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EXTRACTION OF POTASH FROM K-FELDSPAR MINERAL BY ACID AND MOLTEN SALT LEACHING PROCESSES

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ABSTRACT

Potassium is one of the three essential nutrients for the plant growth. It will be supplied in the form of fertilizer with other nutrients such as N, P and K. Feldspars and glauconite minerals are the prominent sources of potash, which contains a good amount of potassium with other associated elements. Feldspar exists in different phases such as microcline, albite and anorthosilicate. The feldspar has an average chemical composition of 62% SiO_2, 26% Al_2O_3, 8% K_2O, 3% Na_2O and 1% CaO as the main constituents. In order to extract potassium, chemical leachants such as HCl, H_2SO_4 and HNO_3 were tried with different concentrations. The recovery of potash is found to be 35% in the case of H_2SO_4 medium. In hydrothermal process, maximum recovery of potash is attained as 71% in H_2SO_4 medium by repeated cycles of leaching. Molten salt extraction was performed at 850°C using $MgCl_2$ and $CaCl_2$ as molten leaching media. The duration of digestion was about 8 hours. After the digestion in the molten melt, the K and Na were leached out by treating with water and acid independently. The product was isolated from the molten melt and analyzed for its concentration using Atomic Absorption Spectroscopy (AAS), X-ray Diffraction technique (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). In the water medium, more than 90% of potash can be recovered as water soluble K using $CaCl_2$ as the flux. In the case of acid medium, same concentration of potash can be extracted along with the dissolution of Ca as $CaCl_2$. While in the case of $MgCl_2$ as the flux, it is noticed that only 35% of K can be recovered. The results indicate that maximum recovery of potash is achieved when the feldspar to flux ratio (Feldspar: $CaCl_2$) is 1:8 to1:10. The results of the above investigation have been presented in this paper.

KEYWORDS: Feldspar, Potash Leaching, X- Ray Diffraction, Hydrometallurgical Route, Molten Salt

INTRODUCTION

Potassic fertilizers are most widely used in agricultural activities for the production of food grains. Potassium is one of the three essential elements namely nitrogen, phosphorus and potassium (N, P, K) for the growth of flora. Potassic fertilizer enhances the food production in Indian agricultural sector [1]. It is estimated that about 5.5 million tons of ores as the source of potash from various minerals such as evaporated deposits, brains, glauconitic etc. [1,2]. About 95% of the potash in worldwide is used in agricultural processes and the rest is utilized for several industrial applications such as glass making, ceramics, plastics, cement and catalysis [3]. The demand for potassic fertilizer is progressively increasing and the source of water soluble potash is limited. The insoluble potash reserves have been widely distributed across the world. Even though potassium bearing minerals are mostly available in the earth's crust, but only water soluble minerals are significant interests. Sylvine (KCl) is most important source of water soluble potash. Sylvinite is the mixture of sylvine and halite in varying proportions which are identified in many geological locations of the world [4]. Feldspar is the most abundant rock mineral in nature and accounts about more than 60% of the earth's crust [5]. The feldspar comprises a group of minerals consisting of aluminum silicate with varying concentration of potassium in the Microcline: $K_2OAl_2O_3.6SiO_2$, Albite Na_2O $Al_2O_3.6SiO_2$ and Anorthrotite $CaOAl_2O_3.6SiO_2$, which contains about 5- 12% of potassium as K_2O [6]. In India, there are not much viable technologies for the production of potash from feldspar minerals such as Sylvite, Kainite, Carnalities, and Polyhalite etc. Hence, our country is importing a large quantity of potash from foreign countries for our agricultural and industrial activities. It is estimated that about 3.6 million tons of potash is required for our use and about 2.4 million tons of potash per annum is solely met by import only [7]. Many methods have been reported on the extraction of potash which is summarized below. It has been reported that the roast leaching method is one of the potential routes for the extraction of potash from glauconitic sand stone with the presence of $CaCl_2$ [8]. An empirical model on the chloredizing roasting in aqueous media for the extraction of potash has been elucidated [9]. The dissolution kinetics of K from glauconitic sand stone in diluted HCl, HNO_3 and H_2SO_4 at different temperatures has been studied [10]. Chemical with biological methods and electro ultra filtration desorption studies have been performed using indigenous glauconitic sandstone [11]. A process has been reported on the extraction of potassium from feldspar mineral using a mixture of magnesium sulfate and calcium carbonate as the molten media [12]. It has been reported that calcium chloride hexa hydrate can be used as the additive to treat K feldspar forming calcium carbonate and soluble potassium as the products [13]. The effects of calcium chloride to sodium chloride, roasting temperature, duration of roasting and the particle size have been studied on the extraction of K from feldspar mineral [14]. Potassium has been recovered as potassium sulfate using potash feldspar and coke as the reducing agent [15]. Thermal decomposition of feldspar with the addition of $CaSO_4$ and CaO has been reported [16]. Extraction of potassium from nepheline syenite by acid leaching and roast-leach methods has been discussed [17]. The extraction of potash from Thailand soils by ionic exchangeable methods has been elaborately studied [18]. In this paper, we are reporting the various methodologies especially hydro and molten salt extraction techniques adopted for the extraction of potash from Indian minerals.

CHEMICAL AND MINERALOGICAL COMPOSITION

A representative sample of Indian feldspar was received from Sun Minerals, Rajasthan, India. The mineral was crushed and sieved through 220 # to obtain a uniform size powder. The feldspar has an average chemical composition of 62% SiO_2, 26% Al_2O_3, 8% K_2O, 3% Na_2O and 1% CaO as the main constituents. Most of the feldspar minerals contain microcline ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), anorthite ($CaAl_2Si_2O_8$), aorthoclase (NaK) $AlSi_3O_8$, sanidine (KNa) $AlSi_3O_8$, labradorite (Ca, Na) Al (Al, Si) Si_2O_8 etc. From the XRD data, it has been identified that the Indian feldspar contains potassium sodium calcium aluminum silicate in anorthic crystal system. The elemental composition and the morphological features of the powder were examined using energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM). The concentration of K and the other constituents of the raw feldspar in the leached solution was assessed using atomic absorption spectroscopy (AAS).

MATERIALS AND METHODS

Acid dissolution is one of most important methods to extract potash from various minerals like glauconitic sandstone, sea bittern, nepheline syenite etc. The chemical and mineralogical composition of the Indian feldspar is given in Table 1. Leachants such as AR grade HCl, H_2SO_4 and HNO_3 acids were used. The reagents procured from Analytical Performance India limited, Gujarat, India. Various concentrations of acids were employed for our investigation. The solid to liquid ratio was kept as 1:30. The suspension containing feldspar powder was stirred at 1000 rpm using a mechanical stirrer and the digestion was performed at room temperature and 90 °C. The duration of digestion was 8 h. The experiments were conducted with roasted and un- roasted samples. The roasting was done at 850 °C for a period of 8 h. The sludge was repeatedly washed with water in order to achieve maximum recovery of K from feldspar. Many of the ores like galena, malachite and pentlandite are being treated by pressure temperature leaching process. Similar technique has been adopted by various authors to leach out K from feldspar mineral using different acids such as HCl, H_2SO_4, HNO_3. For the above purpose, Teflon lined hydrothermal reactor was used. The pressure leaching was performed at 120 °C for 8 h by keeping the reactor in an electrical resistance furnace. After treating for a pre determined period, the solution was decanted from the reactor and assessed for the concentration of K. The molten salt extraction is one of the novel techniques used to extract K from feldspar mineral. Molten salts namely $CaCl_2$ and $MgCl_2$ have been used (Fisher Scientific) for the trapping of K from the feldspar mineral. The ratio of feldspar to flux is varied from 1:1 to 1:10 (Feldspar: $CaCl_2$) and (Feldspar: $MgCl_2$). After the digestion process, the contents are removed from the alumina crucible and leached with water and dilute HCl independently. Finally the concentration of K was assessed by Atomic Absorption Spectroscopy.

RESULTS AND DISCUSSIONS

Dissolution of K in Acid Media

The results of the above investigation are presented in the following section. In the case of acid leaching, the concentration of K is depicted in graph (**Figure 3**). From the graph, it is noted that the extraction of K can be done to a maximum value of 13.1% using 10 M H_2SO_4 as the medium at room temperature. In the case of other media, such as HCl and HNO_3 the leachability is found to be low ranging between 9.2% to 6.2% respectively. From the above data, it is noticed that HNO_3 is found to be a weak leachant than the other acid media namely HCl and H_2SO_4. It is also observed that the concentration of K can be obtained up to18.1% by treating feldspar at 90 °C in H_2SO_4 medium. From the above data, it has been concluded that the leachability of K is found to be low at 90 °C. On roasted samples, the leachablity of K is found to be only 21% in 10 M H_2SO_4 in a single leaching process. On multiple leaching of the sludge (i.e) four times, where the recovery of K is achieved up to 51% in 7 M H_2SO_4 medium. Similar results have been noticed in the case of 7M H_2SO_4 medium. Hence, further studies were performed only in 7M H_2SO_4 medium and the results are presented.

Dissolution of K by Hydrothermal Process

Roasting was performed at 850 °C and subsequently treated by hydrothermally at 120 °C in various acid media such as HCl, H_2SO_4 and HNO_3. The digested liquid and sludge treated solution were assessed in order to identify the concentration of K released from feldspar mineral. From the above process, we have concluding that K can be leached out up to 71% in 7 M H_2SO_4 medium. The maximum leachability in the above medium may be due to the energy of crystal lattice reduced to single oxygen atom as reported by Guo et al. On repeated washing of sludge using hydrothermal process, maximum K can be recovered which may be observed from the XRD spectrum **Figure 1a.** The concentration of K on repeated leaching with different acid media is presented in the graph (4). From the graph, it has been noticed that the maximum recovery of K can be achieved in the first cycle of dissolution reaction rather the subsequent leaching process.

Dissolution of K in Molten Melts

Figure 5 shows the graphical representation of K leached using $CaCl_2$ and $MgCl_2$ as the molten leaching medium. It has been noticed that about 90% of K can be recovered, when the feldspar to molten medium is in the ratio of 1:8 to 1:10 (Feldspar**:** $CaCl_2$). In $MgCl_2$ molten melt, the recovery is found to be only 44%. The maximum recovery of K in $CaCl_2$ melt may be due to the interaction between K^+ and Ca^{2+} ions in the melt. Thermodynamically this reaction is most favored where K and Mg is in a chaos state. From the above studies, it has been concluded that the molten salt extraction of K using $CaCl_2$ melt is found to be the more promising route. The extracted K in the form of solution can directly be used as a liquid fertilizer in agricultural sector.

X-Ray Diffraction (XRD)

Figure 1 Shows the XRD spectrum of raw feldspar and leached potash residues by hydrothermal and molten salt routes. **Figure 1a** represents the original phases of raw feldspar, which contains potassium sodium calcium aluminum silicate in anorthic crystal system. The XRD data matched with the standard JCPDS file (01-084-0710). **Figure 1b** shows the XRD spectrum of leached residue, after treating in 7M H_2SO_4 using hydrothermal process. It has also been noticed that many phases have been destroyed by the high temperature leaching process which ascertains the leachability of K from the mineral. **Figure 1c** shows the XRD spectrum obtained by treating in $CaCl_2$ melt. The spectrum indicates that the absence of peak for K in the treated sludge. In the case of unroasted feldspar, even after the treatment with molten $CaCl_2$ the K cannot be leached out form the mineral. It may be due to the lower diffusion reaction kinetics between the feldspar and $CaCl_2$ medium at high temperature. It is also predicted that the ionic strength of Ca^{2+} is not sufficient to dissociate feldspar fully at this condition.

Figure 2 shows the flow sheet indicating the overall mechanical, hydrothermal and molten salt leaching steps involved in the processing of feldspar mineral. **Figure 2a** indicates the various unit operations carried out such as milling, sieving, mechanical stirring and hydrothermal leaching performed in various acid media at different temperatures. **Figure 2b** shows the sequence of the steps involved in the molten salt extraction of process. **Figure 3a** represents the concentration of K leached out by treating with different concentrations of acid media namely HCl, H_2SO_4 and HNO_3 at room temperature. From the graph, it has been noticed that H_2SO_4 medium has shown maximum leachability. By treating at 90 °C, **t**he leachability of K is found to increase with increase in temperature irrespective of the acids which has been shown **Figure 3b.** Among the three acids**,** H_2SO_4 is found to be the best leaching medium in comparison to other acids.

Energy Dispersive Spectroscopy (EDS)

The Energy Dispersive Spectra (EDS) indicate the various elements such as K, Na, Al, Si, Ca and O present in the raw feldspar. The leached residue obtained by repeated washing after hydrothermal process in 7M H_2SO_4, shows only 4% K values. This result ascertains that the maximum leachability could be possible by treating with 7M H_2SO_4 medium. The residue obtained after treating with molten $CaCl_2$ melt, indicates that the absence of K in the sludge which confirms the maximum leachability of K in molten $CaCl_2$ melt. In the case of $MgCl_2$ melt, the concentration of K is found to be 5.4% even after the treatment which indicates the $MgCl_2$ melt is sluggish in extracting K from the mineral.

Scanning Electron Microscopy (SEM)

Figure 5a shows the SEM image of raw feldspar which exhibits irregular shape with particle sizes ranging from 10 to 20µm. **Figure 5b** shows irregular plate like particles obtained after leaching by hydrothermal process. **Figure 5c** exhibits particles with porous morphology obtained after leaching with $CaCl_2$ melt. **Figure 5d** exemplifies the leached residue obtained from $MgCl_2$ melt which also manifests the particles with irregular size of 10-15µm.

CONCLUSIONS

Based on the results obtained from the above investigation, it has been concluded that potash can be effectively leached out by using H_2SO_4 medium using hydrothermal process. Molten salt extraction yields maximum recovery of potash up to 90% using $CaCl_2$ molten melt. These processes can be improved by adopting mechanized devices to take it into a pilot plant scale for the efficient utilization of Indian K-feldspar.

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APPENDICES

Figure Captions

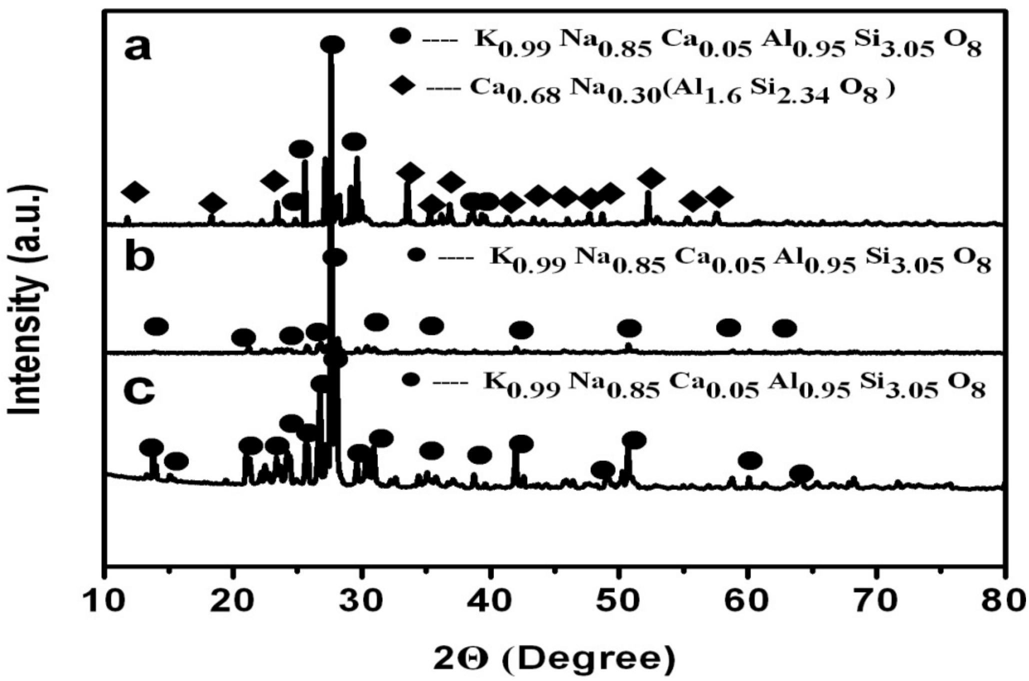

Figure 1: XRD for (a) Raw K-Feldspar, (b) Potash Leached Residue in 7M H_2SO_4 with Four Time Repeated Cyclic Process, (c) Potash Leached Residue in $CaCl_2$ Molten Melt

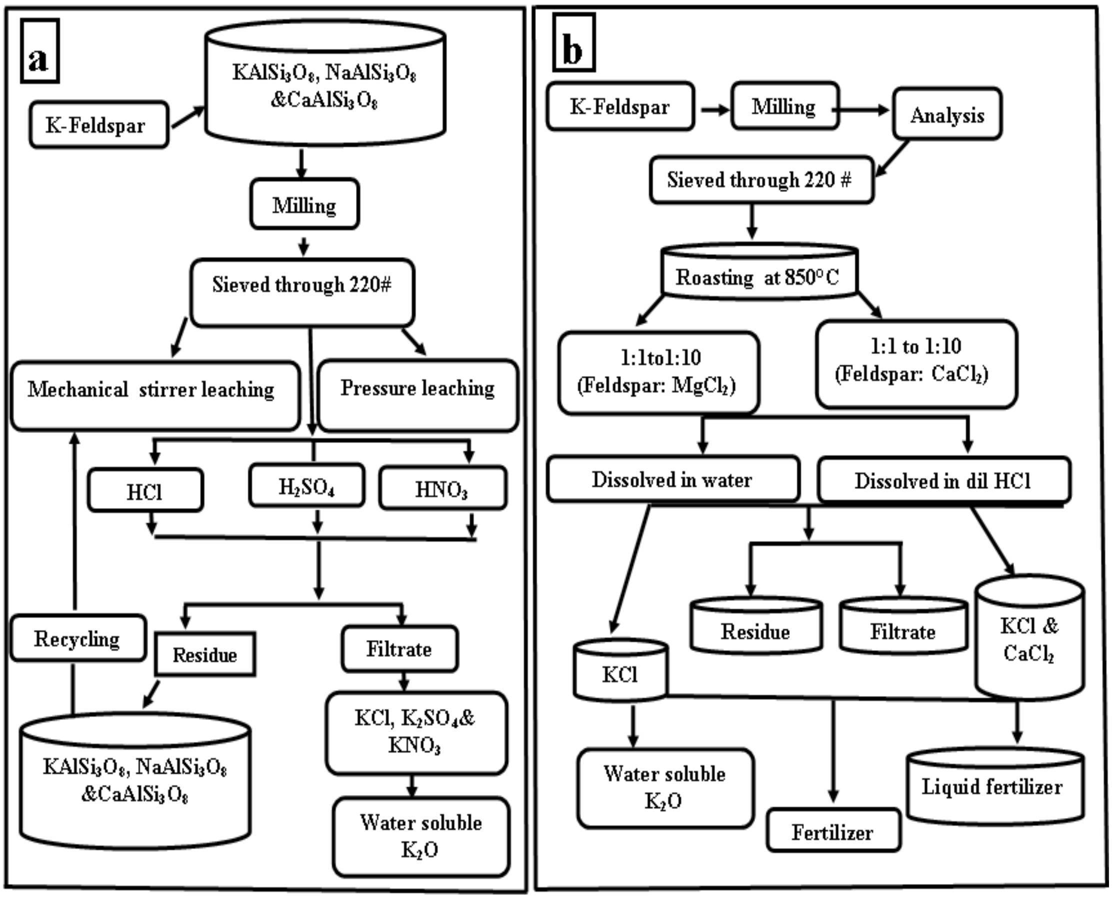

Figure 2(a): Flow sheet for Acid and Hydrothermal Leaching Processes, (b) Flow Sheet for $CaCl_2$ and $MgCl_2$ Molten Salt Process

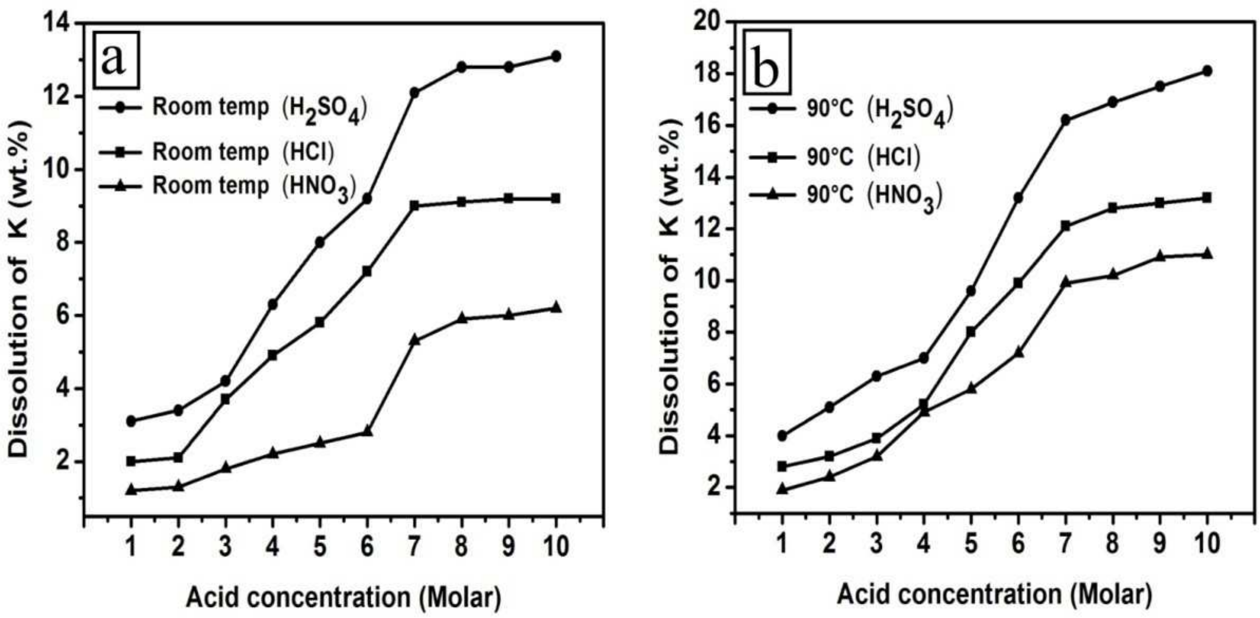

Figure 3: Leaching Studies in HCl, H_2SO_4 and HNO_3 at Room Temperature and at 90° C.

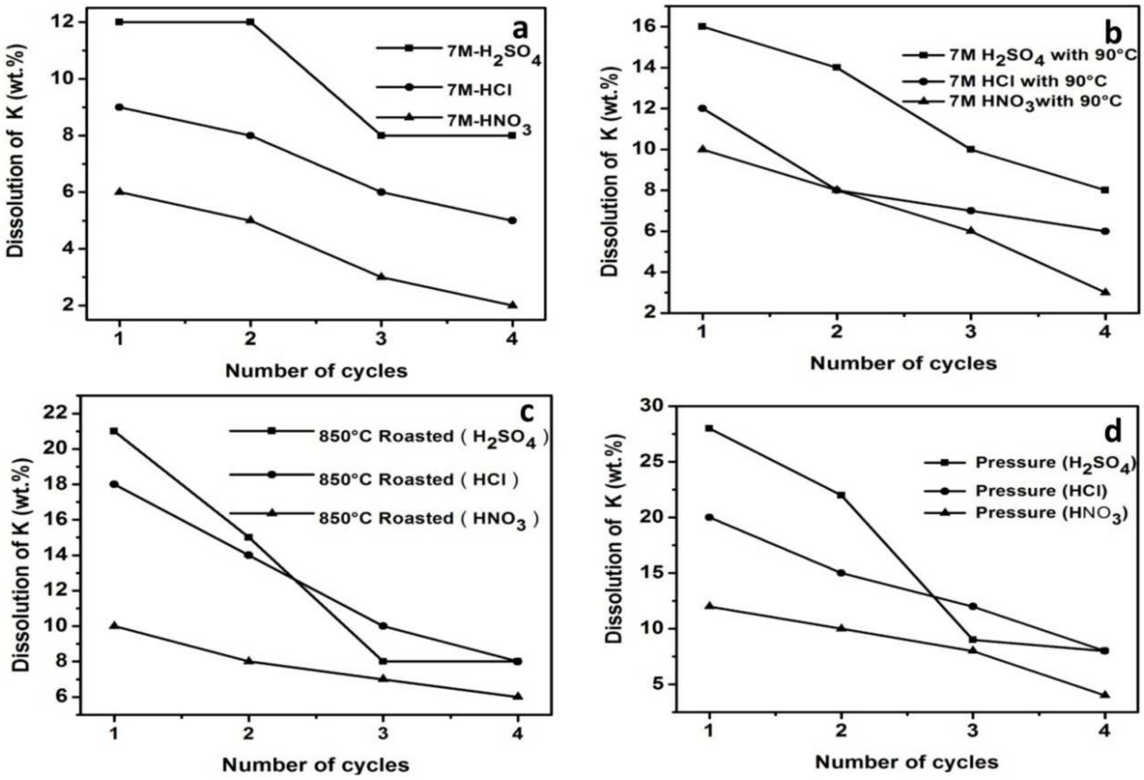

Figure 4: Four Times Repeated Cycles of Leaching Un-Roasted (a) at Room Temperature, (b) at 90°C, and Roasted at 850°C (c) at Room Temperature, (d) at 120 °C Hydrothermal Process

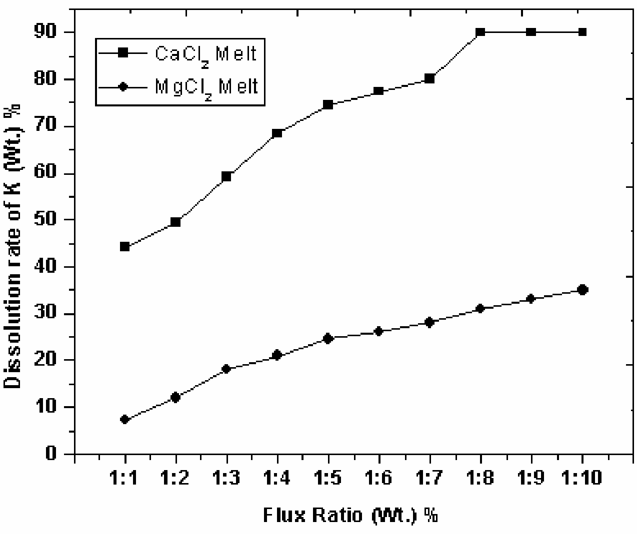

Figure 5: Molten Salt Extraction of Potash by using Additives as $CaCl_2$ and $MgCl_2$

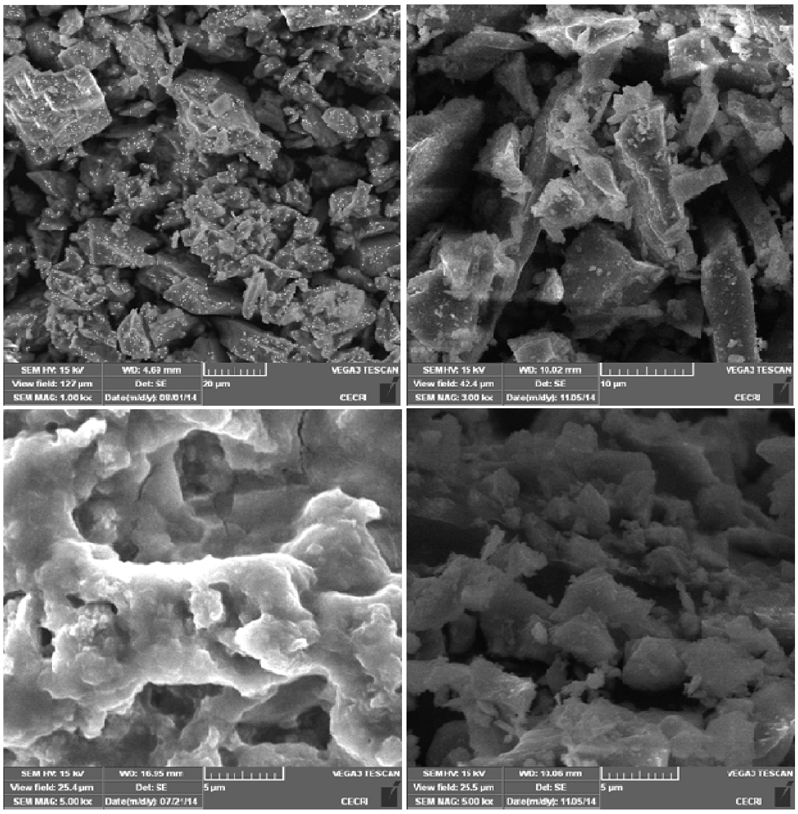

Figure 6(a, b): SEM Image of Raw K-Feldspar and Potash Leached Residue in 7 M H_2SO_4; (c, d) Potash Leached Residue in $CaCl_2$ and $MgCl_2$ Melt