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Determination of Calcium, Magnesium and Aluminium in Magmatic Rocks after Ultrasonic Leaching by Flame AAS

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A method of ultrasonic leaching has been developed for the destructive analysis of magmatic rock samples¹. This method was applied to determine three new elements, Ca, Mg and Al, in magmatic rock samples. The accuracy of the ultrasonic leaching method (C_{ULM}) was tested using standard reference materials (SRMs) and the recovery ratio as $K_1 = C_{ULM}/C_{SRM}$ was defined. Another recovery ratio, K_2 , was also defined from the results of the conventional dissolution method (CDM), that is $K_2 = C_{ULM}/C_{CDM}$. The accuracy and precision of the method are comparable with those of conventional methods. The following recovery ratios were obtained for Ca, Mg and Al, respectively.

$$\begin{aligned} 96\% < K_{1,Ca} < 112\% \text{ and } 95\% < K_{2,Ca} < 112\%, \\ 93\% < K_{1,Mg} < 109\% \text{ and } 94\% < K_{2,Mg} < 108\% \text{ and} \\ 91\% < K_{1,Al} < 102\% \text{ and } 94\% < K_{2,Al} < 107\%. \end{aligned}$$

Key Words: Ultrasonic metal leaching, partial leaching, magmatic rocks, flame-AAS

Introduction

Chemical analysis of geological materials has been conventionally performed by two different groups of methods^{1,2}. One of them is the well-known destructive method which involves the UV-VIS, AAS, ICP-AES or MS and NAA. The other is the non-destructive XRF method. Conventional sample preparation techniques have some serious disadvantages. Many of the techniques used for the analysis of geological materials require a sample dissolution step prior to the measurement step. The sample preparation step is frequently the most time consuming and is a major potential source of error in any geochemical analysis. In addition, there is excess acid consumption in these techniques¹⁻⁶. Despite advances in instrumentation and microcomputer technology, many sample preparation practices are based on nineteenth-century technologies. Furthermore, there is a serious contamination risk associated with these procedures. Sample preparation steps are frequently the major sources of error for overall analysis. An ideal dissolution technique should

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be economical, simple, effective, and selective (for interference problems) and should require minimum solvent usage. In general, partial dissolution of an analyte from a solid sample is not reproducible and total dissolution seems to be the right choice. However, although quantitative leaching of analyte from a solid sample is not possible, a technique in which a representative portion of the sample can be abstracted which reflects the real composition of the corresponding solid material may be proposed, and there is enough supporting evidence for this case⁷⁻⁹.

1. A rock sample can be crushed into certain grain sizes which represent the whole rock without any fractionation.
2. The grain sized rock samples can be partially dissolved using the same chemical treatment or a series of similar treatments with reproducible results (they can be leached).
3. Once an analyte is dissolved, its deposition on solid residue and adsorption onto solid surface can be prevented (e.g. by ultrasonication). Ultrasonic leaching interacts with the pores of the solid and prevents the deposition of dissolved ions on it. When speed of procedure, reproducibility and solvent consumption are considered, the ultrasonic leaching has some advantages over traditional methods¹⁰⁻¹². Therefore, the ultrasonic leaching method (ULM) is thought to be an alternative to conventional total dissolution techniques.

It has been reported that high recoveries of organics from granular activated carbon¹³, sediment¹⁴, fly ash¹⁵, biological materials¹⁶, atmospheric particulate¹⁷ and geological samples^{1,18-21} are possible when analysed by ULM, in a much shorter time than that required for other extraction procedures. Similar results may also be expected for labile (physical bound) metal fractions in atmospheric particulate and on bio-collector sprouts, as reported in previous studies on the physical and chemical effects of ultrasonication²²⁻²⁴.

It is possible that the advantages of a reproducible partial dissolution method are greater than its disadvantages as a sample preparation procedure.

The objective of this study was to investigate the possibility of obtaining a portion of a rock sample by ULM which reflects the real composition of the sample experimentally and statistically²⁵. The conditions of the procedure were optimised for grain size, sample amount, ultrasonication period and ultrasonic power.

We also sought to investigate whether the recovery ratio obtained by ULM and CDM from differs one element to another.

Experimental

The rock sample

Magmatic rock samples were obtained from Cumhuriyet University Engineering Faculty Laboratories in Sivas, Turkey from a sample location in south Giresun, north Turkey²⁶.

The sample used throughout this study, was defined as quartz-syenite by the afore mentioned laboratories²⁶.

Crushing, sieving and fractionating

Firstly, the superficially weathered parts of the rock sample were removed by using a geological hammer. After that, the rock sample was crushed with a Fritsch-Pulverizette type jaw-crusher, with iron-steel jaws,

to obtain suitable grain sizes. All these sample comminution (size-reduction) methods have been tested and recommended by Muller²⁷, who explained that iron contamination from iron–steel jaws can be ignored due to high contamination attaining up to 4-5 weight % in geological sample. For this purpose, the samples were put into the jaw-crusher with a jaw distance 0.5 cm. The sieving of these roughly crushed rock samples was performed with an Endecotts Octagan-200 model shaker with suitable sieves (see Table). The sieving procedure was completed with a shaking rate of 7 for 10 min, which is established as the standard sieving condition for intensive igneous rock samples, i.e., quartz syenite, at the Crushing, Grinding and Sieving Laboratory of the Department of Geological Engineering of Cumhuriyet University. The rock sample was fractionated into five sample grain sizes and described in the Table.

Table. Sample grain size, sieve pore size and sieve pore range

Sample grain size no	Sieve pore numbers, mm	Sieve pore range, mm
5	0.425	-0.425+0.250
4	0.250	-0.250+0.106
3	0.106	-0.106+0.063
2	0.063	-0.063+0.038
1	0.038	-0.038+0.000

A total of 720 test solutions were prepared from six different masses of sample (0.0500, 0.1000, 0.2000, 0.3000, 0.4000 and 0.5000 g) and for three different sonication powers (minimum, medium and maximum ultrasonic power) and eight different sonication times (5, 10, 15, 20, 30, 40, 50 and 60 min) for each sample grain size.

Softening step

The concentration of HF (2.0 cm³ HF + 2.0 cm³ H₂O) as optimised in our earlier work was used in the softening procedures¹.

Dissolution by ULM

The residue from the silica removing procedure was placed in a 120.0 cm³ glass beaker, 25.0 cm³ of 1% HCl (Merck, Darmstadt, Germany) was added and the beakers were kept in an ultrasonic bath, NEY 300 model (50-60 kHz), for leaching. Leaching solutions were centrifuged at 5000 rpm for 10 min to separate the residue and solutions were filtered using Whatman 41-filtration paper. Then 1.0 cm³ of 1% La³⁺ (for improved atomisation efficiency in AAS analysis) and 1.0 cm³ of concentrated HCl were added to samples which were made up 50.0 cm³ with 1% HCl solution and kept in low density polyethylene (LDPE) bottle for analysis⁷.

The optimum ULM dissolution was gained when the ultrasonic time was 30 min, sample mass was 0.0500 g and maximum USP was used for grain size 1.

Determination of elements

The leaching solutions were analysed for the determination of Ca, Mg and Al with a flame atomic absorption spectrophotometer (FAAS-UNICAM 929 model) using the standard addition and calibration curve

techniques. The standard additions technique was used to test possible interferences. There were no significant interference effects. Therefore, the calibration curve technique was used in all analyses. An air-acetylene flame was used for the determination of Ca, Mg and a nitrous oxide/acetylene flame (burner) for Al. The calibration curves were prepared using certificated standard reference materials for the three elements.²⁸ The calibration ranges were 0.15-2.00 mg L⁻¹, 0.05-0.60 mg L⁻¹, and 5.0-50.0 mg L⁻¹ for Ca, Mg and Al, respectively. To match the dynamic range of the calibration curves, the samples were diluted by a factor of 10, 50, or 100 with 1% HCl, as appropriate, to expected levels of the elements' before the determinations. The elements concentrations were obtained as the mean of three readings which provided less than 2% relative standard deviation (RSD %).

Ultrasonic power (USP) and sonication period used for the leaching process

The ultrasonic bath used in this study has eight different power scales and the using power ranges were defined as follows.

First scale: minimum ultrasonic power (min USP).

Fourth scale: medium ultrasonic power (med USP).

Eighth scale: maximum ultrasonic power (max USP).

Twenty-four equal samples for each grain size and sample mass (total of 720 samples) were prepared and sub-samples which contained eight equal samples were grouped. Each of the eight samples were subjected to ultrasonic treatment for 5, 10, 15, 20, 30, 40, 50 and 60 min at minimum, medium and maximum ultrasonic power individually.

Results and Discussion

Solubility of Calcium, Magnesium and Aluminium with ULM

The effects of sonication period, sample mass, grain size and ultrasonic power on ultrasonic leaching were considered as follows:

The effect of sonication period

The solubility of calcium, magnesium and aluminium at grain size 1 and max USP with sample mass and sonication period is given in Figures 1a, 1b and 1c, respectively, and the percentages of each element leached (as oxides) are also in the same figures.

The leached amounts (as %) of calcium oxide, magnesium oxide and aluminium oxide for the whole mass range (0.0500-0.5000 g) increased with sonication period in the first 30 min, and then remained constant. However, the best recovery was observed with a 0.0500 g sample mass (minimum recovery at 0.5000 g sample mass). The constant solubilities for the three oxides at 30, 40, 50 and 60 min (for each sample) were used for reproducibility tests. Similar results were observed for other sample sizes and ultrasonic power.

The solubilities of Ca, Mg and Al (for 0.0500 g sample mass and maximum USP) with grain size and sonication time are shown in Figures 2a, 2b and 2c.

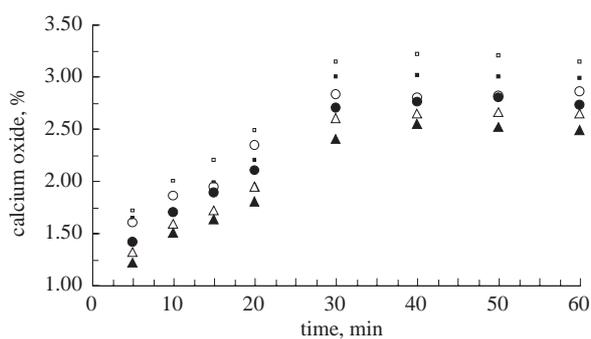


Figure 1a. The change in calcium levels (calcium oxide %) with sample mass and sonication time (grain size 1 and maximum USP)

□ : 0.0500 g, ■: 0.1000 g, ○: 0.2000 g, ●: 0.3000 g, △: 0.4000 g, ▲: 0.5000 g

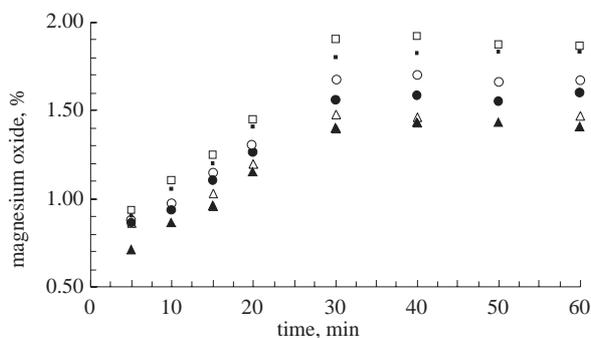


Figure 1b. The change in magnesium levels (magnesium oxide %) with sample mass and sonication time (grain size 1 and maximum USP)

□ : 0.0500 g, ■: 0.1000 g, ○: 0.2000 g, ●: 0.3000 g, △: 0.4000 g, ▲: 0.5000 g,

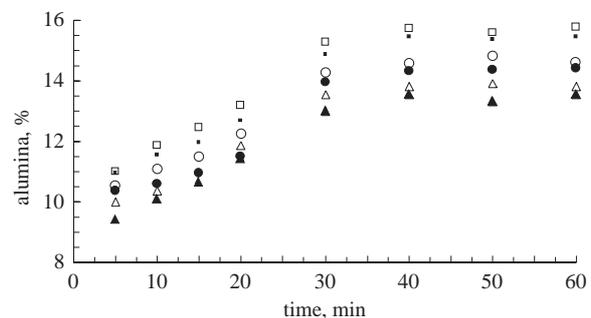


Figure 1c. The change in aluminium levels (alumina %) with sample mass and sonication time (grain size 1 and maximum USP)

□ : 0.0500 g, ■: 0.1000 g, ○: 0.2000 g, ●: 0.3000 g, △: 0.4000 g, ▲: 0.5000 g

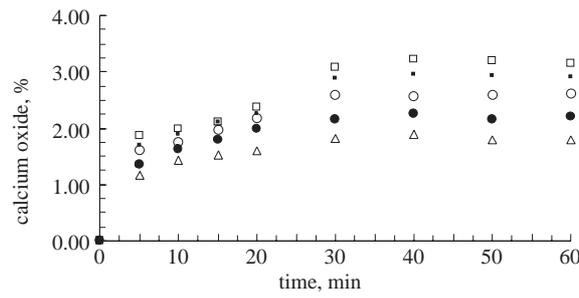


Figure 2a. The change in calcium levels with grain size and sonication time (0.0500 g sample mass and maximum ultrasonic power)

□ : grain size 1., ■: grain size 2., ○: grain size 3., ●: grain size 4., △: grain size 5.

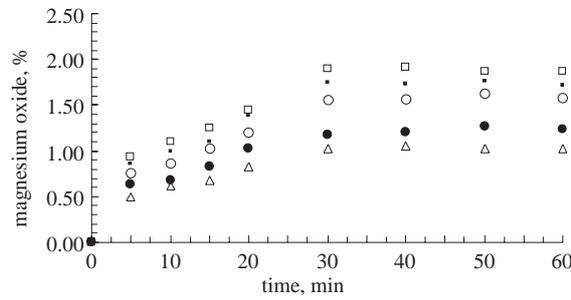


Figure 2b. The change in magnesium levels with grain size and sonication time (0.0500 g sample mass and maximum ultrasonic power)

□ : grain size 1., ■: grain size 2., ○: grain size 3., ●: grain size 4., △: grain size 5.

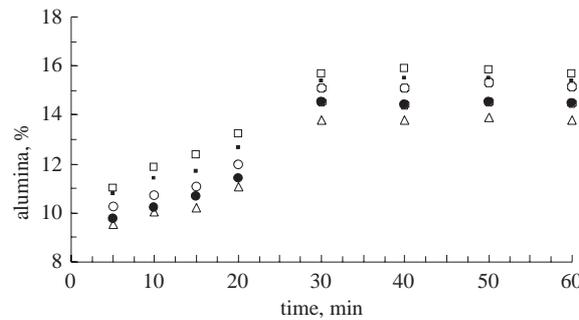


Figure 2c. The change in aluminium levels with grain size and sonication time (0.0500 g sample mass and maximum ultrasonic power)

□ : grain size 1., ■: grain size 2., ○: grain size 3., ●: grain size 4., △: grain size 5.

These curves (Figure 2a-c) exhibited similar behaviour. A linear increase during the first 30 min was observed and the leaching (%) remained constant for all sample grain sizes.

Figures 3a, 3b and 3c illustrate the changes in solubilities of Ca, Mg and Al with sonication time at minimum, medium and maximum ultrasonic power for samples having the same grain size of 1 and constant mass of 0.0500 g.

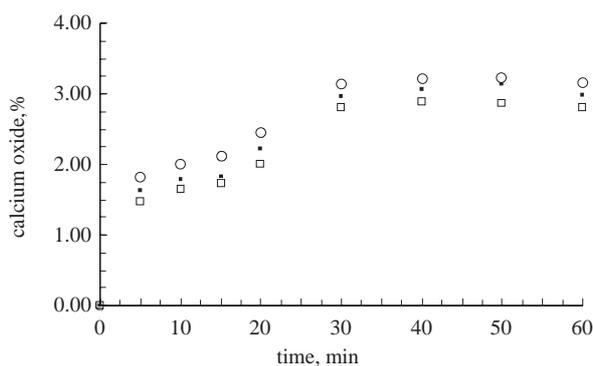


Figure 3a. The change in calcium oxide solubility with USP and sonication time (for samples grain size 1 and mass 0.0500 g)

□ : minimum USP, ■: medium USP, ○: maximum USP

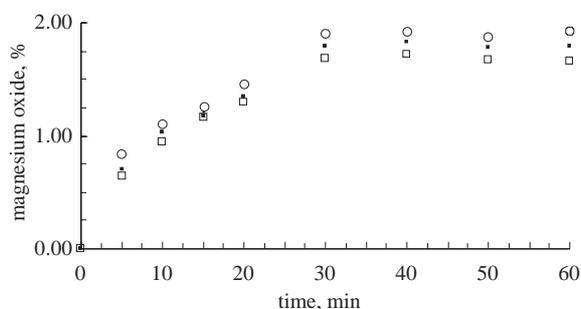


Figure 3b. The change in magnesium oxide solubility with USP and sonication time (for samples grain size 1 and mass 0.0500 g)

□ : minimum USP, ■: medium USP, ○: maximum USP

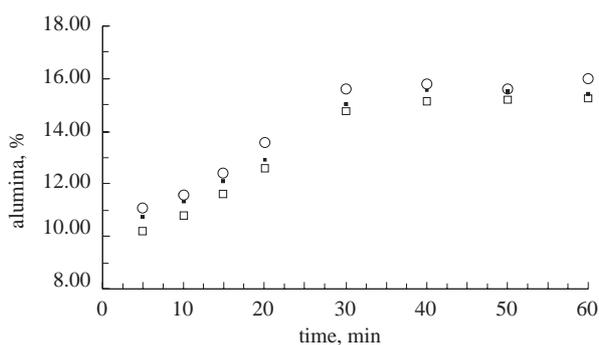


Figure 3c. The change in alumina solubility with USP and sonication time (for samples grain size 1 and mass 0.0500 g)

□ : minimum USP, ■: medium USP, ○: maximum USP

The recoveries of Ca, Mg and Al showed a linear increase during the first 30 min and remained constant afterwards for all ultrasonic powers.

The effect of sample mass

The change in Ca, Mg and Al solubilities of four equal samples for all grain size and sample masses at maximum ultrasonic power (that is, average time periods of 30-60 min of sonication) are given in Figures 4a, 4b and 4c.

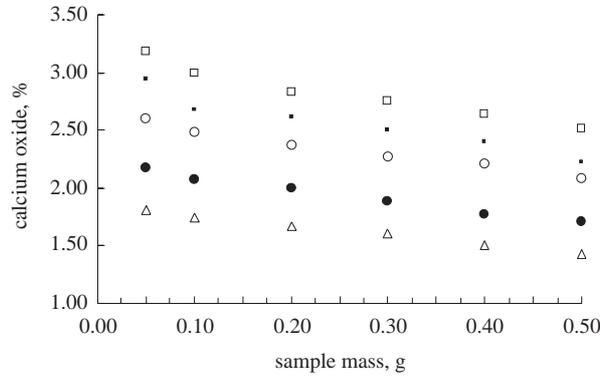


Figure 4a. The change in calcium oxide solubility with sample grain size and sample masses (maximum USP and mean values from 30 to 60 min)

□ : grain size 1., ■: grain size 2., ○: grain size 3., ●: grain size 4., △: grain size 5.

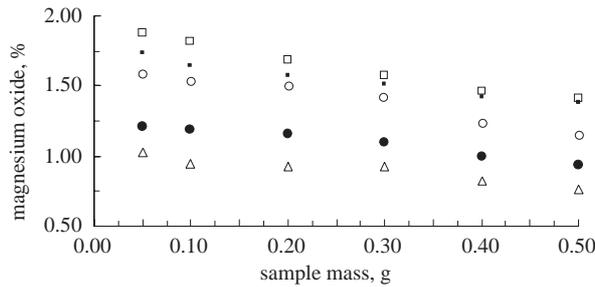


Figure 4b. The change in magnesium oxide solubility with sample grain size and sample masses (maximum USP and mean values from 30 to 60 min)

□ : grain size 1., ■: grain size 2., ○: grain size 3., ●: grain size 4., △: grain size 5.

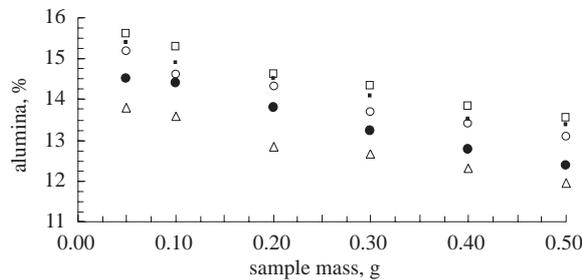


Figure 4c. The change in alumina solubility with sample grain size and sample masses (maximum USP and mean values from 30 to 60 min)

□ : grain size 1., ■: grain size 2., ○: grain size 3., ●: grain size 4., △: grain size 5.

The solubilities decreased with increasing sample grain size for the three elements. The maximum solubilities were observed for a 0.0500 g sample mass and grain size 1. The 0.0500 g of sample portions left

practically no residue, and the recovery from these portions of samples must be equal to that obtained by total dissolution.

Therefore, the solubilities of Ca, Mg and Al for grain size 1 and all sample masses at varied ultrasonic power (minimum, medium and maximum) were investigated and the findings are shown in Figures 5a, 5b and 5c, respectively.

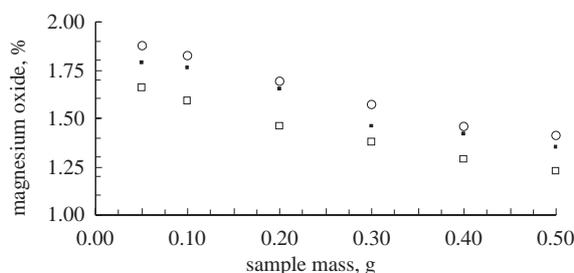


Figure 5a. The change in Ca solubility with sample mass and USP (grain size 1 and mean values from 30 to 60 min)

□ : minimum USP, ■: medium USP, ○: maximum USP

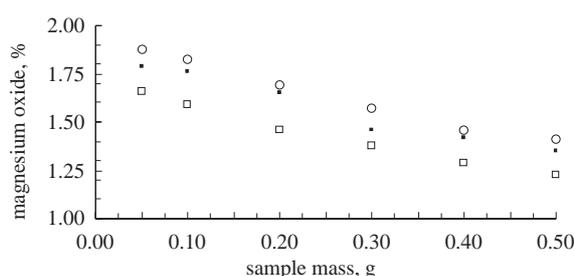


Figure 5b. The change in Mg solubility with sample mass and USP (grain size 1 and mean values from 30 to 60 min)

□ : minimum USP, ■: medium USP, ○: maximum USP

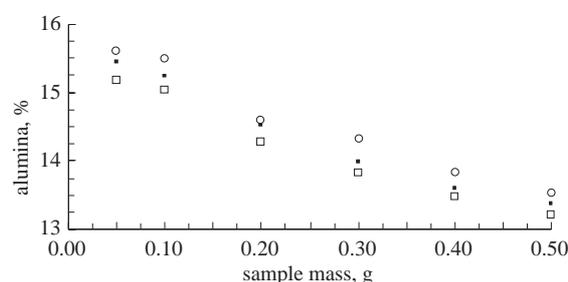


Figure 5c. The change in Al solubility with sample mass and USP (grain size 1 and mean values from 30 to 60 min)

□ : minimum USP, ■: medium USP, ○: maximum USP

The solubilities of Ca, Mg and Al rapidly decreased with increasing sample mass, the recoveries being dependent upon USP. This trend was similar for other sample grain sizes.

The effect of sample grain size

Grain size was previously defined as the sieve pore size range. The effects of sieve pore size range and sample mass on the solubilities of Ca, Mg and Al for all sample masses at maximum USP are given in Figures 6a, 6b and 6c.

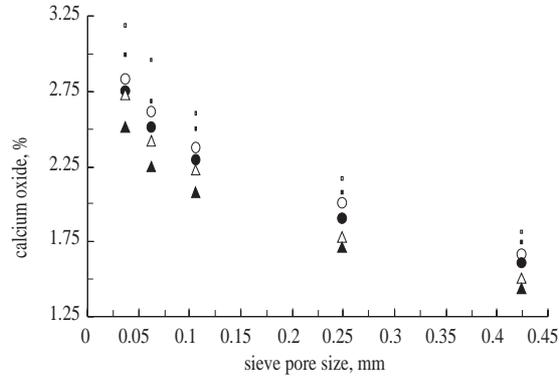


Figure 6a. The change in calcium oxide solubility with sieve pore size and sample masses (for maximum USP and mean values from 30 to 60 min)

□ : 0.0500 g, ■: 0.1000 g, ○: 0.2000 g, ●: 0.3000 g, △: 0.4000 g, ▲: 0.5000 g

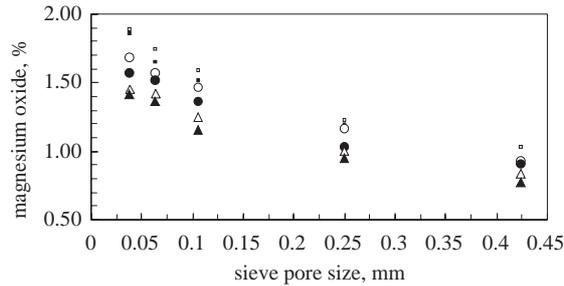


Figure 6b. The change in magnesium oxide solubility with sieve pore size and sample masses (for maximum USP and mean values from 30 to 60 min)

□ : 0.0500 g, ■: 0.1000 g, ○: 0.2000 g, ●: 0.3000 g, △: 0.4000 g, ▲: 0.5000 g

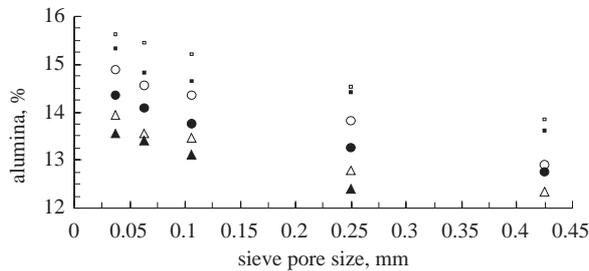


Figure 6c. The change in alumina solubility with sieve pore size and sample masses (for maximum USP and mean values from 30 to 60 min)

□ : 0.0500 g, ■: 0.1000 g, ○: 0.2000 g, ●: 0.3000 g, △: 0.4000 g, ▲: 0.5000 g

Maximum solubilities were obtained for $-0.038 + 0.000$ mm (grain size 1) sieve pore range and samples with 0.0500 g mass. Solubilities decreased up to 0.0106 mm sieve pore size rapidly, and then slowly with

increasing grain size. In all of the above mentioned conditions, the minimum sample grain size produced results equal to total dissolution for maximum USP. The situation is similar to those at other USPs.

The effect of ultrasonic power

The change in solubility with USP is shown in Figures 7a, 7b and 7c for Ca, Mg and Al, respectively.

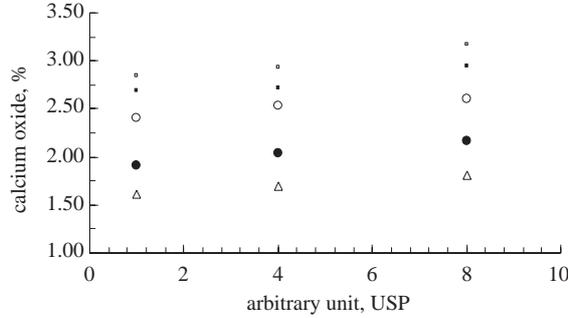


Figure 7a. The change in calcium oxide solubility with USP and grain size (for 0.0500 g sample, mean value from 30 to 60 min)

□ : grain size 1., ■: grain size 2., ○: grain size 3., ●: grain size 4., △: grain size 5.

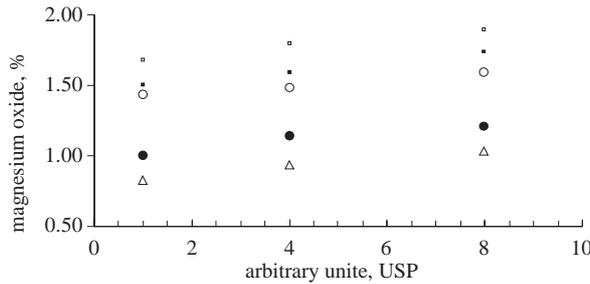


Figure 7b. The change in magnesium oxide solubility with USP and grain size (for 0.0500 g sample, mean value from 30 to 60 min)

□ : grain size 1., ■: grain size 2., ○: grain size 3., ●: grain size 4., △: grain size 5.

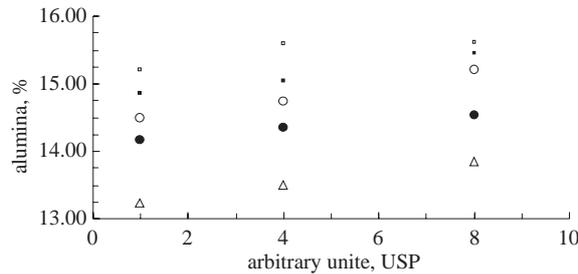


Figure 7c. The change in alumina solubility with USP and grain size (for 0.0500 g sample, mean value from 30 to 60 min)

□ : grain size 1., ■: grain size 2., ○: grain size 3., ●: grain size 4., △: grain size 5.

While solubility increased with increasing USP, it decreased with increasing sample grain size. Maximum recovery was obtained with maximum USP and grain size 1 (-0.038 + 0.000 mm). The results from other sample masses confirmed this trend.

Evaluation of the solubilities of Ca, Mg and Al

The elements, Ca, Mg and Al, are found as CaO, MgO and Al₂O₃ in rock samples forming minerals. These major elements, as the main rock forming components in magmatic rocks, are incorporated in the formation of feldspar and mafic minerals^{29–30}. It has been reported that high recoveries of oxide bound strontium from sediments are possible when analysed by sequential ULM in a much shorter time than that required for conventional sequential extraction procedures³¹. Similar results have also been observed for oxide bound elements (Na, K, Ca, Mg, Al, Mn and Fe) in rock samples by the physical and chemical effects of ultrasonication^{1,21}.

The solubilities of all these three elements exhibited a linear increase for the first 30 min and then remained nearly constant under all conditions studied. However, the solubilities changed significantly, allowing us to determine optimal conditions. Therefore, solubilities at 30, 40, 50 and 60 min sonication time were evaluated as four replicates for reproducibility tests. Maximum Ca, Mg and Al solubilities were obtained with grain size 1, 0.0500 g sample mass and max USP (considered the optimum conditions). In fact, under these circumstances, practically no residual sample was left with ULM. In other words, the results of this procedure practically matched those of the conventional destructive methods.

The results of ULM (C_{ULM}) with corresponding confidence intervals ($p = 0.05$, $N = 4$) were 3.18 ± 0.05 , 1.89 ± 0.03 and 15.61 ± 0.09 in terms of metal oxide percentage at optimal conditions for Ca, Mg and Al, respectively.

The results of the conventional dissolution method²⁸ (C_{CDM}) were 2.96, 1.73 and 15.51 in terms of metal oxide percentage for Ca, Mg and Al, respectively.

The confidence intervals (for CDM) were ± 0.07 , ± 0.04 , and ± 0.11 for Ca, Mg and Al, respectively ($P = 0.05$ and $N = 4$).

When the concentrations of Ca, Mg and Al obtained from ULM at optimum conditions were compared to those of the conventional method, there was no significant difference between the results.

The amount of residues increased with increasing sample mass and grain size, and hence the solubilities of Ca, Mg and Al decreased. Despite this handicap, reproducible partial dissolution was obtained in 30 min of sonication time.

Average Ca, Mg and Al solubilities which gave reproducible results for five different grain sizes and six different sample masses were defined as follows for applied ultrasonic power:

\bar{x} min USP: average as a percentage of four repeated equal measurements at min USP

\bar{x} med. USP: average as a percentage of four repeated equal measurements at med USP

\bar{x} max USP: average as a percentage of four repeated equal measurements at max USP

The percentage recovery ratio for the oxides of Ca, Mg and Al were derived from

Kmin: $(\bar{x}_{minUSP}/C_{CDM}) \times 100$,

Kmed: $(\bar{x}_{medUSP}/C_{CDM}) \times 100$, and

Kmax: $(\bar{x}_{maxUSP}/C_{CDM}) \times 100$.

The percentage recovery ratio (K) depending on applied USP for five different grain sizes and six sample masses were determined.

The recovery efficiencies varied between 40 (for grain size 5, 0.5000 g sample mass and minimum USP) and 107% (for optimum conditions) for CaO, between 34 (for grain size 5, 0.5000 g sample mass and minimum USP) and 98% (for optimum conditions) for MgO, and between 72 (for grain size 5, 0.5000 g sample mass and minimum USP) and 101% (for optimum conditions) for Al₂O₃.

The results of SRMs

Validation of the developed method was performed using standard reference materials (SRM). Values of elemental concentrations (C_{SRM}) were obtained from the certificates of analysis or from the compilation of usable values by Govindaraju²⁷. The SRMs used in this study are as follows:

USGS (AGV-1, G-2, RGM-1 and SDC-1), CRPG (GA, GH, MICA-Fe and MICA-Mg), ANRT (DRN, GSN and UB-N) and GIT-IWG (MA-N, AC-E, AN-G and BE-N).

USGS: United State Geological Survey, Reston.

CRPG: Centre de Recherches Petrographiques et Geochimiques, France.

ANRT: Association Nationale de la Recherche Technique, Paris.

GIT-IWG: Groupe International de Travail - International Working Group (preferred designation of GIT and IWG, France).

The SRMs were leached under optimised ULM conditions using the conventional method, and the experiments were repeated four times. All leachates were analysed using AAS, and results were defined for Ca, Mg and Al as an average percentage including recovery efficiency percentage. $K_1 = (C_{ULM}/C_{SRM}) \times 100$ and $K_2 = (C_{ULM}/C_{CDM}) \times 100$

The percentage confidence intervals (for K_1) were ± 4 , ± 3 , and ± 8 for Ca, Mg and Al, respectively ($P = 0.05$, $N = 4$).

The percentage confidence intervals (for K_2) were ± 5 , ± 4 , and ± 7 for Ca, Mg and Al, respectively ($P = 0.05$, $N = 4$).

Recovery efficiencies were 95-112% for Ca, 93-109% for Mg and 91-107% for Al.

Conclusions

It is claimed that reproducible element recovery ratios can be obtained under well defined partial dissolution conditions. Similar results were obtained for three of the elements investigated. Therefore, it seems that the situation does not depend upon the nature of the element. This conclusion was also supported by the results of our earlier work^{1,21}.

The confidence interval of the method is comparable with those of conventional techniques. Clearly, the method is quicker than its conventional counterparts. The reagent consumption of the method is less than that of total dissolution methods and hence the method is environmentally friendly.

The method can be a speedy, inexpensive, reproducible and safe alternative dissolution process if it is supported by complementary investigations.

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