 1200g for 5 min before the supernatant was gently decanted. The second leaching step was then initiated by adding 100 ml of fresh solution to the remaining solid phase. After the second leaching step had commenced, the procedure was repeated to initiate the third and final step. Each of the three successive leaching steps lasted 24 h.

The pH of the supernatants from each individual leaching step was determined immediately after centrifugation using a Metrohm 713 pH meter and a Aquatrode Plus combined glass electrode before the solutions were sampled by extracting and filtering a volume of 10 ml using a syringe and a 0.45 µm syringe filter. The filtrates were collected in glass vials and acidified using 20 µl of 65% nitric acid.

Finally, the filtrates were analysed using atomic absorption spectrometry (AAS) and a GBC Avanta Σ flame atomic absorption spectrometer. Each determination was obtained by taking the average of three replicate measurements. The pH meter was calibrated prior to each series of measurements, and great care was taken to minimise the risk of contamination throughout the study.

The leaching test was performed on selected PM-activated products which were chosen in order to study the effect of both specific surface area and structural disordering. The highest values of these two parameters were found after milling times of 10 min and 60 min, respectively. The original concentrates were also included as a reference. Three HiCOM products were selected according to the same principle, but also so that they would span the range of the measured specific energy consumption. As these products were expected to be less reactive than the PM-activated materials they were only subjected to the acidic leachant.

3. Results and discussion

3.1. Size distribution, specific surface area and relative degree of disordering

The results from characterisation of the activated products are summarised in Table 2, presenting specific surface area (S_A), size distributions (d_{10} , d_{50} and d_{90}) and the estimated relative degree of disordering (F), and in Fig. 3 displaying the XRD signature of PM-activated K-feldspar concentrate as a function of milling time (t_M). The development of the particle size distributions and the specific surface area is further illustrated in Figs. 1 and 2, respectively.

As is apparent when viewing Fig. 2, the specific surface areas of the PM-activated products reach a maximum after approximately 10 min of milling. Milling beyond this point

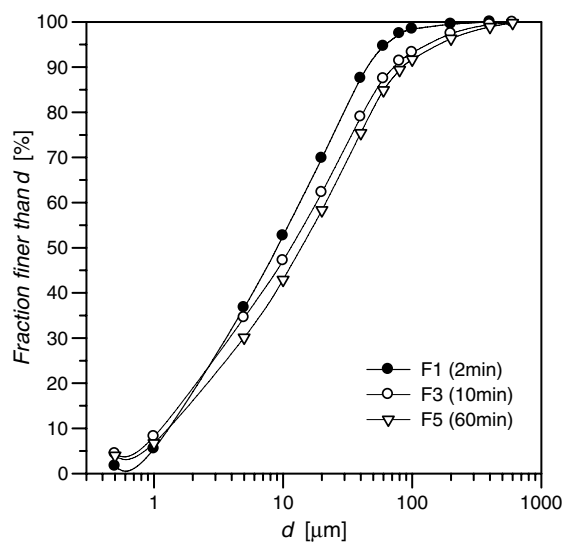


Fig. 1. Size distribution of PM-activated K-feldspar concentrate as a function of milling time.

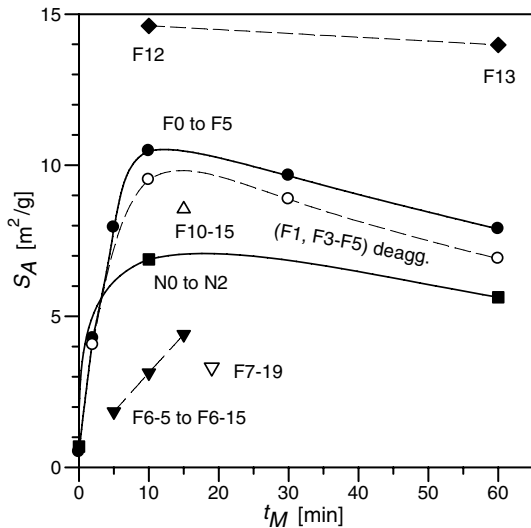


Fig. 2. Specific surface area of the different mill products as a function of milling time.

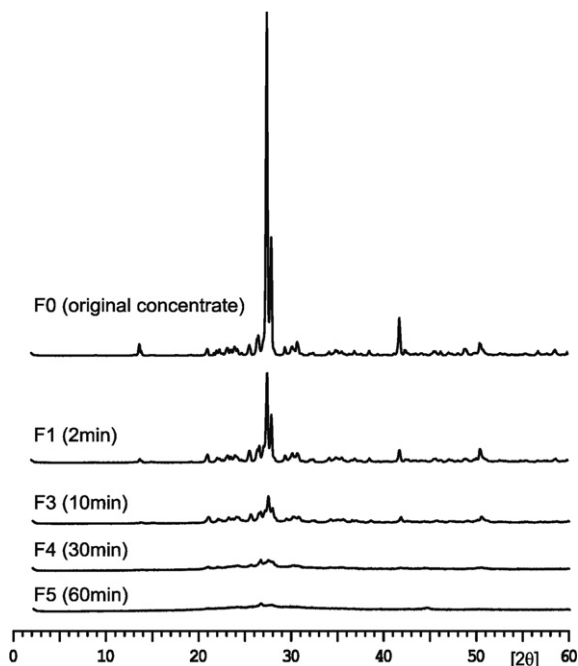


Fig. 3. XRD signature of PM-activated K-feldspar concentrate as a function of milling time.

does not produce a further net increase in surface area. Instead, a significant decrease is observed. This behaviour is common for dry milling, and is usually explained by agglomeration of structurally modified particles following the initial reduction of particle size. In the case of the K-feldspar and nepheline syenite concentrates, this view is supported by the observed changes in their particle size distributions. As can be seen in Fig. 1, 60 min of planetary milling produces a PM-activated K-feldspar material that contains a larger proportion of both fine and coarse particles compared to the material that has been milled for 2 min, whereas the highest proportion of fines is found

after 10 min of milling. The corresponding curves for PM-activated nepheline syenite concentrate are almost identical to those of the K-feldspar material and are therefore not shown.

The addition of water as a grinding aid resulted in higher specific surface areas of the final products, probably by lubricating the system and delaying agglomeration. It is interesting to note that this also affects the relative degree of disordering as described by the calculated F -values shown in Table 2. Whereas 10 min of milling in the dry system resulted in an F -value of 0.70, a small addition of water to the mill chamber produced a corresponding value of 0.89. In the dry system this degree of disordering was obtained after only 2 min of milling. The F -value of the F5 batch could not be calculated due to the total absence of defined peaks in the diffractogram.

The specific surface areas of the HC-activated products are generally lower than those of the PM-activated materials, although the F10–15 batch is comparable to the F3 and F5. Compared to the planetary mill, the HiCOM mill is also less efficient with respect to mechanical activation. When studied as a function of milling time, the F -values obtained for the HC-activated products are considerably higher. By choosing 1000 g of feed, the coarse grinding ball mixture and the higher mill speed a less crystalline product is produced. However, the differences between the different batches are relatively small.

As shown in Fig. 2, the specific surface areas of the PM-activated materials that were subjected to the deagglomeration test are close to but slightly lower than those of the corresponding original activated products. The difference between the two curves could probably be explained as loss of fines during decanting. Hence, the results suggest that the BET values obtained for dry activated products are fairly representative of the initial specific surface areas of the same products in aqueous suspensions.

3.2. Energy consumption of HiCOM milling

The total energy consumption of HiCOM milling is shown in Table 3. The average power (P) drawn by the mill varies from 2.02 kW to 4.80 kW and depends on the mass of the charge, the size of the grinding balls and the mill speed. The latter parameter proved to be critical, since an increase from 750 rpm to 900 rpm resulted in a 50–60% rise in the power consumption.

Due to the lower stability of the reduced charge, the power values found for the batches produced with only 1000 g of the original K-feldspar concentrate in the mill are actually higher than the corresponding values for batches based on twice as much feed material. A certain amount of feed is needed to obtain stable conditions during milling. As expected, the stability of the mill charge is also higher when using the fine grinding ball mixture, thus resulting in a lower power consumption.

In order to span the range of specific grinding energy as well as specific surface area, batches F6-15, F7-19 and F10-

Table 3
Total energy consumption of HiCOM milling

Batch	Feed (g)	t_M (min)	Other settings ^a (rpm/ball mixture)	P (kW)	Sp. energy (kWh/tonne)
F6-5	2000	5	900/FGBM	3.27	136.3
F6-10	2000	10	900/FGBM	3.27	272.7
F6-15	2000	15	900/FGBM	3.27	409.0
F7-10	2000	10	750/FGBM	2.02	168.3
F7-19	2000	19	750/FGBM	2.02	319.8
F8-5	1000	5	900/FGBM	3.75	312.3
F8-10	1000	10	900/FGBM	3.75	624.7
F8-13	1000	13	900/FGBM	3.75	812.1
F9-10	1000	10	750/FGBM	2.49	415.0
F9-13	1000	13	750/FGBM	2.49	539.5
F10-10	1000	10	750/CGBM	3.03	504.5
F10-15	1000	15	750/CGBM	3.03	756.7
F11-8	1000	8	900/CGBM	4.80	640.3

^a CGBM = coarse grinding ball mixture, FGBM = fine grinding ball mixture.

15 were selected for the leaching experiment. The specific grinding energy of these batches varied from approximately 300 to 750 kWh/tonne.

3.3. Reactivity of the mill products

The results from the three-step leaching test were evaluated by calculating the cumulative relative release of potassium, i.e., the ratio between the amount released to the aqueous phase and the total amount initially present in the solid product. Hence, the cumulative relative release of potassium was defined as follows:

$$\beta_n = \frac{\sum_{i=1}^n m_{K,i}}{m_{K,\text{total}}}, \quad (2)$$

where n indicates the leaching step, $m_{K,i}$ is the mass of potassium released during step i and $m_{K,\text{total}}$ is the total amount of potassium initially present in the solid product. Here, $m_{K,i}$ and $m_{K,\text{total}}$ were calculated from the results of the AAS and XRF analysis, respectively.

The results from the leaching test that are shown in Table 4 and Fig. 4 clearly demonstrate how milling has increased the availability of potassium in both the nepheline syenite and K-feldspar concentrates. Note that these release values are relative values, and that 100% release corresponds to 82.9 mg potassium per gram solid for the nepheline syenite and 113.3 mg potassium per gram solid for the K-feldspar material. The difference between the total release of potassium from the original concentrate and the milled products is largest for the K-feldspar material, and less than 10 min of planetary milling is required in order to make this material more soluble than a corresponding nepheline syenite product. When this K-feldspar product (i.e., the F3 material) is exposed to 0.01 M HNO₃, the total release of potassium is 12.6 times higher than that of the original concentrate (F0). The corresponding value for the nepheline syenite material is 2.0. However, since the nepheline syenite material displays a more evenly distributed release of potassium throughout the leaching test, a more prolonged leaching test with additional leaching steps could modify this picture.

The most notable result from the leaching test is the cumulative release values for the F13 material which reached no less than 58%. This material was produced by adding 1.00 ml of water as a grinding aid prior to 60 min of planetary milling. As explained in the following paragraphs, the higher release of potassium from this product is largely due to structural disordering by mechanical activation.

Table 4
Results from the three-step cascade leaching test

Batch	S_A (m ² /g)	F	Leachant	First leaching step			Second leaching step			Third leaching step		
				pH	K (mg/l)	β_1 (%)	pH	K (mg/l)	β_1 (%)	pH	K (mg/l)	β_1 (%)
N0	0.69		Dist. water	8.42	4.1	0.9	6.61	3.3	1.6	6.35	1.9	2.0
N1	6.88		Dist. water	9.88	19.0	4.2	8.99	8.7	6.1	9.14	5.6	7.3
N2	5.63		Dist. water	9.43	15.2	3.3	9.05	5.9	4.6	9.00	5.1	5.7
N0	0.69		0.01 M HNO ₃	3.85	16.7	3.7	3.88	19.2	7.9	3.88	19.2	12.1
N1	6.88		0.01 M HNO ₃	4.09	54.5	12.0	3.97	42.6	21.3	3.88	26.5	27.1
N2	5.63		0.01 M HNO ₃	4.18	53.8	11.8	4.07	34.1	19.3	3.90	24.2	24.6
F0	0.51	1.00	Dist. water	6.01	4.6	0.7	5.65	4.8	1.5	5.64	4.7	2.3
F3	10.47	0.70	Dist. water	10.32	22.3	3.6	9.96	9.6	5.1	9.67	7.1	6.3
F5	7.89	–	Dist. water	10.40	17.4	2.8	10.02	8.8	4.2	9.85	6.0	5.2
F0	0.51	1.00	0.01 M HNO ₃	2.13	5.7	0.9	2.13	3.8	1.5	2.12	4.0	2.2
F3	10.47	0.70	0.01 M HNO ₃	3.07	122.5	19.7	2.42	32.0	24.8	2.25	18.8	27.8
F5	7.89	–	0.01 M HNO ₃	3.01	107.7	17.3	2.37	30.8	22.2	2.24	16.0	24.8
F6-15	4.40	0.89	0.01 M HNO ₃	2.40	40.8	6.5	2.14	7.8	7.8	2.12	6.5	8.8
F7-19	3.31	0.89	0.01 M HNO ₃	2.32	31.3	5.0	2.13	7.1	6.2	2.12	5.6	7.1
F10-15	8.55	0.83	0.01 M HNO ₃	3.08	91.5	14.7	2.39	23.6	18.5	2.19	11.4	20.3
F12	14.61	0.89	Dist. water	8.75	15.7	2.5	8.69	8.3	3.9	8.58	7.4	5.0
F13	13.98	0.59	Dist. water	9.77	21.6	3.5	8.74	10.0	5.1	8.52	9.4	6.6
F12	14.61	0.89	0.01 M HNO ₃	3.05	112.7	18.1	2.51	21.5	21.5	2.25	11.5	23.4
F13	13.98	0.59	0.01 M HNO ₃	4.13	215.4	34.6	3.39	95.2	49.8	3.08	50.6	58.0

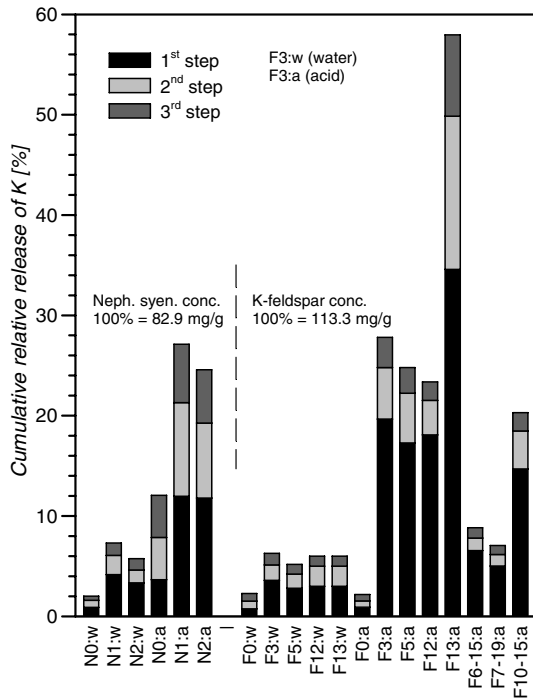


Fig. 4. Cumulative relative release of potassium from original concentrates and mill products.

The leachability of the materials depends on three main parameters; the specific surface area, the degree of structural disordering and the acidity of the leachant. The relative importance of these three factors depends on the mineralogy of the material, as can be seen when comparing the difference between the cumulative release in 0.01 M HNO_3 and distilled water for the two original concentrates (i.e., the N0 and F0 materials). While the nepheline syenite concentrate produces considerably more potassium in solution when exposed to the acidic leachant, there is little difference between the corresponding release values for the K-feldspar concentrate.

When comparing the specific surface areas with the corresponding cumulative relative release values, it becomes clear that surface area is the main factor controlling the availability of potassium when the materials are exposed to a given leachant. This explains why the materials that have been milled for 60 min (N2 and F5) release slightly less potassium than those produced by 10 min of milling (N1 and F3). However, the slight reduction in leachability is proportionally lower than the corresponding reduction in specific surface area, thus indicating an additional contribution by mechanical activation. The importance of structural disordering becomes apparent when comparing the F3 and F5 materials to the corresponding materials produced by adding 1.00 ml of water to the mill chamber prior to milling (i.e., F12 and F13). When water is added as a grinding aid, it is possible to obtain products where both the specific surface area and the degree of structural disordering are high. This is the case for the F13 material which has an F -value of 0.59 and a specific surface area of

13.98 m^2/g . In comparison, the specific surface area of the F12 material is 4.5% higher, but its F -value is as high as 0.89. When both materials are exposed to the acidic leachant approximately 2.5 times more potassium is released from the F13 material, thus demonstrating the importance of structural disordering. It is also interesting to note that the leachability of the F12 material is slightly lower than that of the F3 material in spite of the former's higher specific surface area. Both these materials have been milled for 10 min, but the addition of water appears to delay the mechanical activation effect resulting in an F -value of 0.89 for the F12 material compared to 0.70 for the F3.

As expected, the cumulative release values of the HiCOM products are lower than those of the PM-activated materials. However, the release of potassium obtained for the F10–15 product is comparable to the results from the F3 material. Considering the values of their surface areas, this is not surprising. The relative importance of specific surface area and structural disordering found for the PM-activated materials appears to be valid for the HiCOM products as well.

3.4. Preliminary concept evaluation

The results obtained by high intensive ultrafine grinding of the K-feldspar concentrate are promising, but they also show that further research is required in order to find the optimal milling solution. As demonstrated by this study, enhanced reactivity can be obtained both by increasing the specific surface area and by increasing the level of structural disorder. The products from the HiCOM mill were characterised by relatively low specific surface areas which directly limited the release rates. Based on the results obtained with the planetary mill, further experiments with the HiCOM mill will be conducted in which the use of water as a grinding aid will be explored.

The full potential of the HiCOM mill remains to be discovered. However, as the specific surface area appears to be the single most important variable controlling the reactivity of the mill products, other milling solutions should also be considered. Attritors are generally chosen when surface area is the primary aim and could therefore represent an interesting alternative, although such mills are likely to be less efficient at producing a highly disordered product. Wet milling would represent a further step in this direction and should not be ruled out.

4. Conclusions

The following conclusions were drawn from the experimental study in which materials produced by high intensive ultrafine dry grinding of nepheline syenite and K-feldspar concentrates were characterised and subjected to a leaching test:

1. Intensive grinding could be used to increase the availability (i.e., leachability) of potassium in K-feldspar

containing materials by more than an order of magnitude. Less than 10 min of high intensive planetary milling was required to make the K-feldspar mineral more reactive than the intrinsically more soluble nepheline.

2. The rate of potassium release from the milled products is predominantly a function of their specific surface areas, but a significant part of the observed increase in reactivity must be attributed to the structural disordering caused by mechanical activation.
3. Addition of small amounts of water as a grinding aid resulted in products with considerably higher specific surface areas, but the presence of water also delayed the effect of mechanical activation. However, using water as a grinding aid makes it possible to produce very reactive products characterised by both high specific surface areas and substantial structural disordering.
4. The results obtained by high intensive ultrafine grinding of the K-feldspar concentrate are promising, but they also show that further research is required in order to find the optimal milling solution.

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