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Cite this article as:
Sandeep Kumar Jena, Jogeshwar Sahu, Geetikamayee Padhy, Swagatika Mohanty, and Ajit Dash, Chlorination roasting-coupled water leaching process for potash recovery from waste mica scrap using dry marble sludge powder and sodium chloride, *Int. J. Miner. Metall. Mater.*, 27(2020), No. 9, pp. 1203-1215. https://doi.org/10.1007/s12613-020-1994-3

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International Journal of Minerals, Metallurgy and Materials
Volume 27, Number 9, September 2020, Page 1203
https://doi.org/10.1007/s12613-020-1994-3

Chlorination roasting-coupled water leaching process for potash recovery from waste mica scrap using dry marble sludge powder and sodium chloride

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(Received: 23 October 2019; revised: 11 December 2019; accepted: 1 February 2020)

Abstract: The present paper reports the effective utilization of marble sludge powder (MSP) for the recovery of potash values from waste mica scrap using chlorination roasting–water leaching method. Characterization studies indicated the presence of dolomite as the major mineral phase in MSP, whereas muscovite and quartz were observed in the mica sample. The acid leaching studies suggest a maximum of 22% potash recovery under conditions: 4 M H_2SO_4 acid, particle size of ~100 μm, stirring speed of 600 r/min, leaching temperature of 75°C, and leaching time of 90 min. The chlorination roasting–water leaching process was adopted to achieve the lowest level of 80%–90% potash recovery. The optimum conditions for the recovery of ~93% potash from mica (~8.6wt% K_2O) requires 900°C roasting temperature, 30 min roasting time, and 1:1:0.75 mass ratio of mica : MSP : NaCl. The roasting temperature and amount of NaCl are found to be the most important factors for the recovery process. The reaction mechanism suggests the formation of different mineral phases, including sylvite (KCl), wollastonite, kyanite, and enstatite, during roasting, which were confirmed by X-ray diffraction (XRD) analyses and scanning electron microscopy (SEM) morphologies. The MSP-blended NaCl additive is more effective for potash recovery compared with the other reported commercial roasting additives.

Keywords: potash recovery; mica scrap; marble sludge powder; chlorination roasting; water leaching

1. Introduction

The generation and steady increase of ineffectual solid waste materials due to industrial, mining, agricultural and commercial activities owing to increasing urbanization and growth of population creates various problems in their disposal and recycling; so, there is a need to reduce, recycle, reuse or recover the generated solid wastes as much as possible. Marble sludge powder (MSP), which is generated in marble processing industries during sawing and polishing of marble, is one of the major industrial solid wastes. Marble sludge, in the form of semi-liquid or slurry form, contains around 24wt%–45wt% water along with dust marble particles and 20% of the processed marble is estimated to end up in sludge waste [1–2]. Practically 70% of the total mine's production is discarded as waste during mining, processing, and polishing, resulting in significant environmental issues [2–4]. As per the available data, the world's major marble exporters including Turkey, Italy, China, Greece, Spain, and India, produce a substantially high amount of marble sludge as waste material [5–6].

Most of the waste is dumped unscientifically and improperly in nearby pit or vacant spaces, which deteriorates the local environment in many aspects, including reduction of soil fertility, depletion of water permeability, and increase in the suspended particulate matter in air [7–10]. Reports are available regarding serious human health problems due to inhalation of dry marble sludge powder (MSP)-polluted air [11–13]. In addition, the handling and disposal of the generated marble waste supplements an extra financial burden for marble/dimension stone companies [14–15]. Hence, value addition to this waste by recycling through a proper method is a challenge. However, apart from land filling [16–18], other reports are available regarding the use of marble/granite waste for production of building and construction raw materials [19–23], different class ceramic products [24–26], removal of heavy metal ions [27–30], neutralization of acidic soil [27,31–32], and as inorganic filler materials in tire and polymer production [33–35].

The present study reports a novel application of waste

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MSP for the recovery of potash from low-priced/waste mica scrap material. The potassium value is commercially expressed as the oxide content, i.e., potash (K_2O). The major industrial application of potassium is the manufacture of potassic fertilizer (~95%), apart from glass, ceramic, pigment, and pharmaceuticals productions [36–37]. The demand of potassic fertilizer is growing persistently at 3%–3.5% annually [38–39]. Many agricultural-based countries in Africa, South Asia, Central Europe, and Oceania with no commercial source of potash entirely depend on its import. However, the presence of secondary mineral sources, such as feldspar (4wt%–12wt% K_2O), mica (6wt%–14wt% K_2O), glauconitic sandstone (4wt%–11wt% K_2O), and nepheline syenite (5wt%–10wt% K_2O), which contain a good amount of potash, is the only option for potash recovery. Mica is a highly available mineral in India with a production of 14000 Mt, making the country the top 8th global producer [40]. However, owing to the technological development of new materials, the global demand for mica is declining continuously [41]. Therefore, an attempt has been made here to extract potash values from mica to support the fertilizer industry.

Literature studies suggest three major routes of potash recovery from mica and other potash bearing minerals, such as feldspar, nepheline syenite, and glauconitic sandstone; these routes include bioleaching, chemical leaching, and chlorination roasting-coupled water leaching processes. Dependency on various critical parameters, such as pH, temperature, complexity of mineral structure, and the presence of CO_2 and O_2, for bioleaching extraction processes, renders this route unsuitable due to their low extraction efficiency [42–44]. Similarly, chemical leaching of mica (muscovite/biotite/phlogopite) depends on the nature and concentration of mineral acids used, leaching temperature, leaching time, and particle size of the sample [45–47]. The use of different acids plays an important role and affects the potash recovery value. Potash (K) release from the complex biotite mica structure completely depends on the chain length of the phosphoric acids used and dehydration degree of the system [45], whereas the release of K from muscovite mica depends on the concentration of H_2SO_4 and leaching temperature [46]. Varadachari in 1997 [47] reported a maximum of 14% potash recovery from biotite mica using HCl (9.4 N) at 80°C after 4 h of leaching period. The low recovery of potash using $BaCl_2$ solution, Mehlich solution (H_2SO_4 + HCl), NaOH, and HNO_3 is due to the positioning of K in the complex structure [48–50].

However, the chlorination roasting followed by water leaching is the most efficient method to recover potassium from these rocks/minerals. Various experimental factors, including the roasting temperature, roasting time, and additive ratio with respect to mica scrap/similar K-bearing rocks, largely influence the extraction efficiency [51–52]. $CaCl_2$ is the most commonly used roasting additive for extraction of potassium from mica, feldspar, and glauconitic sandstone [49,53–55]. The comparison of $CaCl_2$ with other alkali/alkaline earth metal chlorides indicates it as a cheaper, non-toxic, and highly efficient choice, as reported in literatures [56–58]. Ca^{2+} replaces K^+ from the complex crystal structure of mica, and subsequently, the released K^+ combines with Cl^- to form KCl. The present work reports the use of MSP (due to high calcium content) as a low-cost roasting additive to recover potassium from mica scrap. Various characterization studies have been carried out to establish the plausible extraction mechanism.

2. Experimental

2.1. Materials and their pre-treatment

The off-white colored slippery and flaky mica scrap sample (Fig. 1(a)) used in this study was collected from a mica sheet manufacturer and exporter located in the state of Jharkhand, India, and further processed in a mortar grinder (Retch model 200M) for size reduction. The as-received dried MSP (Fig. 1(b)) from Rajasthan state, India, was used as such without any further treatment. Figs. 1(c) and 1(d) present the size analysis results for both samples. Under various grinding times of the mortar grinder, the ground products were size analyzed using Indian standard sieves, with 80wt% of the product passing through 100 μm after 6 min grinding (Fig. 1(c)). The other chemicals and standards, for inductively coupled plasma optical emission spectroscopy (ICP-OES) and flame photometry, were purchased from Avantor (India) Ltd, New Delhi.

2.2. Extraction methods

2.2.1. Acid leaching

Acid leaching studies were performed with respect to different mineral acids, including H_2SO_4, HNO_3, HCl, and H_3PO_4, in a glass beaker using a digital magnetic stirrer. The major leaching parameters, such as acid concentration, particle size of mica scrap, leaching time, and leaching temperature, were optimized for maximum recovery of potash. The agitation rate of the slurry sample was maintained at (600 ± 10) r/min. Both flame photometer (Systronic 128μc) and inductively coupled plasma optical emission spectrometer (ICP-OES Perkin Elmer 8300) were used to analyze the leached liquor to determine the potash value.

2.2.2. Roasting–leaching experiments

The roasting–leaching experiments of mica scrap sample involved high-temperature roasting followed by water leaching. Batch-scale roasting experiments were performed in a laboratory muffle furnace with a well-mixed and fixed mass ratio of mica scrap powder (~10 g) and roasting additives in an iron crucible. Roasting parameters, including roasting time, temperature, particle size, and mica-to-additive mass

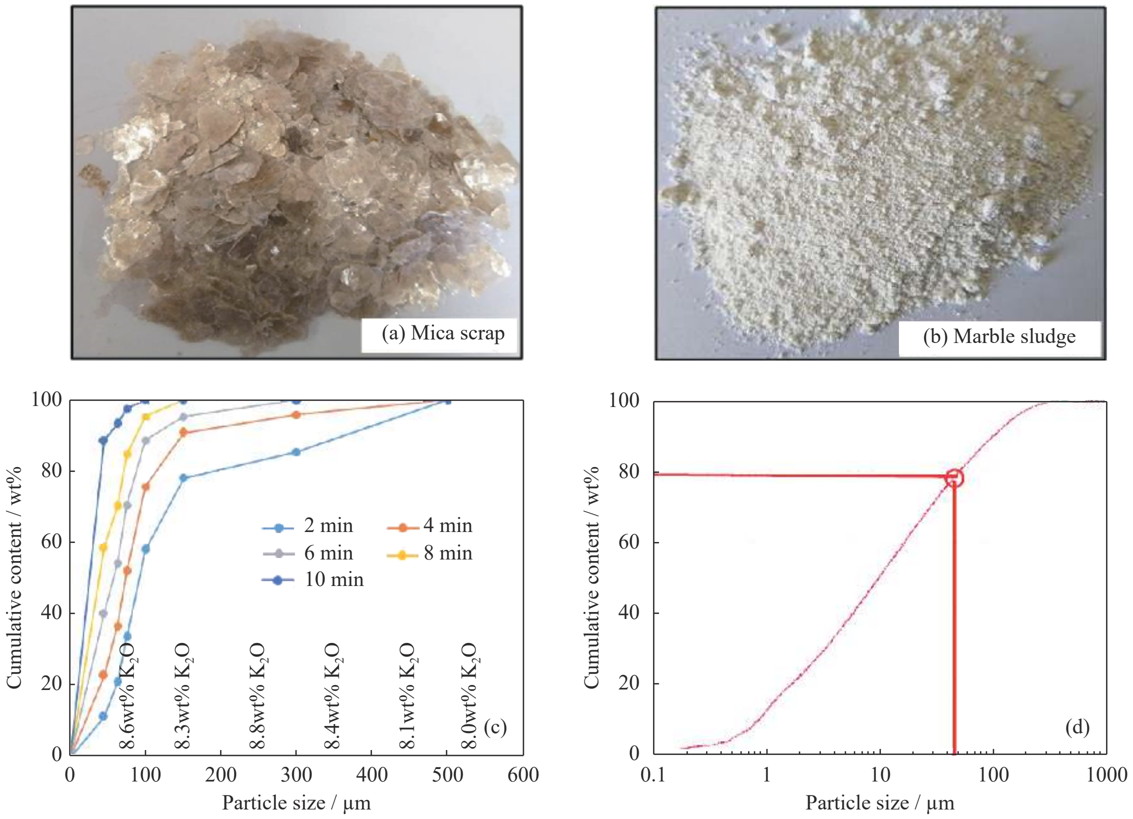


Fig. 1. (a) As-received mica scrap and (c) the particle size analysis of its mortar ground products at different times; (b) the dry MSP and (d) its particle size analysis.

ratio, were varied to recover maximum potash from the feed sample. The different roasting additives used here comprised NaCl, $CaCl_2$, $CaCO_3$, $NaCO_3$, and MSP. After a specific roasting time, the collected hard roasted mass was made into powder form using a hand mortar and allowed to leach with water only. The water leaching experiments are similar to the methods described in section 2.2.1. At the end of water leaching, the solid–liquid phases were separated using laboratory-grade filter papers, and the residual parts were washed carefully 5–6 times. Fig. 2 presents the scheme of the extraction process.

2.3. Characterization studies

The mineralogical characteristics of the feed and processed product samples were studied using X-ray diffraction (XRD, PANalytical X'pert PRO-XRD) equipped with CuK_α radiation (40 kV, 20 mA) source and ZEISS (EVO) scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS). Thermogravimetric analysis (TGA) of the samples was conducted from room temperature up to 1200°C in 80 mL/min Ar flow using Netzsch STA 449F3 Jupiter instrument. The chemical composition of the samples was determined using standard wet chemical analysis meth-

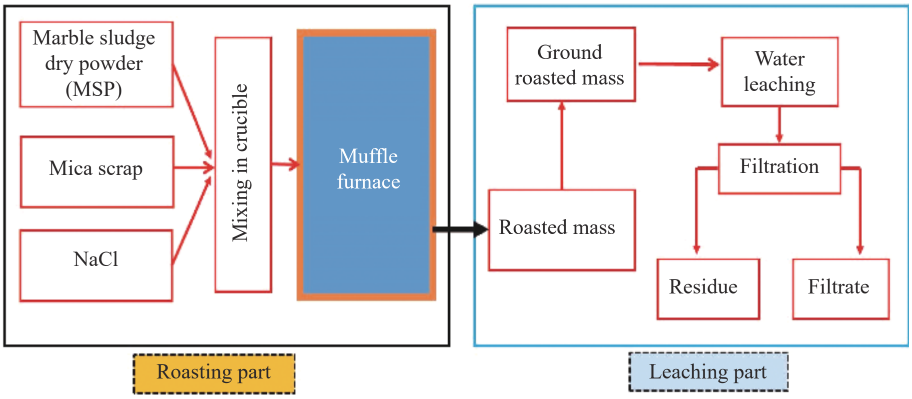


Fig. 2. Experimental scheme for potash recovery from mica scrap using MSP and NaCl.

ods and instruments, such as Systronic flame photometer (Model 128μc) and Perkin Elmer Optima 8300 (ICP-OES).

3. Results and discussion

3.1. Sample characterization

Table 1 presents the chemical compositions of the feed mica scrap and MSP, and the corresponding TGA graph is presented in Fig. 3. The mica sample primarily consisted of three components, such as silica, alumina, and potassium, with a loss on ignition (LOI) value of 5.38wt%. This high LOI value is due to the adsorbed moisture in the mica sample. Moreover, the chemical analysis of all the mortar ground mica products indicated that potassium was equally distributed in all fractions (Fig. 1(c)). The dry MSP has two prime components ($CaCO_3$ and $MgCO_3$) with an extremely high LOI value of 40.45wt% (Fig. 3), and this finding is due to the removal of CO_2 after heating the sample at 900°C for 1 h.

The XRD patterns of the mica scrap and MSP samples, as presented in Figs. 4(a) and 4(b), indicated the presence of various phases. The mica sample consist of muscovite and quartz phases, whereas dolomite and quartz as the major phases present in MSP. Figs. 5 and 6 show the SEM images along with the semi-quantitative analysis and EDS analyses of mica and MSP, respectively. The typical flaky structure of the mica sample was observed, and the semi-quantitative data confirmed the presence of muscovite (K-bearing hydrated aluminum silicate phase). The marble sludge sample has no definite structure with no distinct particle morphology, but the semi-quantitative data analysis indicated the presence of calcium and magnesium oxides as the major constituents.

Table 1. Chemical composition analyses of the feed mica and marble sludge power (MSP) samples wt%

Sample	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	MnO	TiO_2	LOI
Mica	48.60	27.82	4.12	8.62	0.81	2.06	1.05	0.12	0.16	5.38
MSP	4.67	0.41	0.52	0.017	0.014	32.64	21.12	0.02	0.029	40.45

Note: LOI—Loss on ignition.

3.2. Acid leaching studies

Mineral acids, such as H_3PO_4, HCl, HNO_3, and H_2SO_4, were used to study the leaching behavior of the ground mica sample. Fig. 7(a) presents the preliminary studies using these acids of 4 M concentration at a fixed leaching temperature of 75°C, leaching time of 90 min,a stirring speed of 600 r/min, and the sample particle size of ~100 μm. The results indicate that a maximum of 22% potassium could be leached with H_2SO_4, which exhibited a better performance than the other three acids used in the same conditions. In addition, another set of experiments using H_2SO_4 was attempted with varying particle sizes of the mica sample, leaching temperatures, and leaching times to increase the potassium extraction efficiency. The results in Figs. 7(b)–7(d) imply that regardless of the conditions of leaching parameters, the extraction efficiency will be in the maximum range of 24%–26% at the sample particle size of 45 μm, leaching temperature of 95°C, and leaching time of 180 min. Thus, these results reveal that acid leaching is an ineffective method for the recovery of potassium from mica.

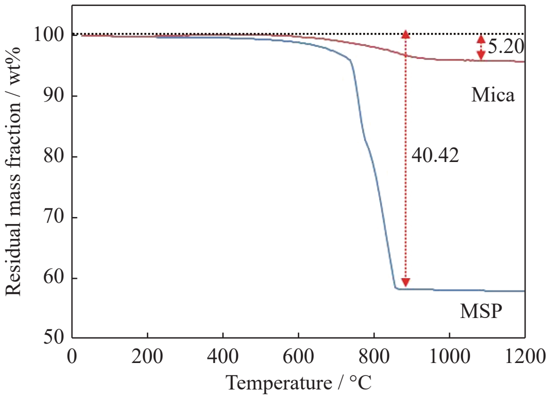


Fig. 3. TGA curves of mica and MSP.

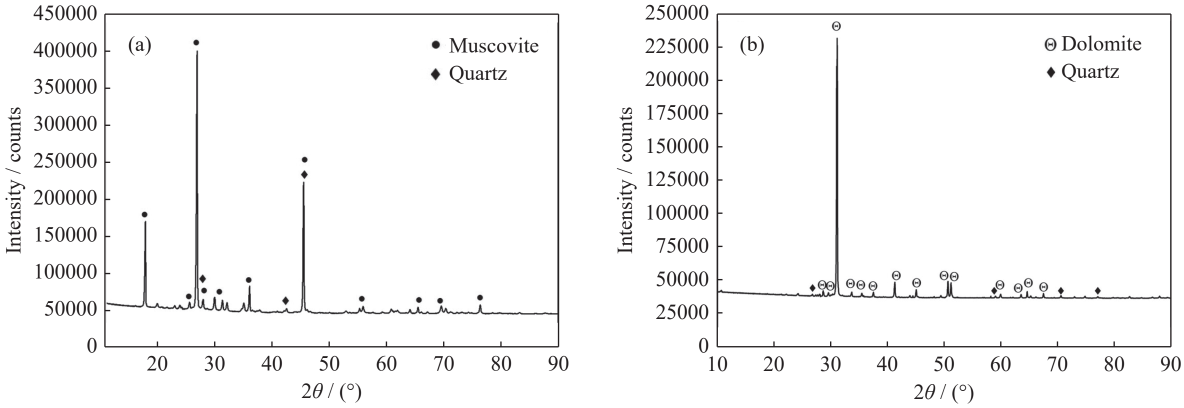
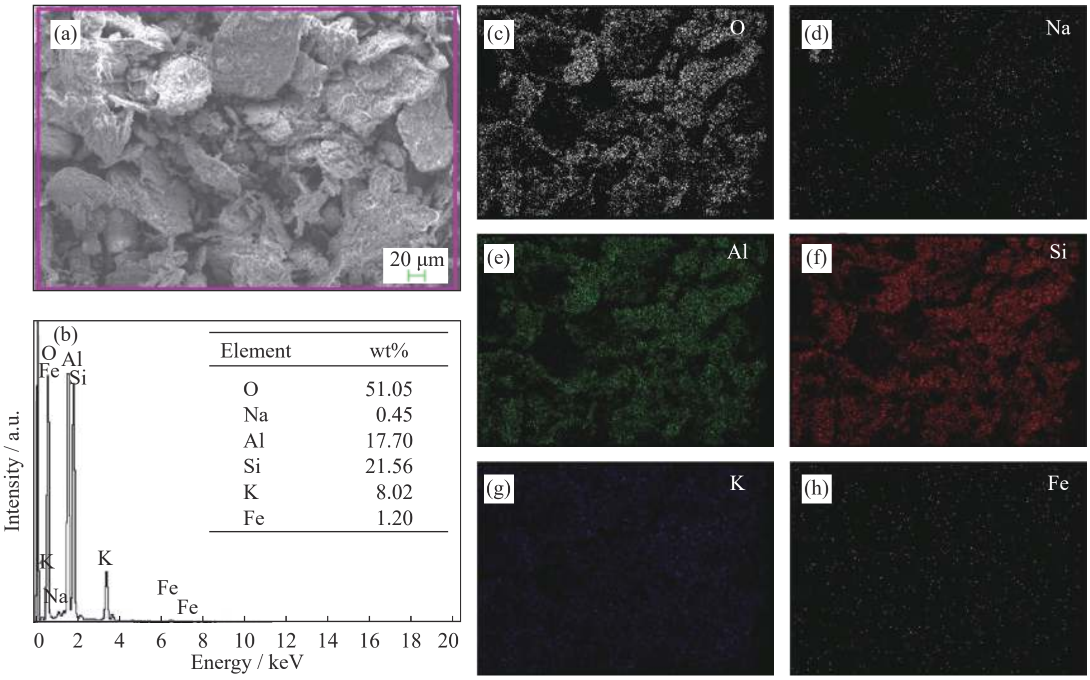
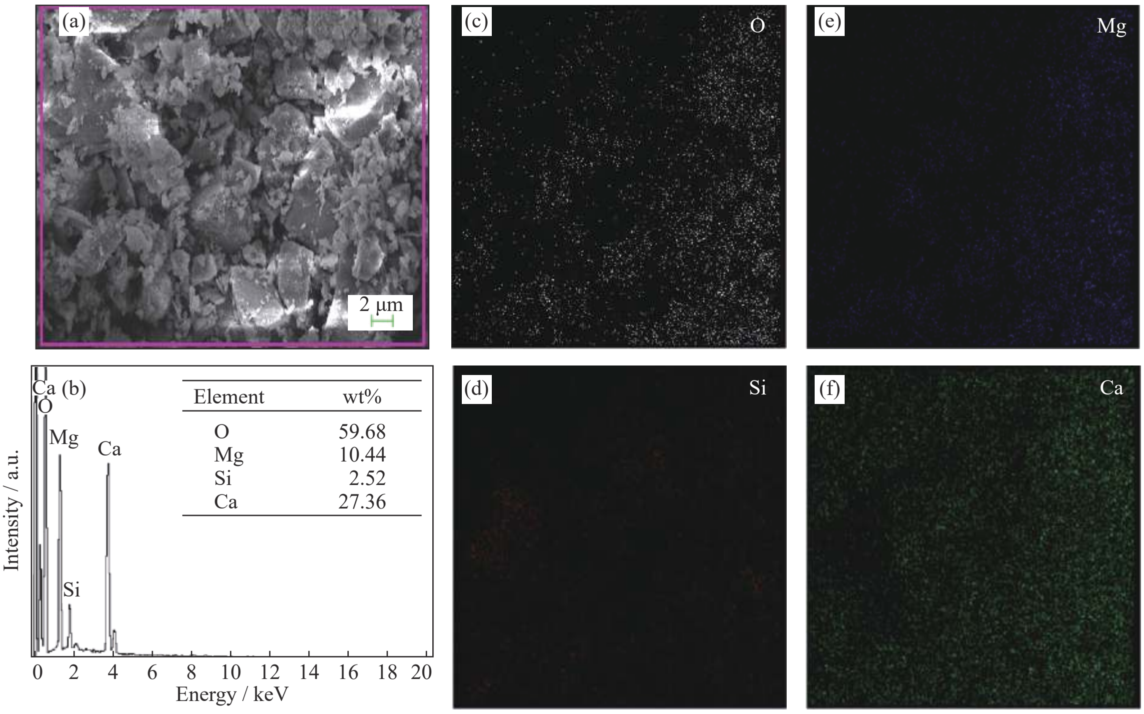


Fig. 4. XRD patterns of (a) feed mica and (b) MSP samples.



Element	wt%
O	51.05
Na	0.45
Al	17.70
Si	21.56
K	8.02
Fe	1.20

Fig. 5. (a) SEM image, (b) EDS analysis, and (c–h) elemental mapping images of the mica sample.



Element	wt%
O	59.68
Mg	10.44
Si	2.52
Ca	27.36

Fig. 6. (a) SEM image, (b) EDS analysis, and (c–f) elemental mapping images of the MSP sample.

3.3. Roasting–leaching studies

3.3.1. Preliminary roasting–leaching experiments

As per the available literatures [51,53,56,59], potassium recovery from mineral sources, including mica, feldspar, nepheline syenite, and glauconitic sandstone, is superior when using the chloridizing roasting–water leaching method compared with acid leaching. Reports on the use of commercial roasting additives, including $CaCl_2$, NaCl, $CaCO_3$, and Na_2CO_3, are widely available for the extraction study of potassium from these minerals. The free-energy–temperature diagram of metal–chloride system suggests that the formation of KCl is favorable than any other metal chlorides [60];

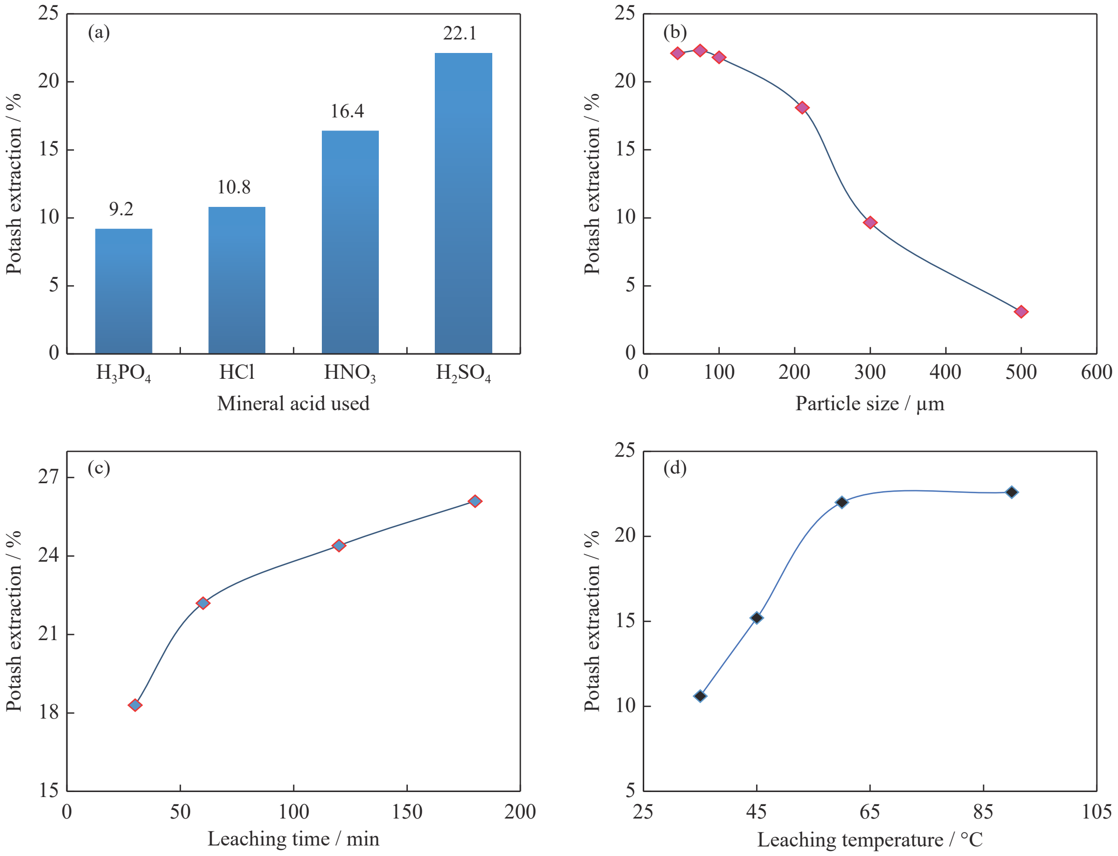


Fig. 7. Acid leaching of mica: (a) effect of mineral acids (4 M acid, 75°C, 90 min, ~100 μm); (b) effect of mica particle size (4 M H_2SO_4, 90°C, 60 min); (c) effect of leaching time (4 M H_2SO_4, 90°C, ~100 μm); (d) effect of leaching temperature (4 M H_2SO_4, 60 min, ~100 μm). Stirring speed of all the experiments was fixed at 600 r/min.

thus, potassium can be possibly recovered as KCl by roasting with metal chlorides, including NaCl and $CaCl_2$. However, calcium-based compounds are better due to the isoelectronic nature of Ca^{2+} and K^+, which easily replace K^+ to form the complex structure smoothly [57–58,61]. The probability for the release of K^+ from the complex structure using Mg^{2+} is low given that the difference in ionic sizes of K^+ and Mg^{2+} is notably large, and they are not in isoelectronic species. Reports are available regarding the use of $MgCl_2$ for the potash extraction purpose, but the comparison with $CaCl_2$ suggests the effectiveness of $CaCl_2$ over the other compounds [62]. Thus, based on these conclusions, preliminary experiments were carried out using different additives (Fig. 8).

The results of this preliminary study indicate that when using $CaCl_2$, potash extraction approximates 98% and is the highest one compared with other additives, whereas $CaCO_3$ results in extremely low recovery value of around 3%. This large difference in extraction value may be attributed to the presence of Cl^-. Ca^{2+} in both the additives can possibly replace K^+ (due to the isoelectronic nature of Ca^{2+} and K^+) from the complex mica structure; however, a chloride source is necessary to combine with the replaced K^+ to form KCl, which is not possible in the case of $CaCO_3$, hence resulting in low potash recovery efficiency. Similar result for MSP as an additive has been observed as in case of $CaCO_3$ roasting. However, roasting of mica with a combination of MSP and NaCl showed a sharp rise in extraction value to around 93%.

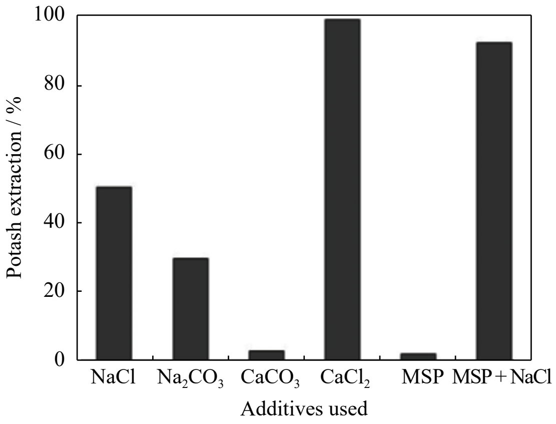


Fig. 8. Comparison of potash recovery using different commercial roasting additives (roasting conditions: roasting temperature of 900°C; roasting time of 60 min; mica particle size of ~100 μm; mica : additive mass ratio of 1:1).

The details of extraction and its possible mechanism using waste MSP and NaCl are presented in sub-section 3.3.2 and section 4, respectively.

3.3.2. Roasting using MSP and NaCl

Experiments were performed under different conditions to evaluate the effect of MSP and NaCl on the extraction of potash values from mica scrap. The effects of other vital roasting parameters, such as roasting time, temperature, and particle size, have been determined, and the results are presented in Fig. 9.

(1) Effect of roasting time.

Fig. 9(a) shows the effect of roasting time while keeping all other parameters constant (a roasting temperature of 900°C, a particle size of ~100 μm, and the mica : MSP : NaCl mass ratio of 1:1:1). A set of experiments has been carried out with a time gap of 10 min and showed that for almost 90% recovery of potassium a minimum roasting time of 30 min is required. However, the increase in roasting time above 30 min showed an insignificant effect on potash extraction.

(2) Effect of roasting temperature.

The roasting temperature plays the most important role during the roasting process as shown in Fig. 9(b). An equal mass ratio of mica, MSP, and NaCl (1:1:1) mixture was roasted for 60 min using a particle size of ~100 μm with varying temperatures from 600 to 1100°C. The roasting temperature plot shows that experiments at 600°C had the lowest potash recovery of around 2%, whereas the highest value was close to 94% at 900°C. A further increase in temperature resulted in slow decrease in extraction value. The results obtained can be explained by considering the melting point of NaCl (801°C) and $CaCO_3$ (825°C). The extremely low potash recovery below 800°C was due to the high melting point of the additives NaCl and $CaCO_3$, which is the minimum temperature required to initialize potassium extraction mechanism. However, as the temperature rose above 800 to 900°C, a sharp change in extraction value occurred, and the maximum was obtained at 900°C. Further increase in temperature beyond 900°C showed a slight decrease in potash recovery due to the formation of water-insoluble potassium phase (leucite, $KAlSi_2O_6$) at such high temperature as reported earlier by Santos *et al*. [63]. In addition, the formed sylvite (KCl) may be volatilized at high temperature, showing a lower value of potassium in the leach liquor [64].

(3) Effect of particle size.

Fig. 9(c) shows the effect of particle size on the extraction

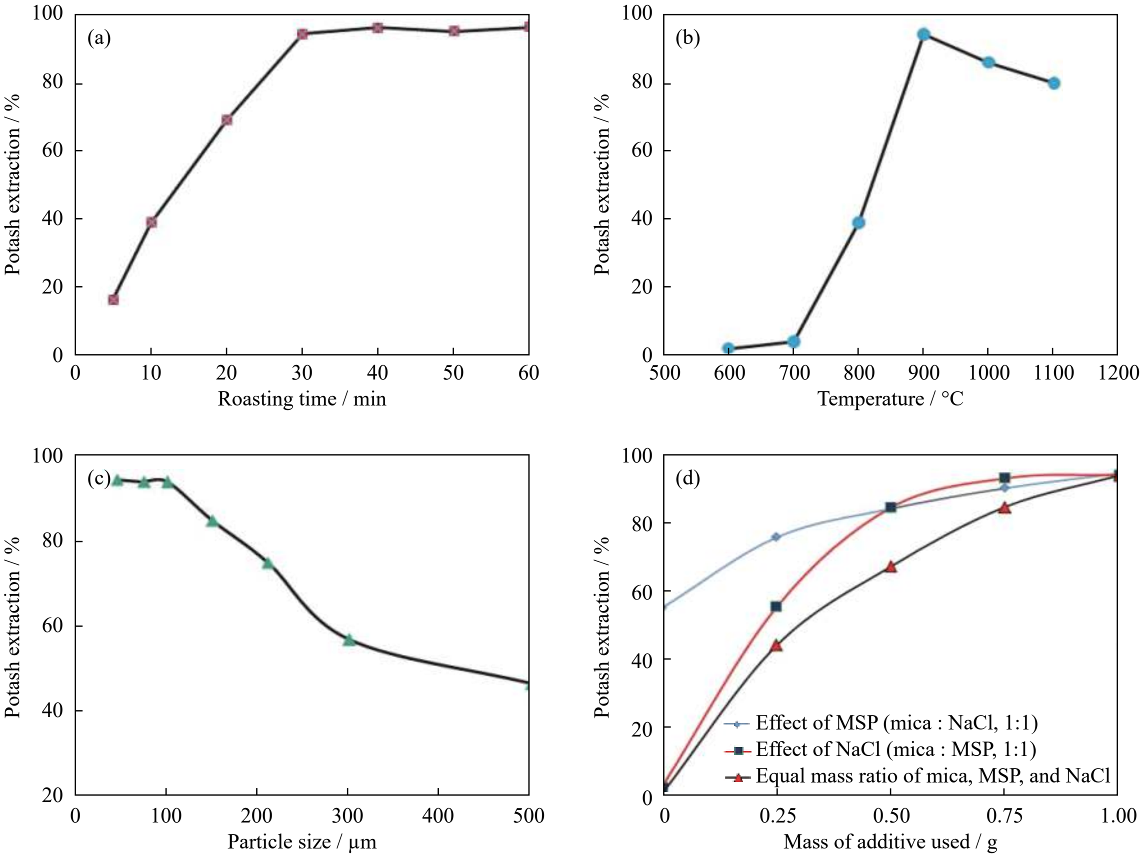


Fig. 9. Effect of different roasting parameters on potash recovery: (a) roasting time; (b) roasting temperature; (c) particle size; (d) mass of roasting additive used.

efficiency of potassium from mica scrap. The particle size of the feed sample was varied during the roasting process under fixed conditions, including a temperature of 900°C, a roasting time of 60 min, and a mass ratio of mica : MSP : NaCl of 1:1:1. The results indicate the lower the particle size, the higher the extraction value, which is due to the generation of a larger surface area of reactivity. The particle size of ~100 μm has a similar recovery as in the case of ~75 μm and ~45 μm. Therefore, 100 μm is the optimum particle size for the recovery of potassium from mica.

(4) Roasting additive ratio.

The effect of roasting additives was studied using different mass ratios of NaCl and MSP at 900°C for 60 min, and the results are shown in Fig. 9(d). In the first part of this study, the mass ratio of mica and MSP were kept fixed at 1:1 with varying amounts of NaCl, whereas in the second part, the mass ratio of mica and NaCl were fixed at 1:1 with varying amounts of MSP. The results show that without the addition of NaCl, extraction of potassium is negligible, thus indicating the necessity of Cl^- [60]. A continuous rise in extraction value occurred as the addition of NaCl increased. Moreover, the use of NaCl as the only roasting additive can extract 56% of potassium, and this value reached 93% upon subsequent addition of MSP. Variation in the amounts of NaCl and MSP has shown almost the same results of extraction (around 84%) at nearly 50wt% of additive addition with respect to mica weight. From Fig. 9(d), the optimum conditions of extraction when comparing all the three curves can be predicted as follows: the mass ratio (mica : MSP : NaCl) of 1:1:0.75, roasting temperature of 900°C, roasting time of 30 min, and particle size of ~100 μm.

(5) Water leaching.

The roasted mass generated in the high-temperature furnace was cooled to room temperature and ground to fine powder before water leaching. Various leaching parameters, including temperature, time, the weight percentage of solid, and stirring speed, exhibited negligible effects on the leaching behavior of the roasted mass. This finding is due to the highly water-soluble nature of sylvite (KCl) formed during roasting.

(6) Product recovery.

The roasted product obtained (900°C temperature, 1:1:0.75 mass ratio of mica : MSP : NaCl, 30 min roasting time) was water-leached with 40wt% solid at room temperature for 15 min using a mechanical stirrer. As the roasted product contained sylvite and halite, it was easily dissolved in the water, whereas the water-insoluble phases remained in the residual part. Then, the filtrate was evaporated at 80–90°C until the formation of white shining crystals followed by cooling at room temperature. Chemical analysis revealed that the dried salt was composed of KCl (24.9wt%) and NaCl (74.7wt%). Further characterization studies by XRD and SEM also confirmed the presence of these two phases as shown in Figs. 10 and 11, respectively. The major chemical composition of the residue is presented in Table 2.

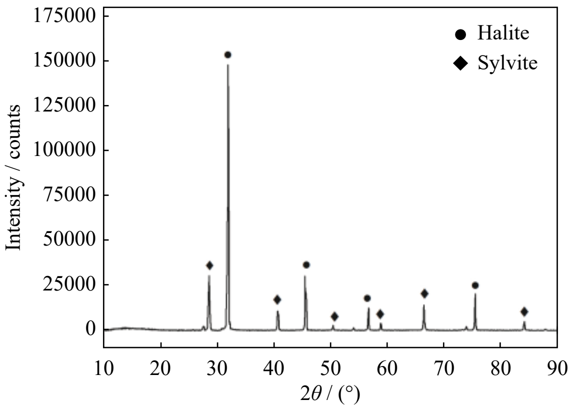


Fig. 10. XRD pattern of the crystallized salt after roasting–leaching experiments.

4. Mechanism of extraction

The mechanism of the extraction process has been established using the XRD and SEM studies of the roasted product and the corresponding roast–leached residue produced under the optimum conditions (the mass ratio of mica : MSP : NaCl of 1:1:0.75, roasting temperature of 900°C, roasting time of 30 min, and particle size of ~100 μm). The extraction mechanism can be discussed in two ways:

(1) Mechanism I.

The heating of mica scrap fine powder at temperatures ranging from 600 to 900°C resulted in dehydroxylation followed by decomposition of the sample (Eqs. (1)–(3)). The comparison of the XRD peaks of feed and calcined mica samples indicated that the peak intensity of calcined mica sample has been lowered, and the numbers of small peaks become less, indicating the physical distortions of AlO_6 octahedron and SiO_4 tetrahedron as reported in literatures [65–66]. The appearance of broad peaks may be due to the generation of small-sized mica particles or conversion of crystalline phases to amorphous phases [67]. The SEM images also showed the breaking of flaky mica structure into finer fractions, indicating a distinct differentiation between the feed mica and calcined mica sample. The XRD and SEM images are presented in Figs. 12 and 13, respectively, for comparison.

$$K_2O\cdot 3Al_2O_3\cdot 6SiO_2\cdot 2H_2O = K_2O\cdot 3Al_2O_3\cdot 6SiO_2 + 2H_2O\uparrow \tag{1}$$

$$K_2O\cdot 3Al_2O_3\cdot 6SiO_2 = K_2O + 3Al_2O_3 + 6SiO_2 \tag{2}$$

$$Al_2O_3 + SiO_2 = Al_2SiO_5 \tag{3}$$

The change in the physical property of mica due to heating possibly generated micro-cracks with loose binding of K, which is different from the untreated feed sample. K present

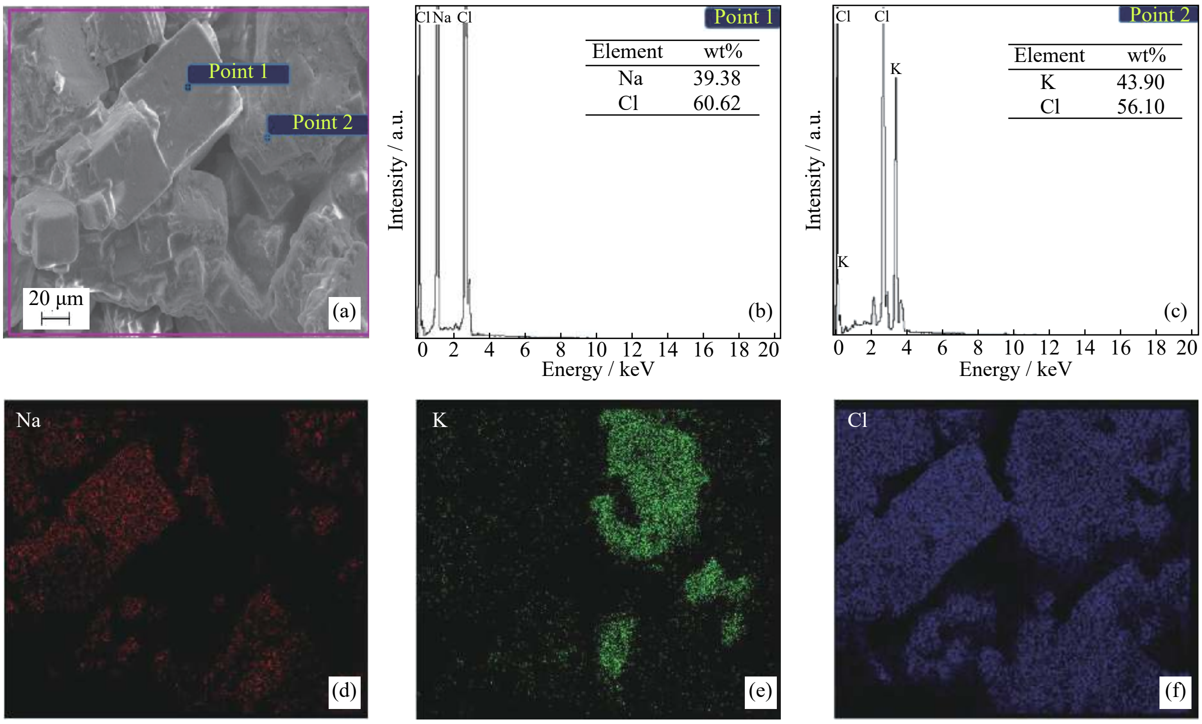


Fig. 11. (a) SEM image, (b, c) EDS analyses, and (d–f) elemental mapping images of the crystallized salt.

Table 2. Major chemical composition of the roast–leached residue

Composition	Content /wt%
SiO_2	36.75
Al_2O_3	18.30
Fe_2O_3	2.96
K_2O	0.42
Na_2O	0.26
CaO	21.34
MgO	14.90
TiO_2	0.10

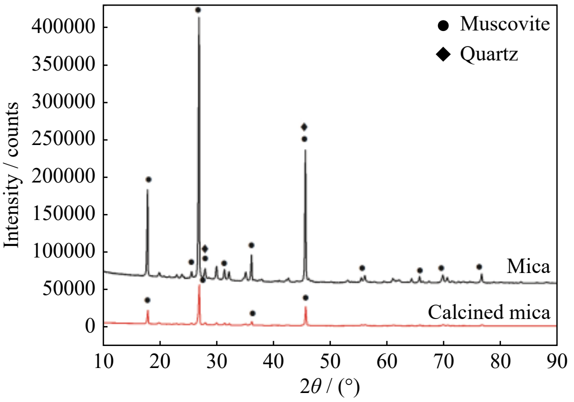


Fig. 12. Comparison of XRD patterns of feed mica and calcined mica samples.

in mica was easily converted into its chloride form (as KCl) when treated with external chloridizing roasting additives at the same calcination conditions.

The decomposition of dolomite occurred within the temperature range of 687–916°C [68]; dolomite combined with molten NaCl (melting point: 801°C) to produce $MgCl_2$ and $CaCl_2$ along with Na_2CO_3 and Na_2O as per the reactions presented in Eqs. (4)–(6). However, the presence of NaCl further lowered the decomposition temperature of dolomite to 20–100°C, facilitating the reaction process [69].

Early stage of heating (below 801°C):

$$CaCO_3 \cdot MgCO_3 = CaCO_3 + MgO + CO_2 \uparrow \tag{4}$$

Heating at above 801°C:

$$CaCO_3 + 2NaCl = CaCl_2 + Na_2CO_3 \tag{5}$$

$$MgO + 2NaCl = MgCl_2 + Na_2O \tag{6}$$

The $CaCl_2$/$MgCl_2$ formed during the initial stages of heating played the most important role in the extraction of potassium. The reaction between $CaCl_2$ and $MgCl_2$ with SiO_2 (generated as per Eq. (2)) produced two new mineral phases, namely, wollastonite ($CaSiO_3$) and enstatite ($MgSiO_3$), which were confirmed in the XRD study of roasted and water-leached products. The appearance of triclinic (wollastonite) and orthorhombic (enstatite) crystal structures in the SEM images of both products also substantiated the formation of these phases. The XRD and SEM images are presented in Figs. 14 and 15, respectively. The appearance of sylvite (KCl) in the roasted product and its disappearance in the water-leached residue were observed in the XRD and SEM studies along with other insoluble phases, including kyanite (Al_2SiO_5) of acicular bladed structure. The possible reactions are presented in two sets of reactions (Eqs. (7) and (8)).

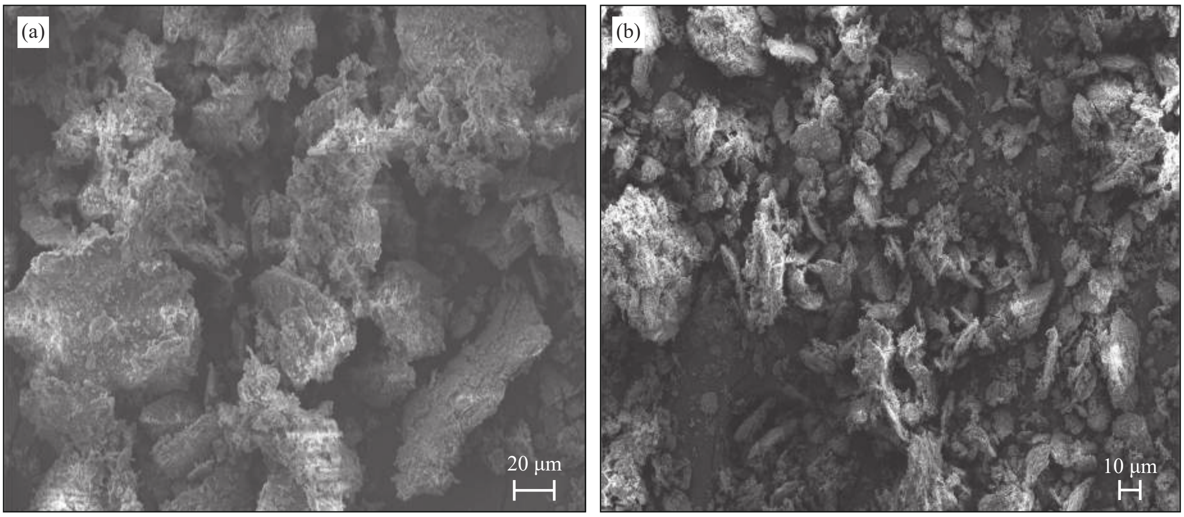


Fig. 13. SEM micrographs of (a) feed mica and (b) calcined mica samples.

$$\left\{\begin{array}{l} CaCl_2 + SiO_2 + 1/2O_2 = CaSiO_3 + Cl_2 \\ CaCl_2 + SiO_2 + H_2O = CaSiO_3 + 2HCl \\ 2HCl + K_2O = 2KCl + H_2O \end{array}\right. \tag{7}$$

$$\left\{\begin{array}{l} MgCl_2 + SiO_2 + 1/2O_2 = MgSiO_3 + Cl_2 \\ MgCl_2 + SiO_2 + H_2O = MgSiO_3 + 2HCl \\ 2HCl + K_2O = 2KCl + H_2O \end{array}\right. \tag{8}$$

(2) Mechanism II.

Muscovite ($KAl_3Si_3O_{10}(OH)_2$) also possibly reacted directly with the quartz present in the mica and MSP samples at high temperature to form K-feldspar ($KAlSi_3O_8$) and aluminum silicate (Al_2SiO_5) with the loss of all the adsorbed moisture [70–71]. Then, $CaCl_2$ (formed by reaction of MSP and NaCl) reacted with K-feldspar to produce anorthite ($CaAl_2Si_2O_8$), which further dissociated in the next step to form wollastonite ($CaSiO_3$) and kyanite (Al_2SiO_5) [52,56–57,72]. The appearance of different possible phases was verified by the XRD and SEM micrographs of the roasted and roast–leached residue as presented in Figs. 14 and 15, respectively. The possible reactions are presented in a set of reactions (Eq. (9)).

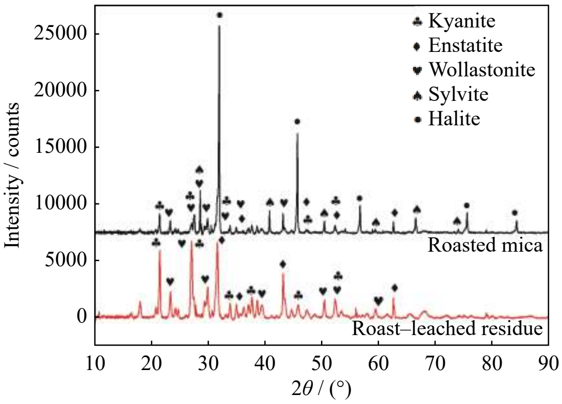


Fig. 14. XRD patterns of roasted mica and roast–leached residue of sample.

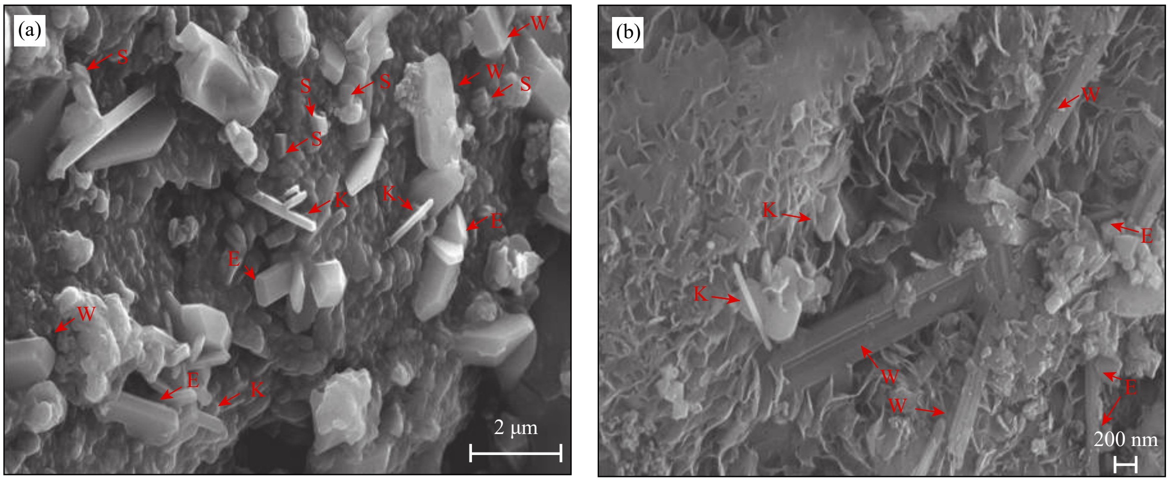


Fig. 15. Scanning electron micrographs of (a) roasted product and (b) water-leached residue showing the formation of different mineral phases under the optimum conditions including the mass ratio (mica : MSP : NaCl) of 1:1:0.75, roasting temperature of 900°C, roasting time of 30 min, and particle size of ~100 μm (S—Sylvite; K—Kyanite; E—Enstatite; W—Wollastonite).

$$\begin{cases} \mathrm{KAl_3Si_3O_{10}(OH)_2 + SiO_2 = KAlSi_3O_8 + Al_2SiO_5 + H_2O} \\ \mathrm{2KAlSi_3O_8 + CaCl_2 = CaAl_2Si_2O_8 + 4SiO_2 + 2KCl} \\ \mathrm{CaAl_2Si_2O_8 = CaSiO_3 + Al_2SiO_5} \end{cases} \tag{9}$$

5. Conclusion

The generation of huge amount of solid waste (MSP) during marble processing creates various environmental problems, such as the reduction of soil fertility, depletion of water permeability, increase in suspended particulate matters in air, and numerous health-related issues. Thus, the generated MSP must be reused for value addition rather than land refilling. In this connection, the MSP wastes were used to recover potash from a low-cost mica scrap waste using chlorination-roasting method. Preliminary studies using H_2SO_4 acid leaching indicated a maximum recovery of 22% potassium from mica scrap using ~100 μm particle size, 600 r/min stirring speed, 75°C leaching temperature, and 90 min processing time. Meanwhile, the roasting–leaching experiments using MSP and NaCl resulted in a recovery of almost 93% potash from the mica scrap under optimum conditions, including the mass ratio (mica : MSP : NaCl) of 1:1:0.75, roasting temperature of 900°C, roasting time of 30 min, and particle size of ~100 μm. A substantial increase in potash recovery occurred when the temperature rose from 800 to 900°C, while the further increase in temperature resulted in decreased recovery value owing to the formation of water-insoluble potassium phases including leucite ($KAlSi_2O_6$) or volatilization of KCl. The formation of different water-soluble and insoluble phases, such as sylvite, wollastonite, halite, enstatite, and kyanite, was evident from the XRD analyses and SEM micrographs of the roasted and roast–leached products. The present report discusses an encouraging process to recover potash for fertilizer application utilizing two cheap industrial waste materials.

Acknowledgements

The authors are thankful to the Director of CSIR-IMMT, Bhubaneswar, India, for his kind permission to publish this paper. The authors also wish to gratefully acknowledge Mr. Sapan K. Kandi and Mr. Debadatta Sahoo for useful discussions during the manuscript preparation.

References

[1] H.A. El-Sayed, A.B. Farag, A.M. Kandeel, A.A. Younes, and M.M. Yousef, Characteristics of the marble processing powder waste at Shaq El-Thoaban industrial area, Egypt, and its suitability for cement manufacture, *HBRC J.*, 14(2018), No. 2, p. 171.

[2] R.S. Kori, P. Jagan, and S.K. Meena, *Guidlines for Management and Handling of Marble Slurry Generated from Marble Processing Plants in Rajasthan*, Central Pollution Control Board, Bhopal [2019-07-09]. https://www.scribd.com/document/410211989/Draft-guidelines-for-M-H-of-Marble-slurry-generated-from-marble-processing-plants-in-Rajasthan-pdf

[3] K. Shreyas, Impact of marble dust on cement concrete, *Int. J. Sci. Technol. Eng.*, 4(2017), No. 6, p. 6.

[4] M. Wijayasundara, P. Mendis, and R.H. Crawford, Net incremental indirect external benefit of manufacturing recycled aggregate concrete, *Waste Manage.*, 78(2018), p. 279.

[5] *The Countries with the Largest Marble Exports in 2017* [2018-12-31]. https://stonenews.eu/countries-largest-marble-exports-2017/

[6] Indian Bureau of Mines, *Indian Minerals Yearbook 2015* (*Part-III: Mineral Reviews*), 54th ed., Government of India, Ministry of Mines, Indian Bureau of Mines [2016-11-20]. http://ibm.nic.in/writereaddata/files/11232016170046IMYB2015_Marble_23112016_Adv.pdf

[7] M. Yavuz Çelik and E. Sabah, Geological and technical characterization of Iscehisar (Afyon-Turkey) marble deposits and the impact of marble waste on environmental pollution, *J. Environ. Manage.*, 87(2008), No. 1, p. 106.

[8] A. Pappu, M. Saxena, and S.R. Asolekar, Solid wastes generation in India and their recycling potential in building materials, *Build. Environ.*, 42(2007), No. 6, p. 2311.

[9] M.A. Montero, M.M. Jordán, M.S. Hernández-Crespo, and T. Sanfeliu, The use of sewage sludge and marble residues in the manufacture of ceramic tile bodies, *Appl. Clay Sci.*, 46(2009), No. 4, p. 404.

[10] E.K. Shirazi, Reusing of stone waste in various industrial activities, [in] *2011 2nd International Conference on Environmental Science and Development*, Singapore, 2011, p. 217.

[11] G. Rego, C. Martínez, A. Quero, T.P. Blanco, and J.M.F. Borque, Efectos del polvo inhalado en los trabajadores de la industria de pizarras, *Med. Clínica*, 116(2001), No. 8, p. 290.

[12] G. Angotzi, L. Bramanti, D. Tavarini, M. Gragnani, L. Cassidoro, L. Moriconi, P. Saccardi, I. Pinto, N. Stacchini, and M. Bovenzi, World at work: Marble quarrying in Tuscany, *Occup. Environ. Med.*, 62(2005), No. 6, p. 417.

[13] M. El-Gammal, M.S. Ibrahim, E.A. Badr, S.A. Asker, and M. El-Galad, Health risk assessment of marble dust at marble workshops, *Nat. Sci.*, 9(2011), No. 11, p. 144.

[14] MSME-Development Institute, *Status Report on Commercial Utilization of Marble Slurry in Rajasthan*, Government of India, Ministry of Micro, Small & Medium Enterprises, Jaipur [2019-07-07]. https://www.pdffiller.com/jsfiller-desk12/?projectId=492304325#df10e63ea090407894eb1d43d40fb651

[15] N. Careddu, G. Siotto, R. Siotto, and C. Tilocca, From landfill to water, land and life: The creation of the centre for stone materials aimed at secondary processing, *Resour. Policy*, 38(2013), No. 3, p. 258.

[16] F.J. Aukour, Incorporation of marble sludge in industrial building eco-blocks or cement bricks formulation, *Jordan J. Civ. Eng.*, 3(2009), No. 1, p. 58.

[17] S.D. Kore and A.K. Vyas, Impact of marble waste as coarse aggregate on properties of lean cement concrete, *Case Stud. Constr. Mater.*, 4(2016), p. 85.

[18] F. Faleschini, M.A. Zanini, C. Pellegrino, and S. Pasinato, Sustainable management and supply of natural and recycled aggregates in a medium-size integrated plant, *Waste Manage.*, 49(2016), p. 146.

[19] E. Tugrul Tunc, Recycling of marble waste: A review based on strength of concrete containing marble waste, *J. Environ. Manage.*, 231(2019), p. 86.

[20] A. Rana, P. Kalla, and L.J. Csetenyi, Sustainable use of marble

slurry in concrete, *J. Cleaner Prod.*, 94(2015), p. 304.

[21] R. Rodrigues, J. de Brito, and M. Sardinha, Mechanical properties of structural concrete containing very fine aggregates from marble cutting sludge, *Constr. Build. Mater.*, 77(2015), p. 349.

[22] M. Singh, A. Srivastava, and D. Bhunia, An investigation on effect of partial replacement of cement by waste marble slurry, *Constr. Build. Mater.*, 134(2017), p. 471.

[23] K. Vardhan, R. Siddique, and S. Goyal, Strength, permeation and micro-structural characteristics of concrete incorporating waste marble, *Constr. Build. Mater.*, 203(2019), p. 45.

[24] H. Al-Hamaiedh, Reuse of marble sludge slime in ceramic industry, *Jordan J. Civ. Eng.*, 4(2010), No. 3, p. 264.

[25] J. Carneiro, D.M. Tobaldi, M.N. Capela, R.M. Novais, M.P. Seabra, and J.A. Labrincha, Synthesis of ceramic pigments from industrial wastes: Red mud and electroplating sludge, *Waste Manage.*, 80(2018), p. 371.

[26] S.K. Amin, E.M. Abdel Hamid, S.A. El-Sherbiny, H.A. Sibak, and M.F. Abadir, The use of sewage sludge in the production of ceramic floor tiles, *HBRC J.*, 14(2018), No. 3, p. 309.

[27] G. Tozsin, Inhibition of acid mine drainage and immobilization of heavy metals from copper flotation tailings using a marble cutting waste, *Int. J. Miner. Metall. Mater.*, 23(2016), No. 1, p. 1.

[28] S. Elabbas, L. Mandi, F. Berrekhis, M.N. Pons, J.P. Leclerc, and N. Ouazzani, Removal of Cr(III) from chrome tanning wastewater by adsorption using two natural carbonaceous materials: Eggshell and powdered marble, *J. Environ. Manage.*, 166(2016), p. 589.

[29] S.E. Ghazy and A.H.M. Gad, Lead separation by sorption onto powdered marble waste, *Arabian J. Chem.*, 7(2014), No. 3, p. 277.

[30] M.R. Lasheen, A.M. Ashmawy, H.S. Ibrahim, and S.M. Abdel Moniem, Immobilization technologies for the management of hazardous industrial waste using granite waste (case study), *Korean J. Chem. Eng.*, 33(2016), p. 914.

[31] N. Bilgin, H.A. Yeprem, S. Arslan, A. Bilgin, E. Günay, and M. Marşoglu, Use of waste marble powder in brick industry, *Constr. Build. Mater.*, 29(2012), p. 449.

[32] G. Tozsin, A.I. Arol, T. Oztas, and E. Kalkan, Using marble wastes as a soil amendment for acidic soil neutralization, *J. Environ. Manage.*, 133(2014), p. 374.

[33] M. Dasgupta, S.D. Gupta, R. Mukhopadhyay, and A. Bandyopadhyay, Derivation of a new compounding ingredient for rubber from waste marble powder and study on its suitability in an inner liner compound of tubeless tyres, *Prog. Rubber Plast. Recycl. Technol.*, 32(2016), No. 2, p. 55.

[34] G. Marras and N. Careddu, Sustainable reuse of marble sludge in tyre mixtures, *Resour. Policy*, 59(2018), p. 77.

[35] T. Thenepalli, A.Y. Jun, C. Han, C. Ramakrishna, and J.W. Ahn, A strategy of precipitated calcium carbonate ($CaCO_3$) fillers for enhancing the mechanical properties of polypropylene polymers, *Korean J. Chem. Eng.*, 32(2015), No. 6, p. 1009.

[36] T. Chaize, *Potash* [2010-03-14]. http://www.dani2989.com/gold/potashgb.htm

[37] B. Mukherjee, *Uses of Potassium* [2019-07-05]. https://biologywise.com/potassium-uses

[38] D.A.C. Manning, Mineral sources of potassium for plant nutrition. A review, *Agron. Sustainable Dev.*, 30(2010), p. 281.

[39] P. Heffer and M. Prud'homme, Short-term fertilizer outlook 2015 – 2016, [in] *International Fertilizer Industry Association Strategic Forum*, Paris, 2015.

[40] S.M. Jasinski, Mica, [in] *Mineral Commodity Summaries* 2018, U.S. Geological Survey (USGS), p. 108 [2019-07-10]. https://s3-us-west-2.amazonaws.com/prd-wret/assets/palladium/production/mineral-pubs/mcs/mcs2018.pdf

[41] Indian Bureau of Mines, Mineral reviews, [in] *Indian Minerals Yearbook* 2018, Vol. III [2019-06-22]. https://ibm.gov.in/index.php?c=pages&mindex&id1347

[42] W.X. Liu, X.S. Xu, X.H. Wu, Q.Y. Yang, Y.M. Luo, and P. Christie, Decomposition of silicate minerals by Bacillus mucilaginosus in liquid culture, *Environ. Geochem. Health*, 28(2006), p. 133.

[43] Z. Luo, J. Yang, H.W. Ma, M.T. Liu, and X. Ma, Recovery of magnesium and potassium from biotite by sulfuric acid leaching and alkali precipitation with ammonia, *Hydrometallurgy*, 157(2015), p. 188.

[44] T.M. Bhatti, J.M. Bigham, A. Vuorinen, and O.H. Tuovinen, Weathering of phlogopite in simulated bioleaching solutions, *Int. J. Miner. Process.*, 98(2011), No. 1-2, p. 30.

[45] C. Varadachari, An investigation on the reaction of phosphoric acid with mica at elevated temperatures, *Ind. Eng. Chem. Res.*, 31(1992), No. 1, p. 357.

[46] N.N. Xue, Y.M. Zhang, T. Liu, J. Huang and Q.S. Zhang, Effects of hydration and hardening of calcium sulfate on muscovite dissolution during pressure acid leaching of black shale, *J. Cleaner Prod.*, 149(2017), p. 989.

[47] C. Varadachari, Potash fertilizer from biotite, *Ind. Eng. Chem. Res.*, 36(1997), No. 11, p. 4768.

[48] P. Meng, Z.L. Huang, Z.Q. Li, M.W. Hu, C.L. Chen, and R. Chi, Conditions and mechanism for extracting potassium from muscovite in potassium-bearing shale by the barium ion-exchange method, *Int. J. Miner. Process.*, 142(2015), p. 107.

[49] A. Kumar, Y.P. Singh, G. Pradhan, and N. Dhawan, Utilization of mica for potassium recovery, *Mater. Today*: *Proc.*, 5(2018), No. 9, p. 17030.

[50] A.A.S. da Silva, J.A. Sampaio, A.B. da Luz, S.C.A. França, and C.M. Ronconi, Modeling controlled potassium release from phlogopite in solution: Exploring the viability of using crushed phlogopitite rock as an alternative potassium source in Brazilian soil, *J. Braz. Chem. Soc.*, 24(2013), No. 8, p. 1366.

[51] S.K. Jena, N. Dhawan, D.S. Rao, P.K. Misra, B.K. Mishra, and B. Das, Studies on extraction of potassium values from nepheline syenite, *Int. J. Miner. Process.*, 133(2014), p. 13.

[52] S.K. Jena, N. Dash, and S.S. Rath, Effective utilization of lime mud for the recovery of potash from mica scraps, *J. Cleaner Prod.*, 231(2019), p. 64.

[53] S. Shekhar, D. Mishra, A. Agarwal, and K.K. Sahu, Physico–chemical treatment of glauconitic sandstone to recover potash and magnetite, *J. Cleaner Prod.*, 147(2017), p. 681.

[54] S.K. Jena, P.K. Misra, and B. Das, Studies on extraction of potassium from feldspar by roast–leach method using phosphogypsum and sodium chloride, *Miner. Process. Extr. Metall. Rev.*, 37(2016), No. 5, p. 323.

[55] M.T. Serdengeçti, H. Baştürkcü, F. Burat, and M.O. Kangal, The correlation of roasting conditions in selective potassium extraction from K-feldspar ore, *Minerals*, 9(2019), No. 2, p. 109.

[56] B. Yuan, C. Li, B. Liang, L. Lü, H.R. Yue, H.Y. Sheng, L.P. Ye, and H.P. Xie, Extraction of potassium from K-feldspar via the $CaCl_2$ calcination route, *Chin. J. Chem. Eng.*, 23(2015), No. 9, p. 1557.

[57] S.K. Jena, N. Dash, A.K. Samal, and P.K. Misra, Competency of chlorination roasting coupled water leaching process for potash recovery from K-feldspar: Mechanism and kinetics aspects, *Korean J. Chem. Eng.*, 36(2019), No. 12, p. 2060.

[58] S.K. Jena, N. Dhawan, S.S. Rath, D.S. Rao, and B. Das, Investigation of microwave roasting for potash extraction from neph-

eline syenite, *Sep. Purif. Technol.*, 161(2016), p. 104.

[59] A.K. Mazumder, T. Sharma, and T.C. Rao, Extraction of potassium from glauconitic sandstone by the roast–leach method, *Int. J. Miner. Process.*, 38(1993), No. 1-2, p. 111.

[60] L.S. Darken and R.W. Gurry, *Physical Chemistry of Metals*, CBS Publishers and Distributers, Delhi, 1987.

[61] L. Li, S.M. Lei, Y.Y. Liu, and H.H. Luo, Extraction and reaction mechanism of potassium from associated phosphorus and potassium ore, *J. Wuhan Univ. Technol. -Mater. Sci. Ed.*, 31 (2016), No. 6, p. 1255.

[62] M. Kumanan, G. Sathya, V. Nandakumar, and L.J. Berchmans, Extraction of potash from k-feldspar mineral by acid and molten salt leaching processes, *IASET Int. J. Metall. Mater. Chem. Eng.*, 7(2016), p. 1.

[63] W.O. Santos, E.M. Mattiello, A.A. Pacheco, L. Vergutz, L.F. da Silva Souza-Filho, and D.B. Abdala, Thermal treatment of a potassium-rich metamorphic rock in formation of soluble K forms, *Int. J. Miner. Process.*, 159(2017), p. 16.

[64] E.M.M. Ewais, Y.M.Z. Ahmed, A.A.M. El-Amir, and H. El-Didamony, Cement kiln dust/rice husk ash as a low temperature route for wollastonite processing, *J. Silic. Based Compos. Mater.*, 66(2014), No. 3, p. 69.

[65] M. Lin, Z.Y. Pei, and S.M. Lei, Mineralogy and processing of hydrothermal vein quartz from Hengche, Hubei Province (China), *Minerals*, 7(2017), No. 9, p. 161.

[66] Z.Y. Pei, M. Lin, Y.Y. Liu, and S.M. Lei, Dissolution behaviors of trace muscovite during pressure leaching of hydrothermal vein quartz using H_2SO_4 and NH_4Cl as leaching agents, *Minerals*, 8(2018), No. 2, p. 60.

[67] O. Palchik, J.J. Zhu, and A. Gedanken, Microwave assisted preparation of binary oxide nanoparticles, *J. Mater. Chem.*, 10(2000), No. 5, p. 1251.

[68] M. Olszak-Humienik and M. Jablonski, Thermal behavior of natural dolomite, *J. Therm. Anal. Calorim.*, 119(2015), No. 3, p. 2239.

[69] T.N. Chernykh, A.V. Nosov, and L.Y. Kramar, Dolomite magnesium oxychloride cement properties control method during its production, *IOP Conf. Ser: Mater. Sci. Eng.*, 71(2015), art. No. 012045.

[70] H.W. Day, The high temperature stability of muscovite plus quartz, *Am. Mineral.*, 58(1973), p. 255.

[71] J.A. Schramke, D.M. Kerrick, and A.C. Lasaga, The reaction muscovite + quartz = andalusite + K-feldspar + quartz. Part I. Growth kinetics and mechanism, *Am. J. Sci.*, 287(1987), No. 6, p. 517.

[72] L. Shi and H.J. Luo, Preparation of soil nutrient amendment using white mud produced in ammonia–soda process and its environmental assessment, *Trans. Nonferrous Met. Soc.*, 19 (2009), No. 5, p. 1383.