

THERMAL AND CHEMICAL PROCESSING OF SILICATE ROCK FOR POTASSIUM RELEASE

A DISSERTATION

**Submitted in partial fulfilment of the
requirements for the award of the degree**

of

MASTER OF TECHNOLOGY

in

**DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING
(With specialization in Industrial Metallurgy)**

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MAY, 2016

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ACKNOWLEDGMENTS

This thesis was a journey filled with lessons, hardship, joys, celebrations and special moments that ultimately lead me to my destination, now it is time to express my sincere vote of thanks to many people who were co-passenger of mine throughout this journey.

The first and foremost, I would like to express my deepest gratitude to my thesis supervisor Dr. Nikhil Dhawan, Assistant professor, Department of metallurgical and materials engineering, Indian Institute of Technology Roorkee. I have never met such a down to earth person in my life, his words of encouragement and motivation has made a deep impression on me. He was very much supportive and always free to listen to me and clear my doubts, whenever I need. His skill and enthusiasm have boosted my interest in this field.

Now I would like to express my sincere thanks to Mr. Naresh Sharma, Mr. R. K. Sharma, Mr. Rajendra Sharma for their help and support towards completion of my dissertation work. I would like to thank technical and administrative staffs of the MMED who help me in all possible ways during my M.Tech work. I sincerely want to credit my friend Yogendra, Niranjana, Vignesh, Neeraj, Vikash, Apeksha and many friends for their direct or indirect contribution during project work.

My deepest gratitude goes to my parents Mr. R.N.Pradhan and Mrs. Neera Pradhan for their constant love, support and caring through out my life. I could not imagine this journey without my siblings Megha and Sagar for their unconditional love, concern and support in spite of all my flaws.

(Gulshan Kumar Pradhan)

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ABSTRACT

Potassium is vital for the growth of healthy plants and crops. India does not have any commercial resources of potash, a large quantity is imported every year from the global market to meet the agricultural demand. In this context, the extraction of potassium values from different indigenous sources is highly essential. Available potassium source in India are only silicates minerals in which potassium is present in insoluble form which are widely available. A silicate K-rock from Banda (Uttar Pradesh) is procured. Detailed characterization is carried out using optical microscopy, XRD, TG/DTA and FESEM/EDS. The major phases are muscovite, orthoclase, phlogopite, rutile and quartz. Potash bearing mineral are muscovite, orthoclase and phlogopite and contains approximately 9.08% K_2O . Extraction of potassium from complex silicate structure has been done using following possible routes, heat treatment using muffle furnace, microwave assisted heating and through mechanical activation using planetary ball mill followed by heat treatment in muffle furnace. In each route optimisation of flux dosage, temperature and time has been done. Using muffle furnace maximum potassium extraction of 83% was achieved by $CaCl_2$ (fused) treated sample whereas in mechanical activation followed by muffle furnace it was 84.52%. Extraction percentage was same for both the case but temperature required for treatment was reduced from 900°C to 700°C. Same was the case for NaOH treated sample, temperature for treatment came from 600°C to 300°C in addition to potassium extraction reached to 87%. This outcome gave indication that mechanical activation has vital role in the liberation of K from the structure so the parameter in mechanical activation was varied, so after varying the milling time using $CaCO_3$ as flux, K extraction was achieved 91% without any heat treatment.

1.1 IMPORTANCE OF POTASSIUM AS FERTILISERS

Fertilizers are very important component for production of crops as a substitute for nutrients which has been removed from the soil during harvesting, chemical weathering and erosion. There are total seventeen elements which are essential for plants growth and development, out of which primary plant food elements are nitrogen (N), phosphorus (P) and potassium (K). Fertilisers are materials which are essential to provide NPK in easily available form i.e., soluble for plant uptake. P and N are the essential for the formation of nucleic acids, vital for photosynthesis and uptake of other nutrients. K is important for growth of stems and leaves, ability to fight with disease and pests and movement of protein, starch and sugar for size and quality of fruits and grains. N-fertilizers are manufactured from ammonia which is synthesised by reacting atmospheric N_2 with H_2 in high temperature pressure environment. P-fertilizers are acquired from phosphate rocks mainly apatite. K-fertilizers are presently obtained from rocks that are mixtures of soluble KCl salt referred to as potash [1].

1.2 SOURCE AND EXTRACTION OF POTASSIUM

Potassium containing rocks are mined and refined from underground ore deposits, salt lakes and brines. In Saskatchewan, Canada, most of the deposits are more than 900 meters below the surface. In Canada deposits are of high grade, thick and easy to mine, once a shaft is up to the level of the bed. Solution mining is one of another method for the extraction of potash from underground deposits. In this method, water is injected into the deposit through a well to dissolve the salts, and a solution containing the KCl and NaCl is pumped out through another nearby well. This method is advantageous when the deposit is irregularly distributed or situated too deep for conventional mining. Another way of extracting potash is by evaporating water which are at it saturation of potassium, sodium and magnesium salt from salt lakes and subsurface brines. This technique is used in the United States at the Great Salt Lake and

Bonneville Salt Flats in Utah, in Searles Lake in California, and in Israel and Jordan at the Dead Sea [2].

Extraction of soluble salt from conventional way of extraction will be the dominant way of extraction up to the time until these sources are available. A possible substitution to these soluble salts are the K-bearing silicate rocks. The principle potash fertiliser minerals, together with the dominant rock-forming potassium silicate minerals are listed in Table 1.1.

Table 1.1: List of Principle potash fertiliser ore mineral and dominant rock forming potassium silicate mineral. [3]

Mineral	Formula	Weight % K	Weight % K ₂ O	Availability in India
Potash ore minerals				
Sylvite	KCl	52.35	63.07	NO
Carnallite	MgCl ₂ .KCl.6H ₂ O	14.05	16.93	NO
Kainite	KMgSO ₄ Cl.3H ₂ O	15.69	18.9	NO
Langbeinite	2MgSO ₄ .K ₂ SO ₄	18.84	22.7	NO
Silicate minerals				
Potassium feldspar	KAlSi ₃ O ₈	14.03	16.9	YES
Leucite	KAlSi ₂ O ₆	17.89	21.55	NO
Nepheline	(Na,K)AlSiO ₄	13.00	15.66	NO
Kalsilite	KAlSiO ₄	24.68	29.73	NO
Muscovite	KAl ₃ Si ₃ O ₁₀ (OH) ₂	9.03	10.88	YES
Biotite	K ₂ Fe ₆ Si ₆ Al ₂ O ₂₀ (OH) ₄	7.62	9.18	YES
Phlogopite	K ₂ Mg ₆ Si ₆ Al ₂ O ₂₀ (OH) ₄	9.38	11.3	YES

The natural way of deriving potassium from soil is from potassium silicate minerals, which can be subdivided into feldspars, feldspathoids, micas, clay minerals, especially illite. Clay mineral are responsible for the exchangeable K due to the cause of deep weathering. Whereas in silicate mineral having K at its interlayer bonded in between two TOT layer are potential source of fixed K [3].

1.3 POTASSIUM PRODUCTION AND CONSUPTION IN WORLD

Potash production in world has increased to 34.5 Mt in 2013 from 33.1 Mt in 2012. Principal producing countries are Canada, Russia, China, and Belarus which accounts for 72% of total production. From 2012 to 2013 global potash capacity has increased to some extent to 49.8 Mt from 49.6 Mt [4].

Table 1.2: World's potash production by country [4].

Country	Production (Thousand metric ton of K ₂ O)	
	2012	2013
Canada	8,976	10,140
Belarus	4840	4243
China	4100	4300
Russia	5563	6100
Israel	2100	2100
Germany	3149	3200
Jordan	1092	1080

Global consumption of all forms of potash was estimated at 33.4 Mt K₂O in 2013, a slight increase from 2012. Apparent consumption of all forms of potash in 2013 increased by 4% over that of 2012. The principal use of potash was as an agricultural fertilizer (plant nutrient) as a source of soluble potassium [4].

1.4 POTASSIUM IN INDIA

The entire requirement of potash in India is met by imports since there is no commercial production in the country. The potash is mainly used as fertiliser and other uses of potassium minerals are in the manufacturing of glass, explosives and chemicals. The current import of potash is around 3.5 million tonne which entails 77 billion per annum and projected more in future if no indigenous production comes up. Thus, there exists huge investment opportunities for potash mining in India as an import substitute mineral[5].

1.5 SILICATE ROCK AS POTASSIUM SOURCE

The potassium silicate minerals occur in mixed form with other silicate minerals, and thus overall K content gets diluted. Though K is the seventh most abundant element in the earth's continental crust, the composition of which is dominated by rocks of granitic composition and the products of their weathering and erosion. One of the essential components of granitic rocks is potassium feldspar also named as orthoclase or microcline, which also contain the micas biotite and muscovite. Granitic rocks weathering product are mainly secondary muscovite and chemically-similar illitic clays. Some of the common silicate minerals are potassium feldspar,

muscovite and biotite, the other potassium silicate minerals are rare. Nepheline occurs in very specific igneous rock types that occur irregularly, mainly as intrusive rocks but also within lavas [6].

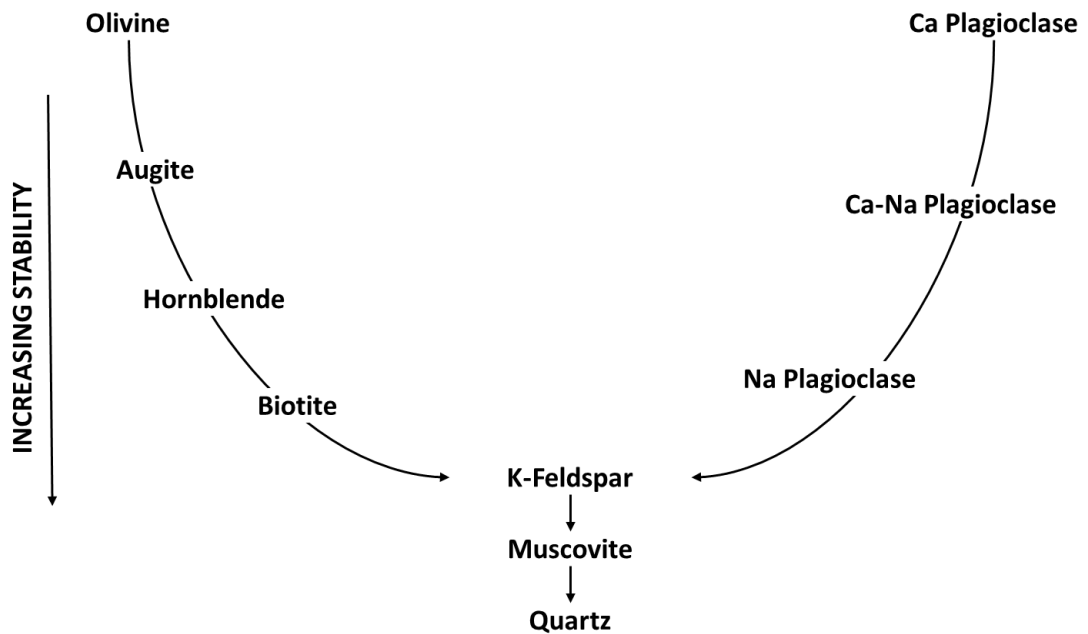


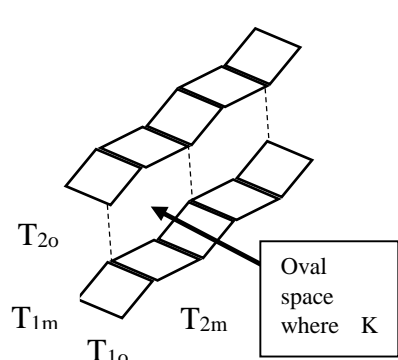
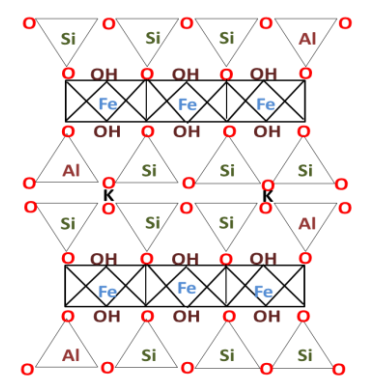
Fig. 1.1. Stability of mineral during weathering process.

It is important to note that main potassium silicate rock group occurs under mica family and feldspar family. The comparison of both the families is given in the below table.

Table 1.3: Comparison of mica group and feldspar group which are major potassium containing mineral group

CHARACTERSTICS	FELDSPAR GROUP	MICA GROUP
Silicate structure	Tectosilicate structure	Phyllosilicate structure
Chemical formula	$KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$	Lepidolite $K(Li,Al)_3(AlSi_3O_{10})(O,OH, F)_2$; ; Biotite $K(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$; Phlogopite $KMg_3(AlSi_3O_{10})(OH)_2$; Muscovite $KAl_2(AlSi_3O_{10})(OH)_2$

<p>General formula</p>	<p>$XAl_{(1-2)}Si_{(3-2)}O_8$ The X in the formula can be sodium, Na and/or potassium, K and/or calcium, Ca</p>	<p>$XY_{2-3}Z_4O_{10}(OH, F)_2$ with $X = K, Na, Ba, Ca, Cs, (H_3O), (NH_4)$; $Y = Al, Mg, Fe^{2+}, Li, Cr, Mn, V, Zn$; and $Z = Si, Al, Fe^{3+}, Be, Ti$</p>
<p>Crystal structure</p>	<p>1. Feldspar are tectosilicate mineral comprises of 3-dimensional framework of SiO_4 and AlO_4. 2. Oval space formed between two crank shaft arrangements is occupied by positively charged cations which can be potassium, sodium, calcium etc. this space is sufficiently flexible to adjust cations of different sizes.</p>	<p>1. Micas are phyllosilicate or sheet structured mineral which consists of sheets of silica (SiO_4) tetrahedrons. These sheet pointing towards each other arrange themselves in T-O-T form, where O is the octahedral spacing between the two tetrahedral arrangements of silicate sheet. 2. The sheets are bond by the cations, these cation balance the charge between the two sheets. Deficiency of charge occurs due to the replacement of Si from its tetrahedral position by Al. The charge balancing cation between the T-O-T layers is generally Potassium in muscovite, a mineral from the mica mineral family.</p>
<p>Physical properties</p>	<p>1. Feldspar in impure form can be of any colour from colourless to white. Orthoclase and microcline which are the type of feldspar have a reddish shade, whereas plagioclases are found white to gray. 2. Looking the whole group feldspars can be found transparent to opaque with non-metallic lustres. On fracture it appearances is glassy and pearly on cleavage surfaces. 3. Feldspar displays cleavage at perfect 90° and Mohs hardness is 6.</p>	<p>1. According to the colour of mineral mica can be divided into two group, the light colour and black colour. Muscovite and lepidolite comes under light colour mineral whereas biotite and phlogopite are dark-coloured mineral. 2. Forming in thin sheets due to the perfect cleavage is undoubtedly the most widely familiar characteristic of the micas. 3. The rock-forming micas exhibit certain characteristic colours. Muscovites range from colourless, greenish to blue-green to emerald-green, pinkish, and brownish to cinnamon-tan. Paragonites are colourless to white; biotites may be black, brown, red to red-brown, greenish brown,</p>

		<p>and blue-green. Phlogopites resemble biotites but are honey brown.</p>
<p>Atomic arrangement</p>	 <p>A 3D schematic diagram of the biotite crystal structure. It shows a central layer of tetrahedra labeled T_{1o} and T_{1m}, with outer layers labeled T_{2o} and T_{2m}. A box labeled "Oval space where K" points to a specific site in the structure.</p>	 <p>A 2D atomic arrangement diagram of biotite. It shows a central layer of tetrahedra with Fe ions (blue) and OH groups (red) in the center. The outer layers consist of Si (green) and Al (red) ions. Two K ions (black) are located in the interlayer spaces. The diagram is labeled "BIOTITE" and "K(Fe)₃(AlSi₃O₁₀)(OH)₂".</p> <p style="text-align: center;">BIOTITE $K(Fe)_3(AlSi_3O_{10})(OH)_2$</p>

2.1 OVERVIEW

As per present scenario the world potash fertiliser production needs to be enhanced so as to balance the demand and supply. Soluble potash salt source are only present in few country such as Canada, Belarus and Russia account for almost 75% of total production[4]. This shows that rest of the world is completely dependent on these countries. Therefore, an alternative way of extractive potassium from potassium aluminosilicate rock should come to forefront [3].

Granitic rocks contain higher K content rock, but dissolution of K is much lower than other K bearing rock such as nepheline. In granitic rock mainly potassium feldspar group mineral falls which has complex tectosilicate structure where K^+ sits in the oval space between the crank shaft structures as shown above. At present high cost of conventional way of extracting potassium fertiliser calls for further research for the use of silicate minerals as alternative sources of K. Since 54% of earth crust is compose of feldspar which shows that such soils occur almost in all the developing countries. Hence, this approach provides an opportunity to develop indigenous silicate rock sources of K as an alternative to sometimes prohibitively expensive commercial fertilisers.

Table 2.1. Summarised key findings from literature review.

S.no	MATERIAL	KEY FINDING	Ref
1	Silicate rocks	Silicate rock can be used as a source of potassium.	[3]
2	Muscovite	K ions in the zone of transition between collapsed and expanded areas of the mineral are loosened.	[7]
3	Potassium feldspar	Chemical method can change most insoluble potassium into water soluble form.	[8]
4	Potassium bearing shale	Using cation exchange k of muscovite can be replaced by barium ion.	[9]
5	Biotite and muscovite	Octahedral vacancies cause less release of k from interlayer.	[10]
6	Biotite and muscovite	K release in soil is only related to biotite whereas muscovite behave as inert source.	[11]

7	Phonolite rock powder	Thermal treatment makes modification in rock mineralogical composition.	[12]
8	Biotite	Biotite can be dissolved in inorganic acid and recover potassium.	[13]
10	Glauconite rock	Calcination in the presence of fluxing agents is efficient in the release of K.	[14]
12	Microcline	Reaction between liquid $MgCl_2$ and microcline at 800 °C generated liq. KCl, enstatite ($Mg SiO_3$), magnesium aluminate spinel and Cl_2 At 900°C, % extraction of K was found to be 93%	[15]
13	K bearing mineral	$Al_2(SO_4)_3$ was used slightly in excess to ensure complete conversion of K present in mineral to K_2SO_4 .	[16]
14	Mica rich soil	H^+ encourages release of interlayer K^+ because of bonding of H^+ than K^+ on less specific soil exchange sites, hence extraction of K by a H^+ saturated amberlite ion exchanger may simulate plant root behaviour in sorbing K^+ released from soil minerals.	[17]
15	K bearing mineral	K was recovered in form of K_2SO_3 .	[18]
16	K bearing mineral and K feldspar	K was extracted as KCl. The reaction of K-feldspar with $CaSO_4$ is a solid-solid reaction and reaction depends on ion diffusion and solid reaction activity. Solid -Solid reactions can be sharply accelerated at temp near melting point of reactants.	[19] [20]
17	K- feldspar	At 800 °C, conversion of K-feldspar reached 84.7%.	[21]
18	Nepheline syenite	Extraction of 99.6% K_2O was observed at 900°C.	[22]
19	K-bearing mineral	Aspergillus was chosen over other microbes because it grew fast and showed strong affinity for K-bearing mineral.	[23]
20	K feldspar	Kalsilite and hydroxyl cancrinite were the products obtained after breaking of crystal structure of K-feldspar due to alkaline-hydrothermal process.	[24]
21	Orthoclase	Soluble potassium salts could be formed.	[25]

2.2 LITERATURE GAP/ PROBLEM FORMULATION

Lot of work has been done for potassium extraction from all groups of silicate rocks mostly feldspar group and mica group, with different possible routes as per the availabilities. But the main insufficiency in literature is as following:

1. **Treatment of muscovite:** Muscovite is a weathered mineral and is resistant to chemical attack and leaching.
2. **Appropriate flux:** In different silicate mineral number of flux has been used with varying dosage percentage but appropriate flux with respect to cost, availability, effect to environment and more such aspects have not been considered.
3. **Possible process route:** Cost of potash is approx. Rs.36 per Kg so the process route should be such that the extraction of potassium is economical.
4. **Waste utilization and by-product:** Potash content in silicate rock is around 5-12%, which means lot of by-product and waste is going to be produced. So suitable use and utilization method should be considered.

CHAPTER 3 EXPERIMENTAL PROCEDURE

3.1 OVERVIEW

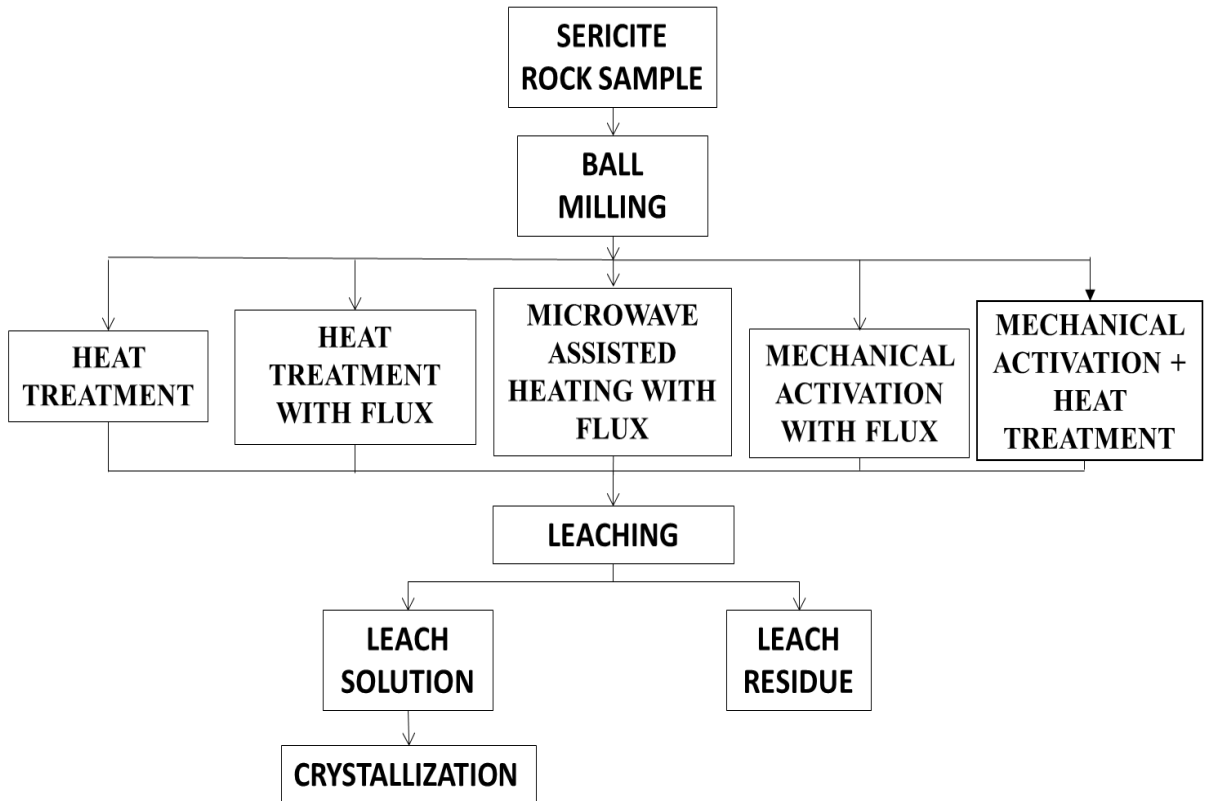


Fig. 3.1. Flow sheet of experimental procedure.

Process route of extraction:

1. Direct leaching of K-rock fine in water or in acid (HCl, H₂SO₄ and HNO₃) followed by leaching.
2. Heat treatment using muffle furnace with and without flux with varying dosage percentage followed by water or 2% citric acid leaching.
3. Mechanical activation using planetary ball mill with or without flux with varying dosage percentage followed by-
 - a) Direct water or 2% citric acid leaching.
 - b) Heat treatment using muffle furnace and water or 2% citric acid leaching.
4. Heat treatment using microwave assisted heating followed by water leaching.

3.2 MATERIAL

The sample used in the experiments was received from Banda (U.P) India. Detailed chemical analysis of K-rock sample was done through classical wet analysis method. Similarly, SEM/EDS were also conducted. The complete chemical analysis is shown in Table1. K-rock mainly contains SiO₂ and Al₂O₃. K₂O is 9.08% which is high enough for indigenous sources for K.

Table 3.1 Chemical analysis of K-rock.

Components	%Results from IBM chemical analysis
Na ₂ O	0.29
CaO	1.69
MgO	1.00
Fe ₂ O ₃	2.80
SiO ₂	43.01
Al ₂ O ₃	31.56
K ₂ O	9.08
TiO ₂	1.56
LOI	7.06

3.3 GRINDING

The sample was crushed in roll crusher and ground in ball mills and sieved by 200 mesh sieve. Sample was received as bulk so grinding was performed using ball mill of size 18”×18” and 6”x10” to grind at different sizes. After grinding, the powder was sieved in different size fractions minus 200 mesh size (75 microns) was used for experiments.

3.4 CHARACTERIZATION

Microstructural study was done using Leica Microscope. X-ray diffraction has been done using Rigaku smart labs diffractometer. After every process of treatment sample were analysed and after comparing all the peaks after each treatment revealed occurrence and disappearance of

different phases during treatment. X ray diffraction analysis was carried out of powder sample from 5° to 60° at speed of 2° per minute.



Fig. 3.2. Photograph of X-Ray diffraction machine.

SEM/EDS studies have been performed using Field Emission Scanning Electron Microscope (FE-SEM Quanta 200 FEG) which helped in varying the phase by shape of the crystal formed and using energy dispersive spectroscopy mass balance was performed during all the stage of experiment. Thermogravimetric/ Differential Thermal Analyser (TG/DTA) SII 6300 EXSTAR was used to calculate the weight loss during heating due to loss of dihydroxylation and oxidation and also revealed about the occurrence of reaction at particular temperature. And analysis of leach solution has been done using Flame photometer.

3.5 HEAT TREATMENT

Thermal treatment has been done with and without flux in muffle furnace and domestic microwave. K-rock received after grinding below 200 mesh was used of thermal treatment. K-rock was mixed with the required percentage of flux thoroughly and then heat treatment was performed in muffle furnace, but in the case of microwave furnace fine charcoal powder was also used aside of flux as an additional heat source.

3.5.1 MUFFLE FURNACE:

Most conventional way of heat treating for research purpose based laboratory. Crucible containing sample is placed in the centre of the furnace and treated for required time as per the experiment.



Fig. 3.3. Photograph of muffle furnace.

3.5.2 DOMESTIC MICROWAVE:

Microwave energy is in frequency range of 0.3 GHz to 300 GHz. Selective and rapid heating are the prime advantages of microwave heating. The absorption of microwaves depends upon the dielectric constant of the underlying material. It is expected in materials such as rocks/ores where lot of minerals are present, selective heating can play a vital role. For e.g. iron based minerals are heating at very fast rate and often catches fire on their own. The effectiveness of microwave is often related with the exposure time and power level.

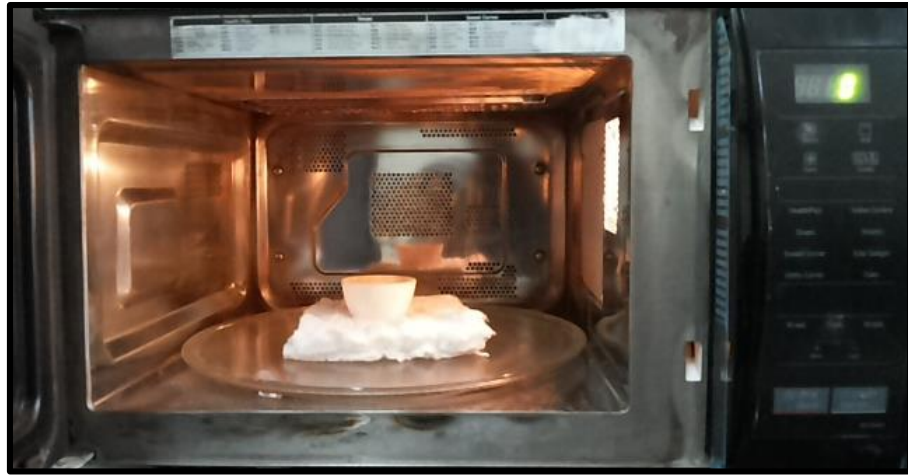


Fig. 3.4. Photograph of domestic microwave.

3.5.3 MECHANICAL ACTIVATION

Due to high impact energy or any mechanical energy if any material possess or leads to development of surface energy or causes change in structure and if any flux is present also leads to chemical reaction or any composition change. This principal was utilised using RETSCH PM 400/2 planetary ball mill, where ball to powder ratio was kept above 20. Mixture of K-rock and required flux percentage was kept in the vial and processed for 8 hours.



Fig. 3.5. Photograph of planetary ball mill.

3.6 LEACHING

Leaching was performed in magnetic stirrer at room temperature at 900 rpm. Heat treated sample was mixed with leaching solvent in the ratio of 50 ml for 1 gram heat treated sample. Before mixing in leaching solvent weight loss was calculate for each experiment performed. Due to heat treatment K-rock and flux gets fused and forms a solid porous mass which was further ground using a agate mortar for further leaching. After 30 min of leaching the leached liquor was filtered and leach residue and solvent were separated. After leaching any formed K-phase (KOH, K_2O , K_2CO_3 and KCl) according to the flux used dissolves in solvent and remaining undissolved mass gets filtered. After drying of filtered mass it is weighed so as to verify the mass balance. On the other side the solvent containing dissolved K-phase is analysed using flame photometer technique.



Fig. 3.6. Photograph of magnetic stirrer.

Solution analysis has been done using Flame photometer. It analyses the solution only if its range lies between 5 to 100 ppm for high concentration and 0 to 5 ppm for low concentration. If dissolved K amount is higher than the limit than necessary dilution is needed so as to fall within its range. And each time before analysis machine need to be calibrated using standard K solution.



Fig. 3.7. Photograph of flame photometer.

4.1 CHARACTERIZATION OF FEED:

Analysis of as received feed sample was done in SEM/EDS and XRD which conforms that the amount of potassium is 8.94% and Si and Al are the highest occurring element in the K-rock and using XRD peaks major K bearing phase was muscovite, orthoclase and phlogopite as shown in Fig 4.1 and Fig 4.2.

DG-DTA analysis shown in Fig 4.3 shows rapid mass loss of 1.23% up to 130°C temperature, this was due to dehydration of water which are attached to surface by vander-wall force and also present as interlayer cation. From 130°C to 550°C sample is thermally stable. As further increase in temperature from 600°C to 800°C a 2.15% mass loss was observed due dehydroxylation of OH⁻ group present in octahedral position.

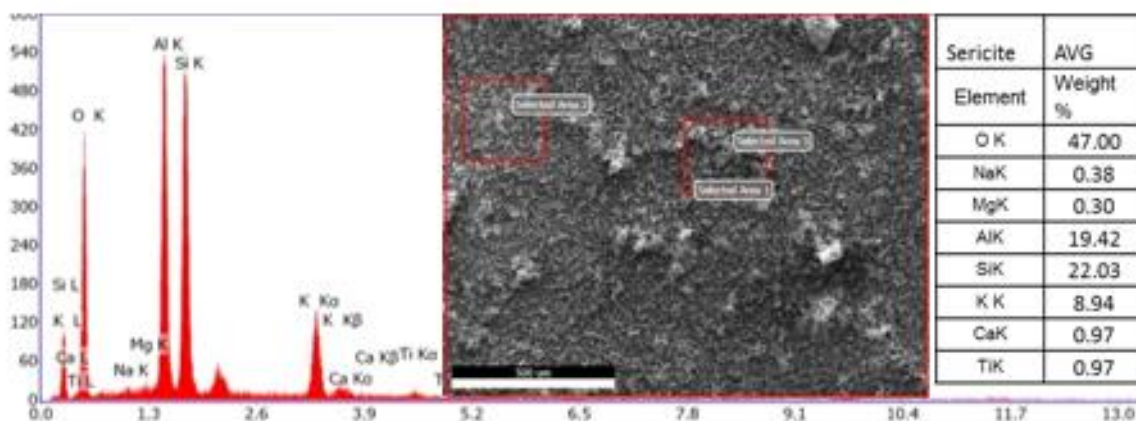


Fig. 4.1. EDS analysis of sericite feed sample.

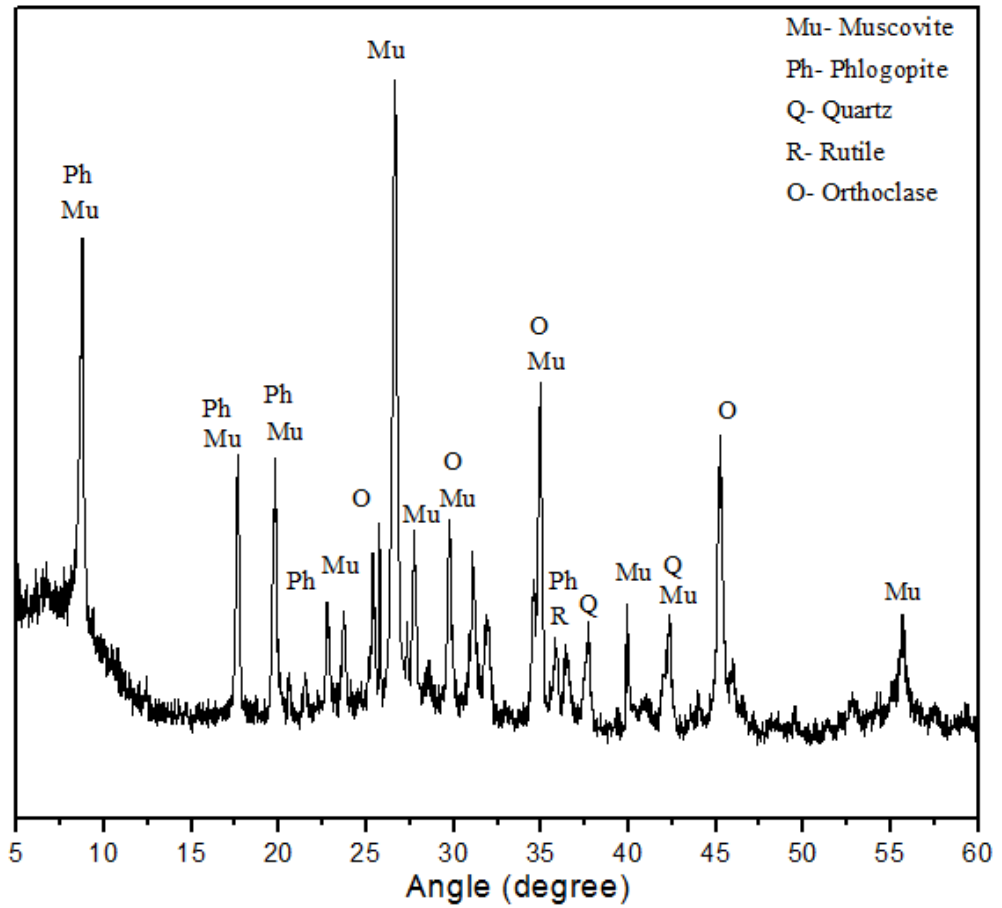


Fig. 4.2 XRD analysis of as received feed sample.

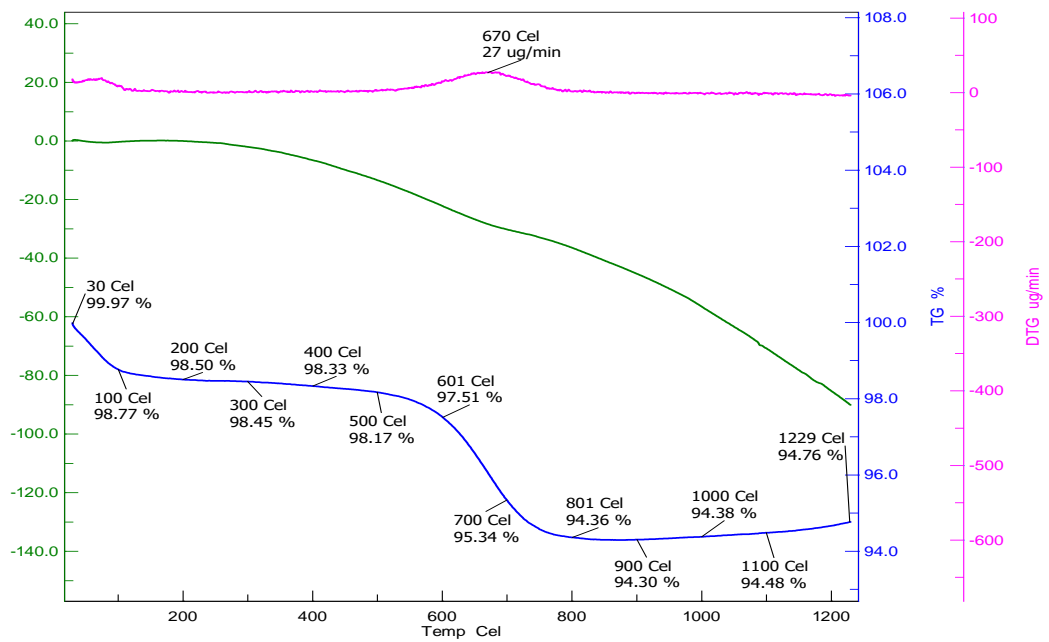


Fig. 4.3. TG/DTA analysis of feed sample.

4.2 PRIMARY TREATMENT OF K ROCK SAMPLE:

Behaviour of sericite feed was observed by directly leaching the sample using water and acid lixiviates and find the extraction of potassium was only limited to 2-5%, then heat treating at 600°C and 900°C was done and the result was same, potassium extraction was only limited to 2-3%. This results shows that the potassium is locked form and need to be liberated using flux, excessive milling and change in structure.

4.3 EXPERIMENTS USING MUFFLE FURNACE:

Chemical and thermal treatment of Sericite using CaCl_2 (fused), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and CaCO_3 at 900°C for 1 hour in muffle furnace.

The solubility of K with different fluxes and variation in dosage depicts that CaCl_2 (fused) is better in making larger part of K dissoluble from complex silicate structure using water leaching. CaCl_2 (fused) was examined further for the treatment. But before treating with CaCl_2 (fused), effect of non-chloride based flux (i.e. CaCO_3 , CaO , CaSO_4 , $\text{Ca}(\text{OH})_2$ and $\text{Ca}_3(\text{PO}_4)_2$) was examined at 1200°C for 1 hour followed by water leaching.

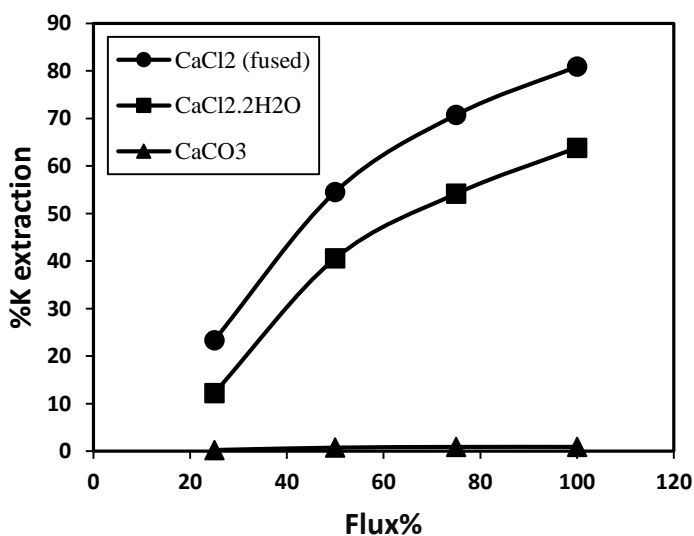


Fig. 4.4. Variation in dosage of different flux in %K extraction using water leaching

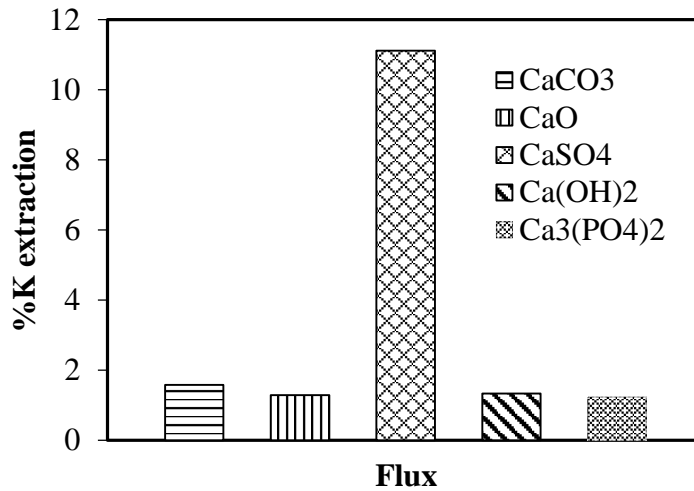


Fig. 4.5. Effect of non-chloride based fluxes (50%) in %K extraction at 1200°C for 1 hour.

The reason to use non-chloride based fluxes is to find the different fluxes which can be used to break the structure as well as which are cheap and easily available as by-product or waste of other industries. All non-chloride based fluxes were not good enough to make K dissoluble from the silicate structure. From these it can be inferred that KCl formation is easy then other forms.

Other than chloride and non-chloride based fluxes, direct HCl leaching was also performed. Direct acid leaching means without prior heat treatment. In solid fluxes it was required to provide heat as to make proper interaction between flux and K-rock sample, as at high temperature it melts and proper interaction takes place as well as due to temperature it provide energy to reaction which are taking place. HCl leaching was conducted at different concentrations 1 M to 6 M and it could only dissolve approximately only 1-5% K.

Direct HCl leaching shows that structure is too complex to react (it is locked), though treating with CaCl₂ (fused) with prior heat treatment it was making interlayer K to avail but without heat treatment it doesn't show any possibility to make interlayer K available.

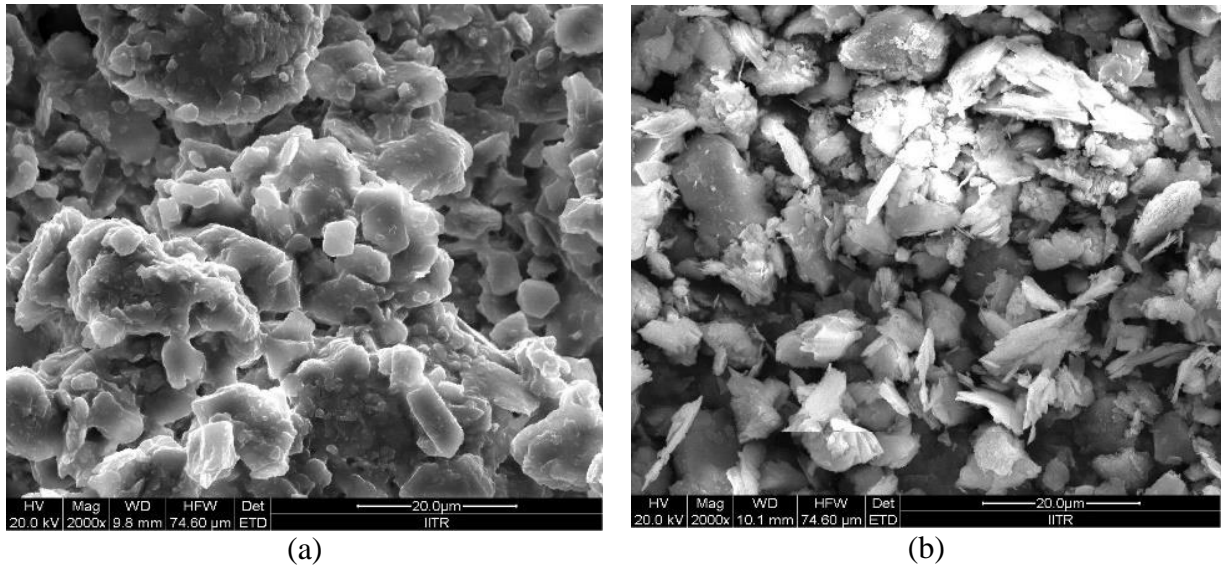


Fig. 4.6. SEM image of CaCl_2 (fused) treated sample at 900°C for 60min (a) Heat treated sample (b) leach residue sample.

In TG-DTA analysis shown in Fig 4.7 mass loss was also observed as in feed but in this $\text{S}+\text{CaCl}_2$ hand mix sample mass loss was 18.82% reaching to 600°C . This mass loss was due to dehydration and dehydroxylation. As further increase in the temperature there was an endothermic peak in the DTA curve at around 735°C which shows a formation of a new phase sylvite which was proven using XRD analysis. Above 900°C there was sudden mass loss, this was due to evaporation of sylvite phase, though the evaporation temperature is above 1400°C but due to formation of $\text{CaCl}_2\text{-KCl}$ eutectic system evaporation of KCl started at 900°C .

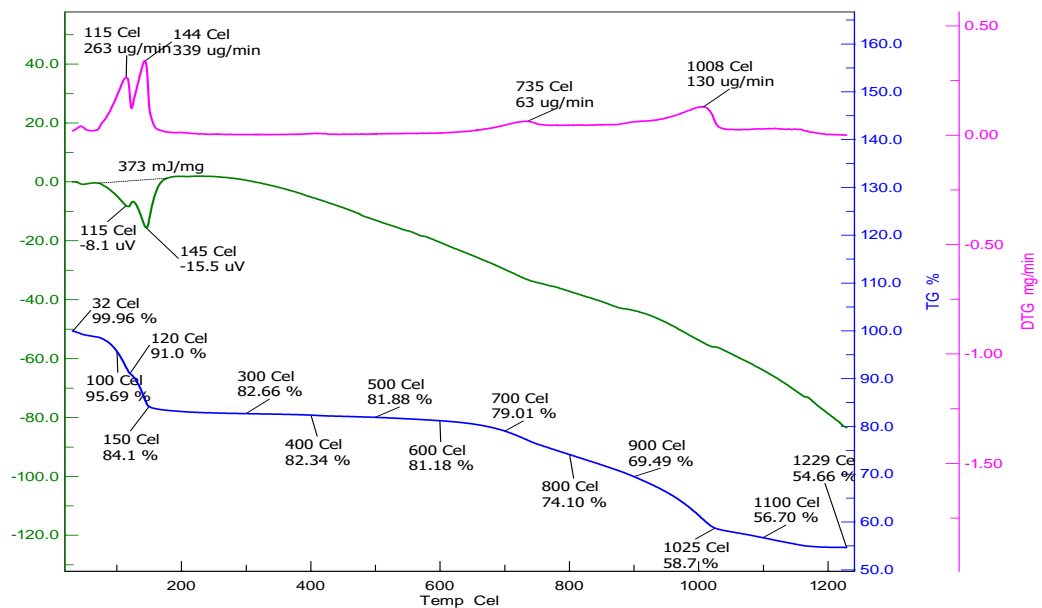


Fig. 4.7. TG/DTA analysis of 50% CaCl_2 (fused) sample.

Chemical and thermal treatment of K-rock was performed using CaCl_2 (fused) flux at different temperature and heat treatment timing. As from prior experiments it has been depicted that higher the percentage of flux higher is the %K extraction, but going beyond 100% flux is not cost worthy so at 60% and 90% dosage different experiments were performed. From Fig 4.8 temperature was optimised, it shows up to 900°C %K extraction increases, then raising the temperature further it starts decreasing. So at 900°C variation on time of heat treatment was performed and Fig 4.9 shows that 30 min is sufficient to heat treat the K-rock sample.

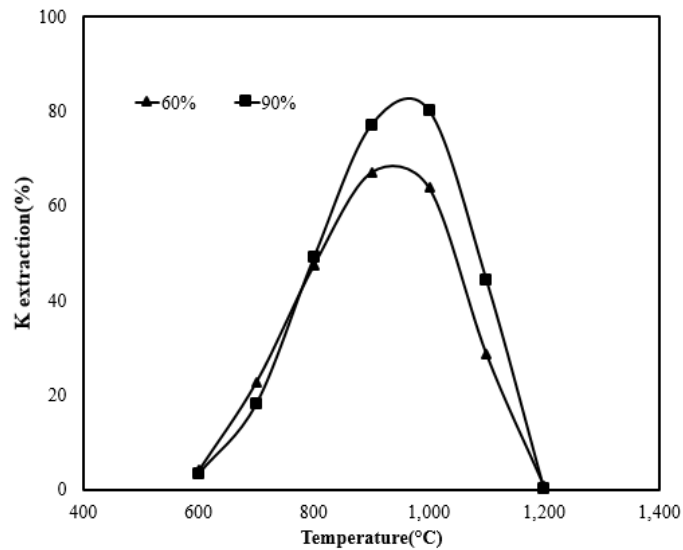


Fig. 4.8. Effect of variation in temperature in %K extraction.

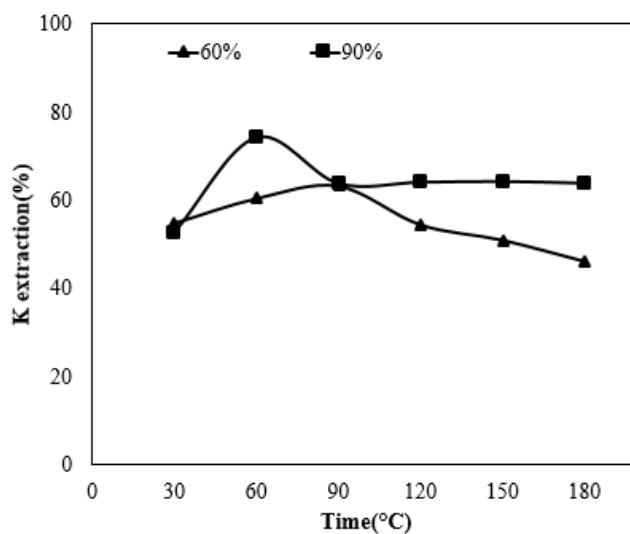


Fig. 4.9. Effect of variation in time of heat treatment in %K extraction.

After heat treatment at 900°C sample was water leached for 30 min, variation of leaching time was also performed and shown in Fig 4.10 that the leaching time doesn't have any major effect on %K extraction as it is approx. constant on increase in time.

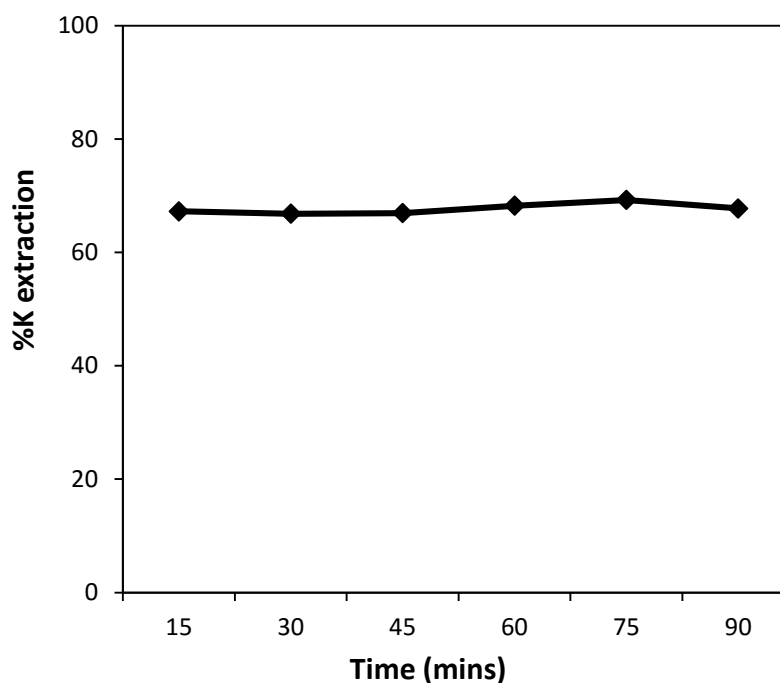


Fig. 4.10. Effect of leaching time in %K extraction

From different experiments it has been proven that thermal treatment is necessary for the attacking the interlayer K in complex silicate structure with appropriate flux which melts at low temperature or forms eutectic at lower temperature so as to react with it and forms K- phase which is easily dissoluble in water.

Using muffle furnace for thermal treatment and CaCl₂ (fused) as flux for 900 °C for 30 min and got the limit up to which maximum interlayer K was attacked by flux and converted into dissoluble K-phase. So as to increase the %K extraction attacking tetrahedral silicate layer rather than the interlayer K was done. To attack tetrahedral silicate layer NaOH was used, it forms a silica gel and the TOT layer gets rupture and makes interlayer K available to react and form soluble K-phase.

After experiments FESEM/EDS of leach residue was done and it shows that K has been dissolved and only contains 0.64 weight%.

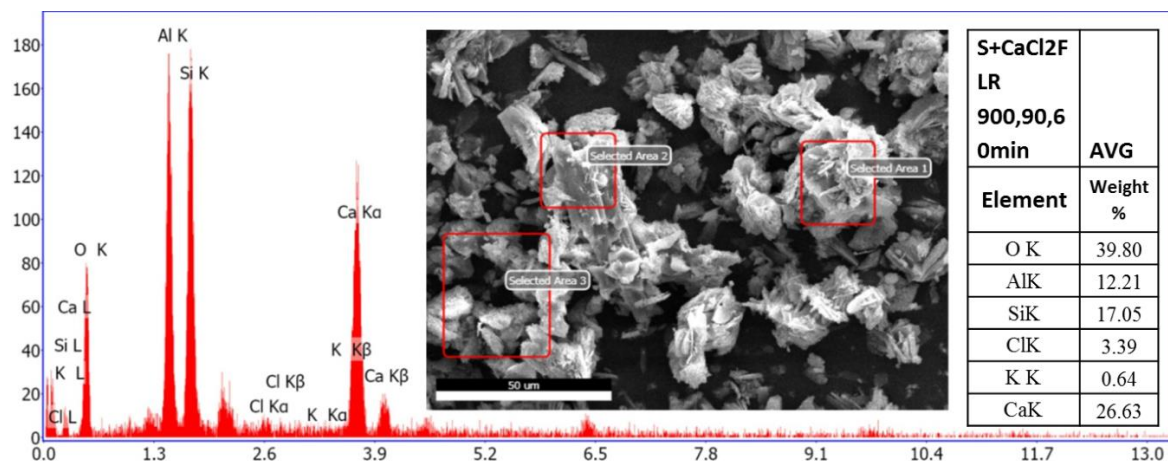


Fig. 4.11. SEM/EDS report of leach residue.

L9 Taguchi orthogonal array was used to conduct experiments with three factors. The three factors were CaCl_2 (fused) dosage, temperature and heat treatment time whereas a corresponding potassium extraction as obtained from leaching experiments was considered as the response variable. The control factors with their selected levels for the experiments are given in Table 4.1.

Table 4.1. Control factor and level for design.

Control factor	Level		
	1	2	3
CaCl_2 fused (%)	30	60	90
Temperature (°C)	700	800	900
Time (min)	30	60	90

Using the Taguchi design for four factor and three level total nine experiments were performed, for all design experiments % K extraction was as given in table. This data were further analysed using contour plot of % K extraction having two variables at a time.

Table 4.2. Taguchi design experiment and respective % K extraction having factor CaCl₂ dosage, temperature and time.

S.No	CaCl ₂ fused (%)	Temperature (°C)	Time (min)	K extraction (%)
1	60	900	90	61.51
2	30	900	60	30.61
3	90	900	30	54.27
4	30	800	90	27.91
5	90	800	60	42.79
6	60	800	30	32.80
7	90	700	90	16.47
8	60	700	60	9.47
9	30	700	30	5.34

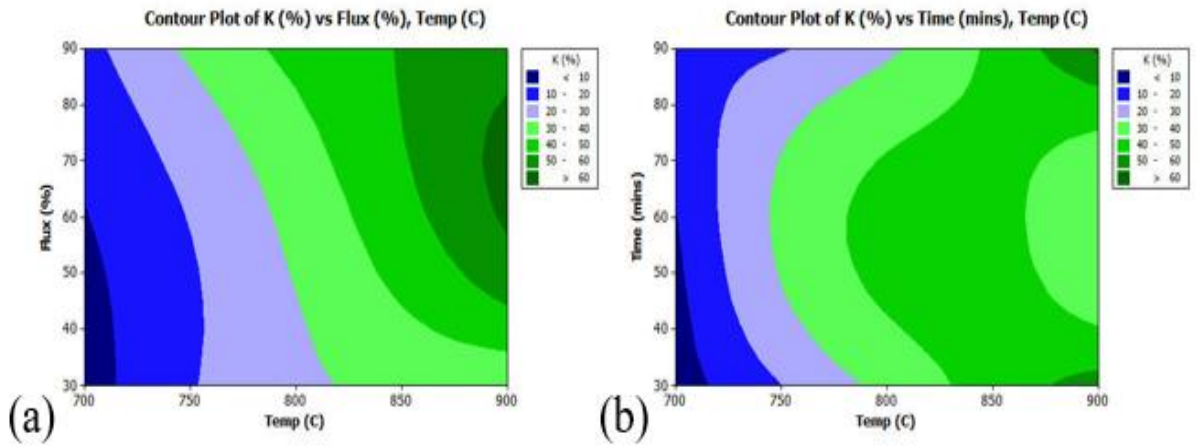


Fig. 4.12. Contour plot of (a) K% vs flux% and temperature (b) K% vs time and temperature.

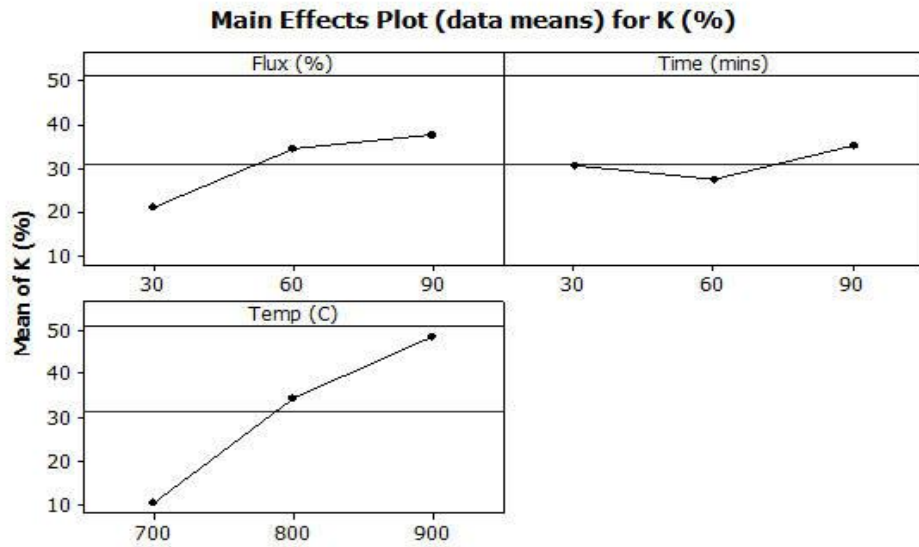


Fig. 4.13. Main effect plot for K%.

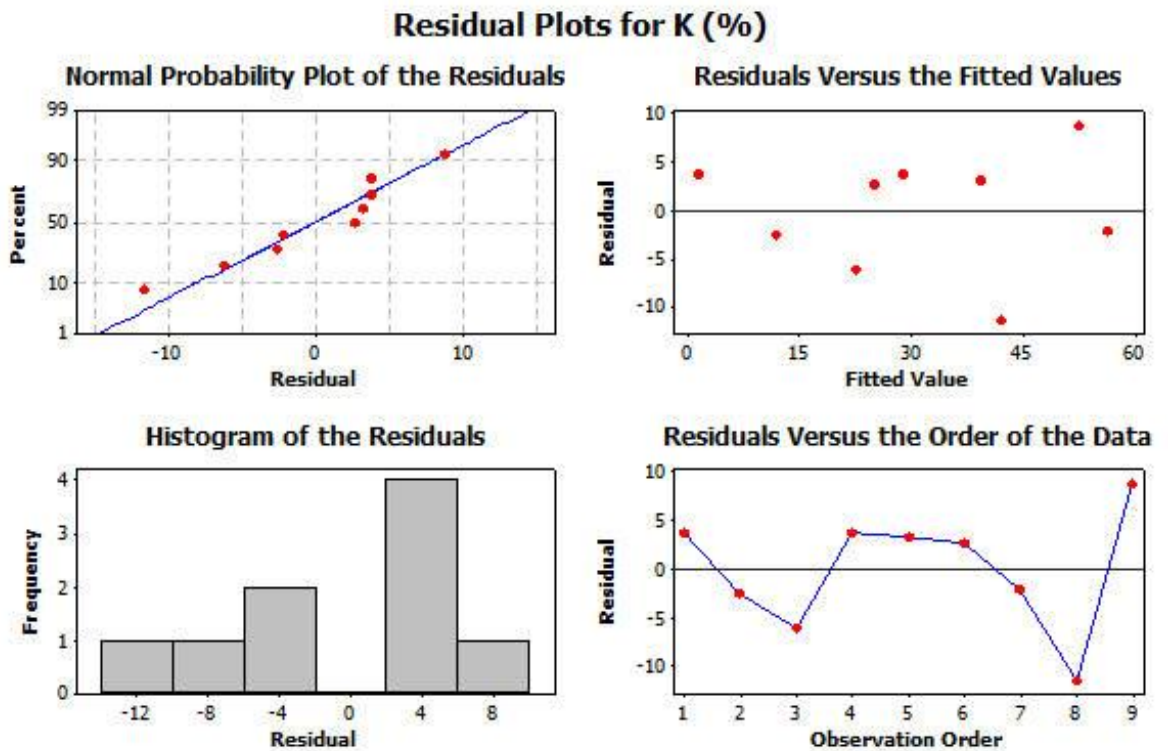


Fig. 4.14. Residual plot for K%.

The regression equation is

$$K (\%) = - 143 + 0.276 \text{ Flux } (\%) + 0.075 \text{ Time (mins)} + 0.192 \text{ Temp (C)}$$

Using CaCl_2 (F) it was able to extract maximum upto 80% so NaOH was tried. As NaOH is a strong base and the OH^- reacts very strongly.

Experiments using NaOH as flux was performed followed by 2% citric acid leaching, first temperature variation was done so as to find out the optimum temperature. From the Fig 4.15 it is clear the maximum extraction is at 600°C .

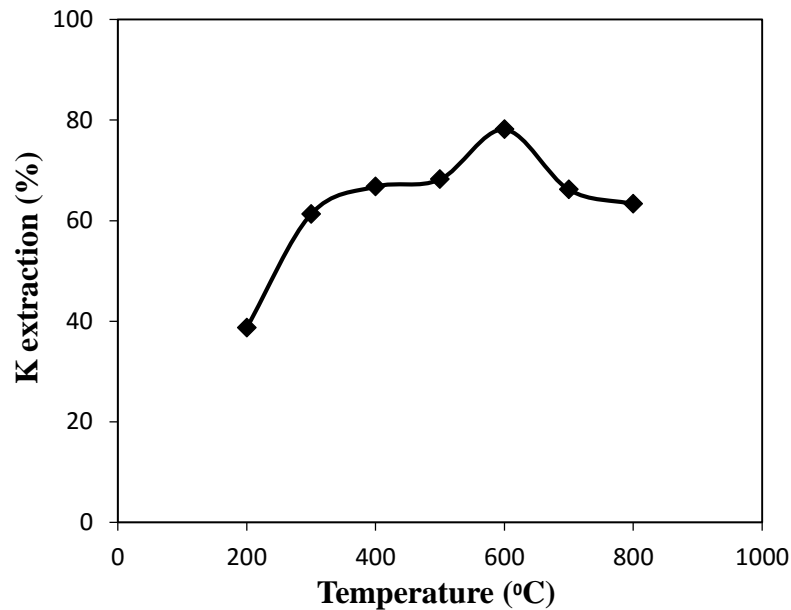


Fig. 4.15. Effect of temperature in %K extraction using NaOH as flux 90% followed by 2% citric acid leaching

It is clear that 600°C is finest to perform the experiment, but in this experiment by default 90% flux was used so to optimise the flux% experiment was performed at 600°C for 150 min varying the dosage. K extraction percentage increases as the flux % has increased, maximum at 90% flux got the maximum %K extraction which can be seen in the Fig 4.16. Temperature and flux % has been optimised, so using 600°C and 90% flux again experiment was performed to find out the optimum time for heat treatment.

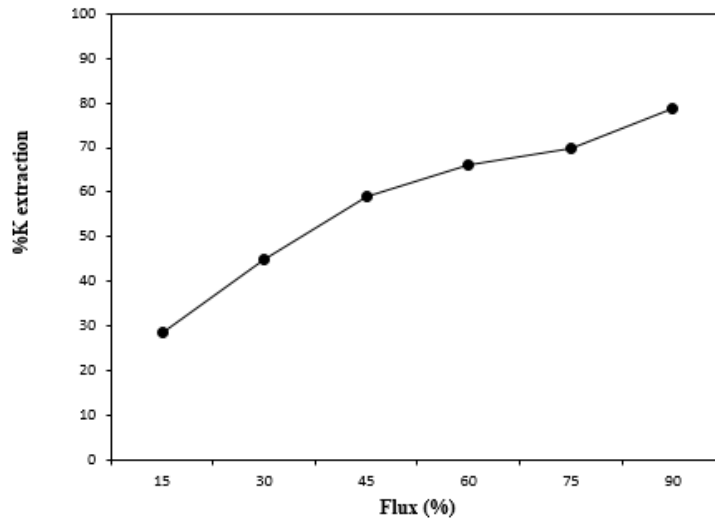


Fig. 4.16. Effect of variation of flux% in %K extraction using NaOH as flux at 600°C followed by 2% citric acid leaching.

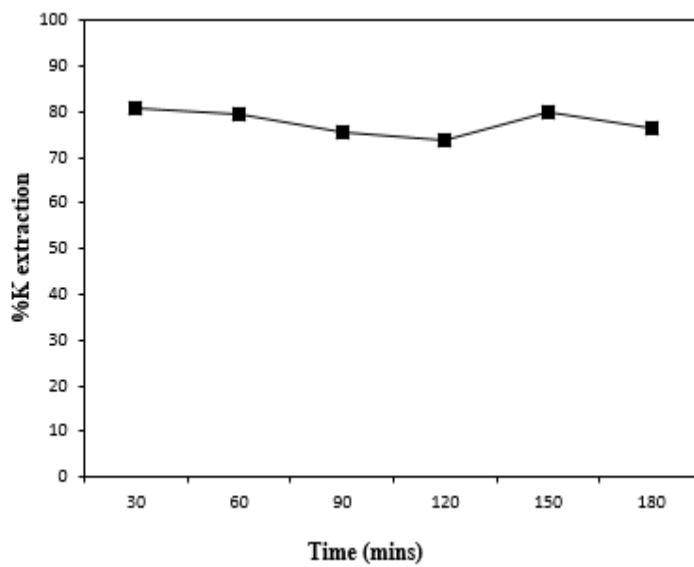
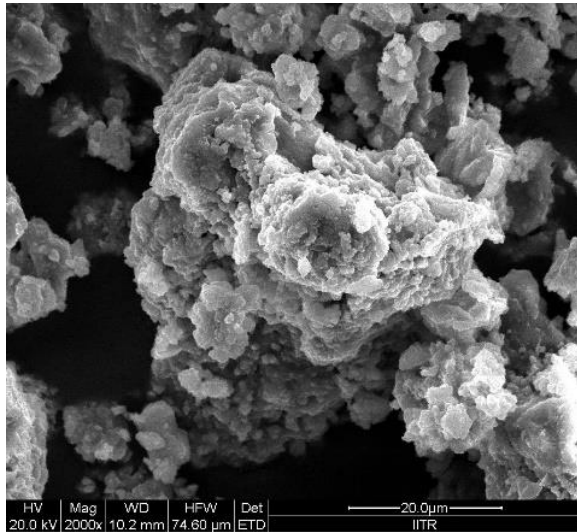
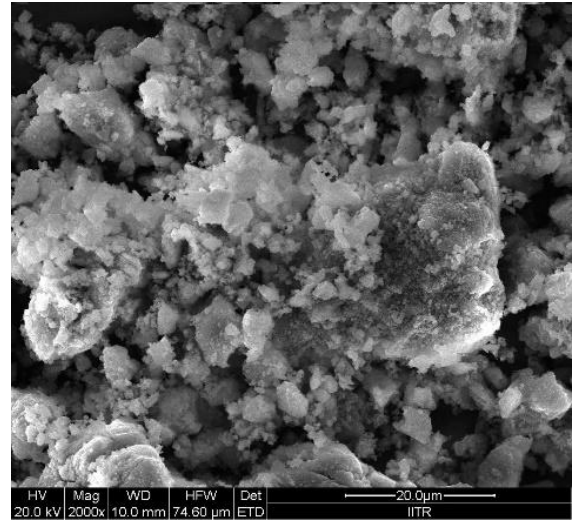


Fig. 4.17. Effect of variation of time in %K extraction using NaOH as flux 90% followed by 2% citric acid leaching.

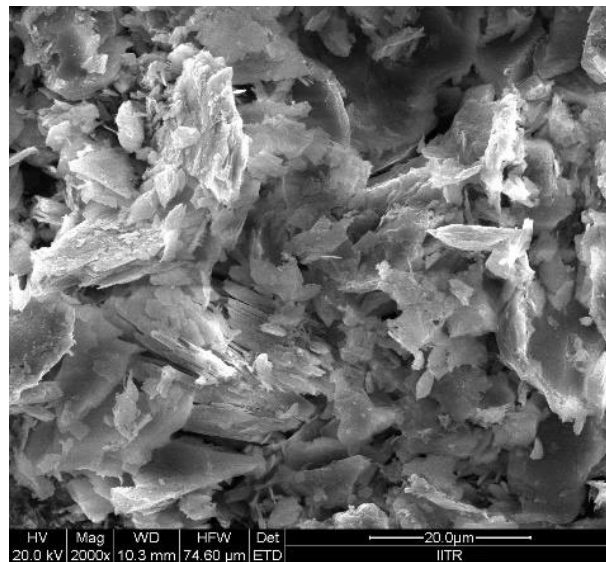
Observing all the experiments performed using NaOH as flux varying temperature, flux and time it predict that at 600°C and 90% flux for 30 min of heat treatment it gives maximum %K extraction.



(a)



(b)



(c)

Fig. 4.18. SEM image of NaOH treated sample at 600°C for 150 min for 90% flux (a) Heat treated sample (b) First leach residue sample (c) Second leach residue sample.

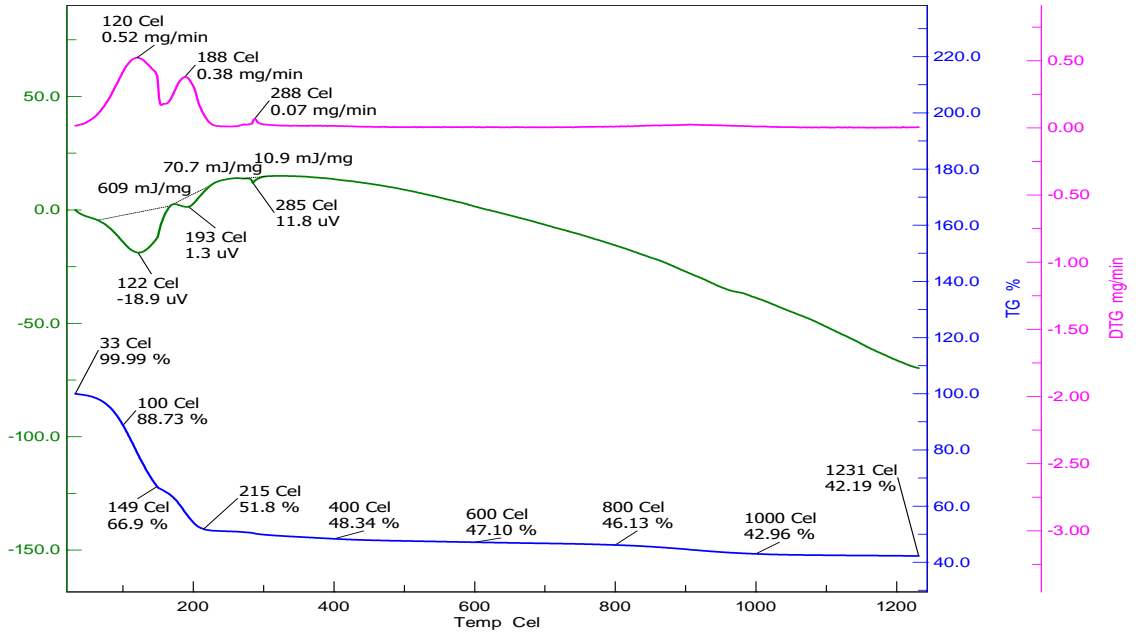


Fig. 4.19. TG/DTA analysis of 90% NaOH handmix sample.

Leaching in citric acid solution unwrapped path for other fluxes which were unable to extract K in previous experiments using water leaching, in this Na_2CO_3 was used as a flux followed by 2% citric acid solution leaching.

As in previous fluxes we got maximum extraction at 900°C so going beyond this temperature doesn't give any reason, so at 800°C and 900°C varying the Na_2CO_3 percentage we got that it gives max extraction at 90% flux and is higher for 900°C as shown in Fig 4.20. So choosing 90% flux and 900°C variation in thermal treatment was performed and from Fig 4.21 we can easily observe that maximum %K extraction is at 60 min.

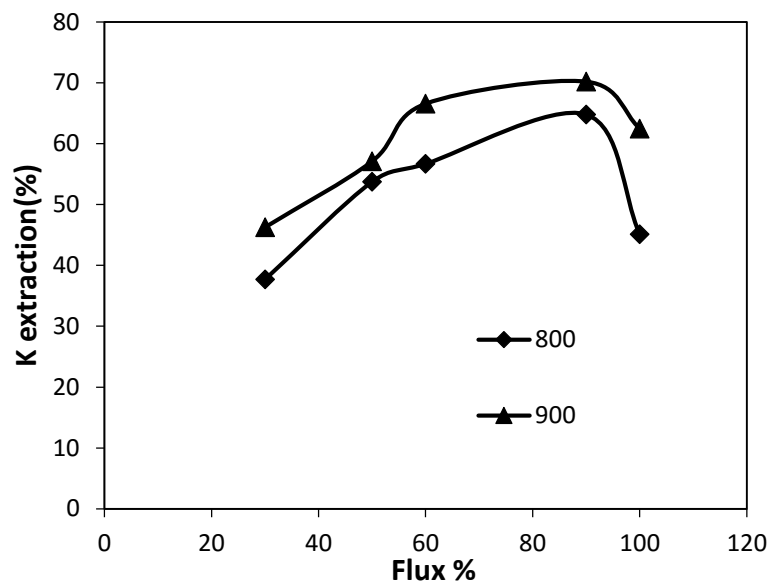


Fig. 4.20. Effect of variation of flux in %K extraction using Na_2CO_3 at 800°C and 900°C followed by 2% citric acid leaching.

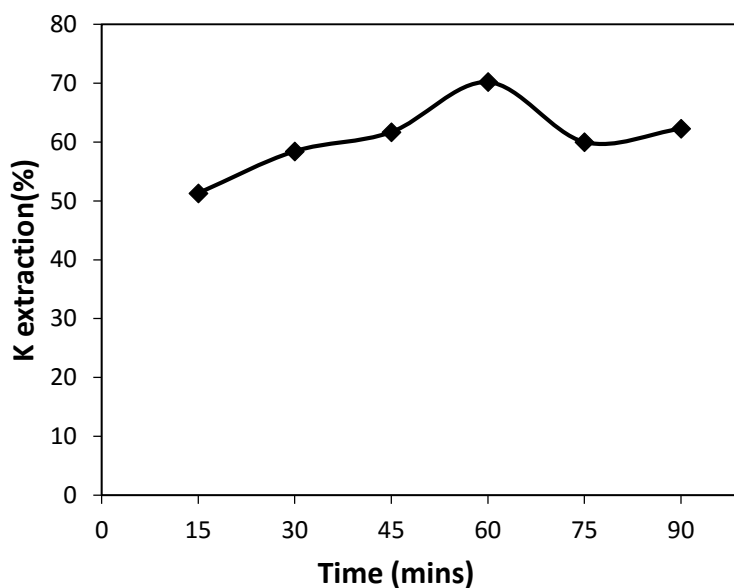


Fig. 4.21. Effect of variation in time of heat treatment in %K extraction using Na_2CO_3 as flux (90%) at 900°C .

K extraction using CaCl_2 (fused) as flux gives 83% extraction at 1000°C in 60 min whereas using NaOH as flux gives 80.95% at 600°C in 30 min, which easily proclaims that NaOH is better than CaCl_2 (fused) as it requires less temperature for treatment as well as less time.

Table 4.3. Comparison of CaCl₂ (fused), NaOH and Na₂CO₃ as flux in extracting K from K-rock using muffle furnace.

Parameters	Flux		
	CaCl ₂ (fused)	NaOH	Na ₂ CO ₃
K extraction (%)	83	80.95	70.56
Time (mins)	60	30	60
Temperature(°C)	1000	600	900
Flux (%)	90	90	90
Cost of flux (Rs. Per Kg)	498	500	579
Medium of leaching	Water	2% Citric acid sol	2% Citric acid sol

4.4 EXPERIMENTS USING MICROWAVE ASSISTED HEATING:

As result of treatment in muffle furnace was restricted to 83% in CaCl₂ (fused), Microwave assisted heating was performed. Advantage of using microwave assisted heating is that it gives sudden heating shock, due to which complex silicate structure ruptures and release of K from interlayer becomes easy.

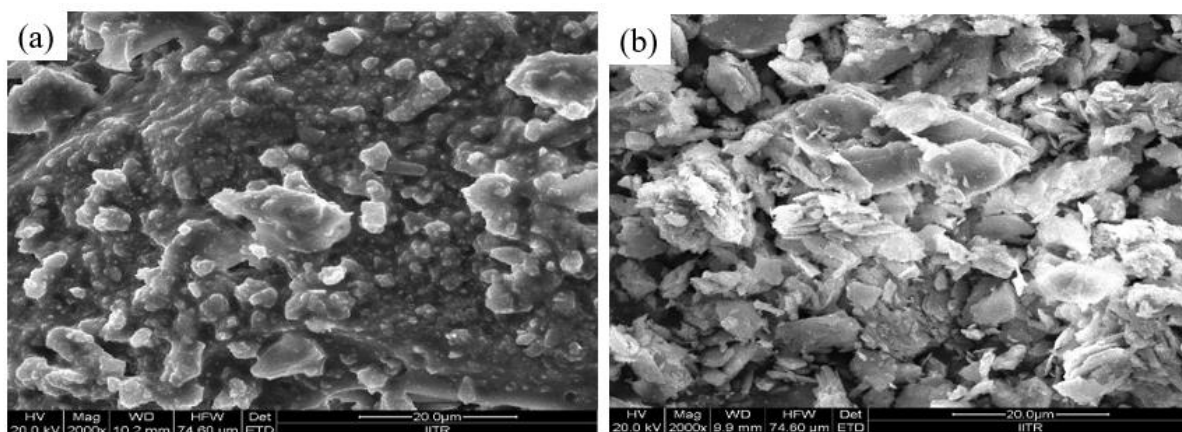


Fig. 4.22. SEM image of CaCl₂ (fused) treated in microwave furnace (a) Heat treated sample (b) leach residue sample.

K-rock fine powder was mixed with CaCl₂ (fused) flux and charcoal powder and was placed in domestic microwave for random time and, followed by water leaching. K% extraction in this random experiment was observed.

Table 4.4. Effect of microwave assisted heating in % K extraction varying power.

Flux (%)	Charcoal (%)	Time (min)	Power (W)	K extraction (%)
50	25	6	540	51.81
50	25	6	720	57.01
50	25	6	900	60.97

This experiment proved that microwave assisted treatment was effective to extract K from the interlayer, but optimisation was needed. So the design of experiments was carried out by using a statistical design based on Taguchi methodology.

L9 Taguchi orthogonal array was used to conduct experiments with four factors. The four factors were Charcoal dosage, CaCl₂ dosage, microwave exposure time and power, whereas a corresponding potassium extraction as obtained from leaching experiments was considered as the response variable. The control factors with their selected levels for the experiments are given in Table 4.5.

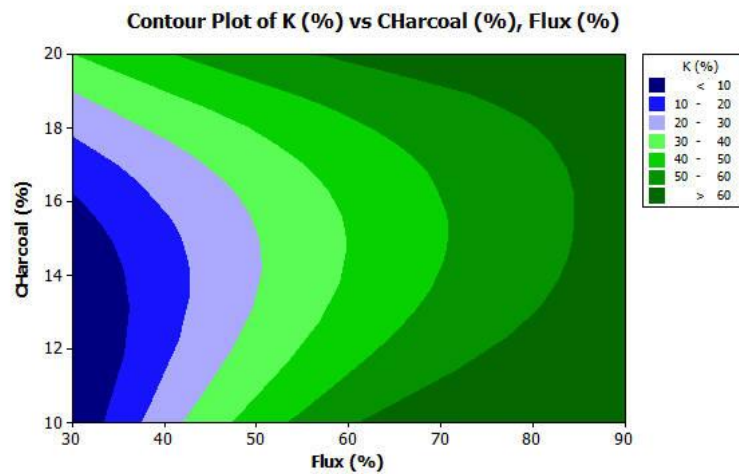
Table 4.5. Control factor and level for design.

Control factor	Level		
	1	2	3
CaCl ₂ fused (%)	30	60	90
Charcoal (%)	10	15	20
Time (min)	4	6	8
Power (W)	540	720	900

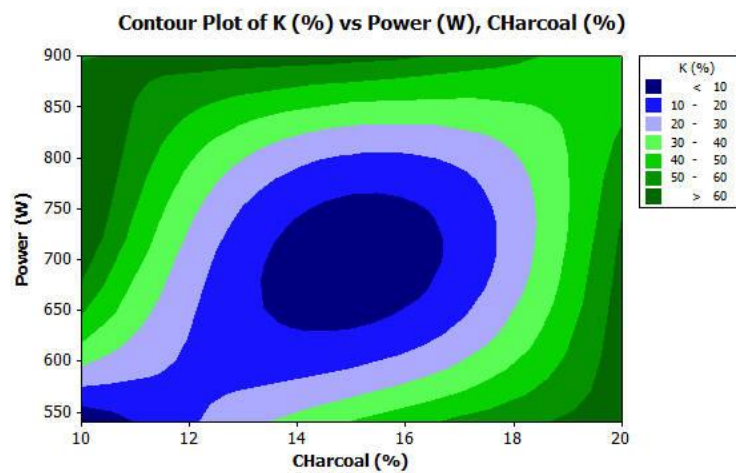
Using the Taguchi design for four factor and three level total nine experiments were performed and one experiment for extreme value of all factor was performed, for all design experiments % K extraction was as given in table 4.6. This data were further analysed using contour plot of % K extraction having two variables at a time.

Table 4.6. Taguchi design experiment and respective % K extraction having factor CaCl₂ dosage, Charcoal dosage, microwave exposure time and power

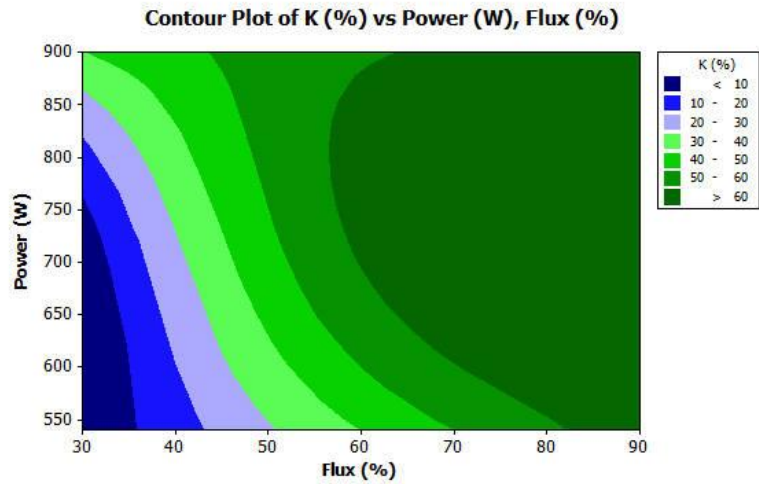
S.No	CaCl ₂ fused (%)	Charcoal (%)	Time (min)	Power (W)	K extraction (%)
1	30	10	4	540	1.1
2	30	15	6	720	4.2
3	30	20	8	900	39.5
4	60	10	6	900	58.6
5	60	15	8	540	40.2
6	60	20	4	720	61.5
7	90	10	8	720	68.6
8	90	15	4	900	63.4
9	90	20	6	540	65.2
10	90	20	8	900	66.8



(a)



(b)



(c)

Fig. 4.23. Contour plots showing the effects of (a) Charcoal and CaCl₂ (fused) (b) Power and charcoal (c) Power and CaCl₂ (fused) on K recovery.

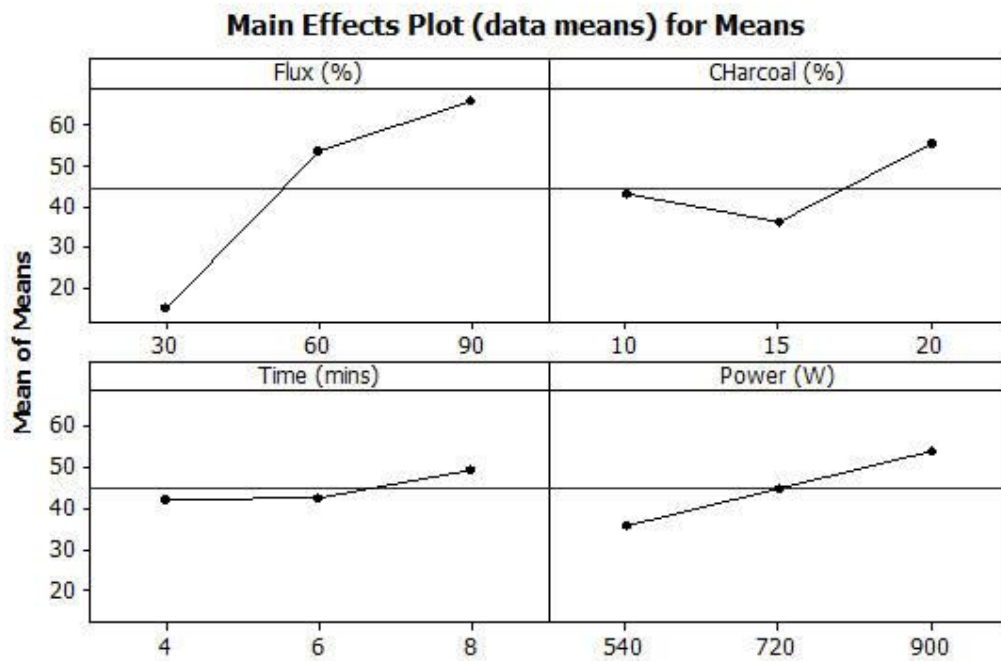


Fig. 4.24. Main effect plot for mean.

The regression equation is

$$K (\%) = - 72.9 + 0.847 \text{ Flux } (\%) + 1.26 \text{ Charcoal } (\%) + 1.86 \text{ Time (mins)} + 0.0509 \text{ Power (W)}$$

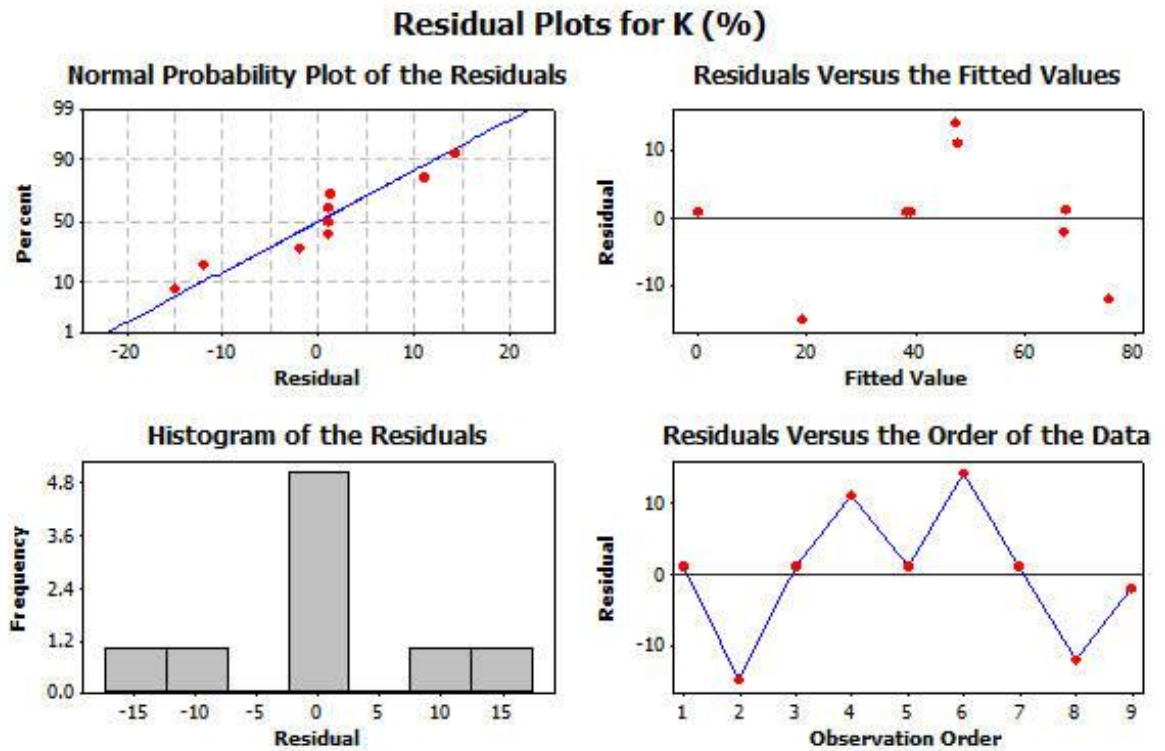


Fig. 4.25. Residual plots for K%.

By means of Microwave assisted heating using CaCl_2 (fused) as flux, maximum % K extraction was 68.6% which is less than muffle furnace heat treated. This shows that muffle furnace is more effective but we need to work on to find out way to reduce heat treating temperature so as to make it more economical.

4.5 EXPERIMENTS USING MECHANICAL ACTIVATION (MA) FOLLOWED BY MUFFLE FURNACE HEATING:

K has been extracted to maximum 83% using CaCl_2 (fused) as flux in muffle furnace, to go beyond this increase in temperature and flux % is not working, so mechanical activation has been used. In this K-rock and flux were mixed in required percentage and mechanically activated (MA) using planetary ball mill for 8 hours, followed by water leaching. Experiments were performed, first to direct MA was leached in water to check whether by MA was it possible to extract K. Result of direct leaching in water was only 17% but it shows that MA is working. Next step was to heat treat using muffle furnace, 60% CaCl_2 (fused) was used as flux and at 600°C, 700°C, 800°C and 900°C with varying time 15min, 30 min, 45min and 60 min shown in graph. This experiment provided some good results, in graph we can see that

increasing temperature %K has increased but has given maximum at 800°C and at 15 min only. This shows that MA has worked, as during MA due to high impact, flux and K-rock has fused to such extent that energy required to form reaction has decreased and reaction kinetics has also increase at much low time i.e. only 15 min it showed complete possible extraction.

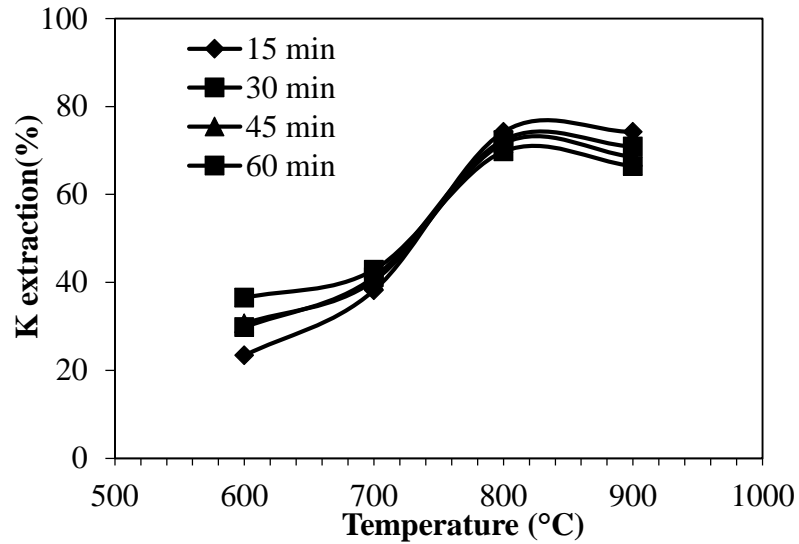


Fig. 4.26. Effect of temperature for different time in % K extraction using MA then muffle furnace heating followed by water leaching.

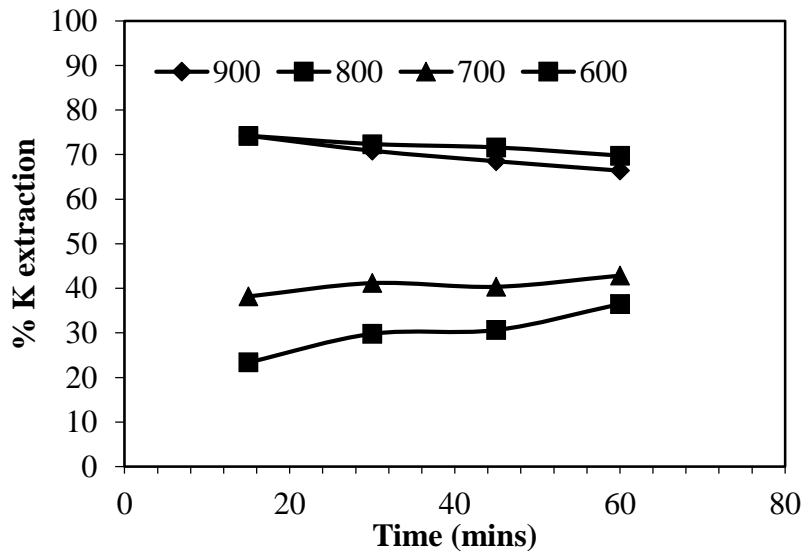


Fig. 4.27. Effect of time for different temperature in % K extraction using MA then muffle furnace heating followed by water leaching.

So, Taguchi design was performed to optimise the %K extraction using L9 Taguchi orthogonal array was used to conduct experiments with four factors. The three factors were CaCl₂ dosage, time and temperature, whereas a corresponding potassium extraction as obtained from leaching

experiments was considered as the response variable. The control factors with their selected levels for the experiments are given in Table 4.7.

Table 4.7. Control factor and level for design.

Control factor	Level		
	1	2	3
CaCl ₂ fused (%)	30	60	90
Time (min)	30	60	90
Temperature (°C)	700	800	900

Using the Taguchi design for three factor and three level total nine experiments were performed, for all design experiments % K extraction was as given in Table 4.8. This data were further analysed using contour plot of % K extraction having two variables at a time.

Table 4.8. Taguchi design experiment and respective % K extraction having factor CaCl₂ (fused) dosage, temperature and time.

S.No	CaCl ₂ fused (%)	Time (min)	Temperature (°C)	K extraction (%)
1	60	90	900	44.05
2	30	60	900	7.53
3	90	30	900	82.47
4	30	90	800	10.36
5	90	60	800	85.45
6	60	30	800	72.11
7	90	90	700	84.52
8	60	60	700	38.52
9	30	30	700	12.71

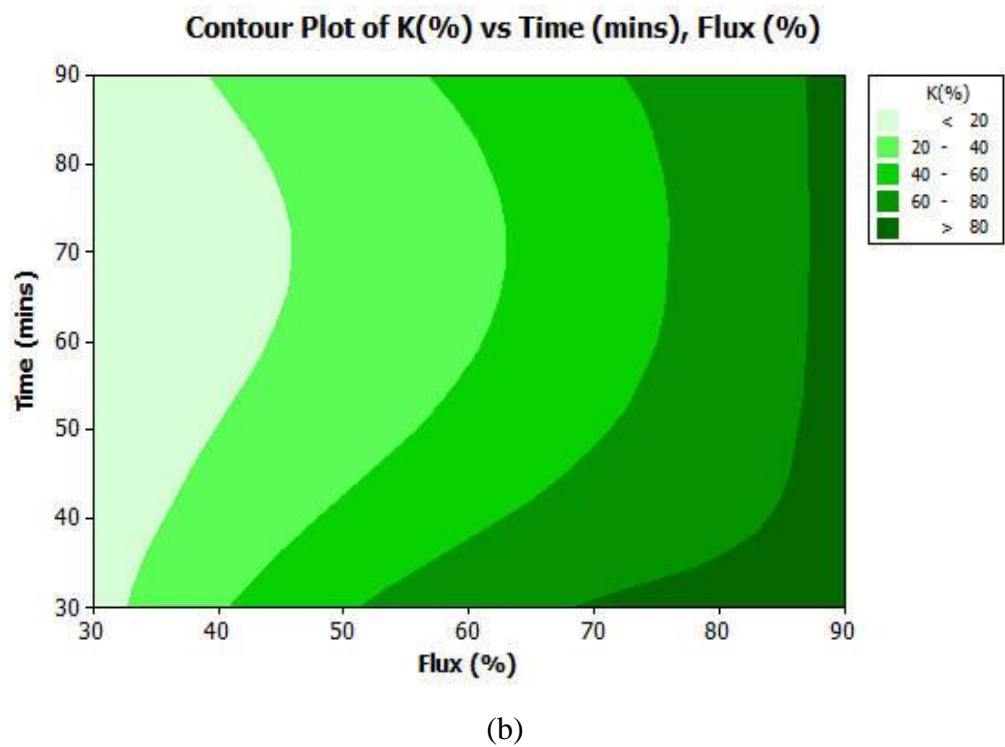
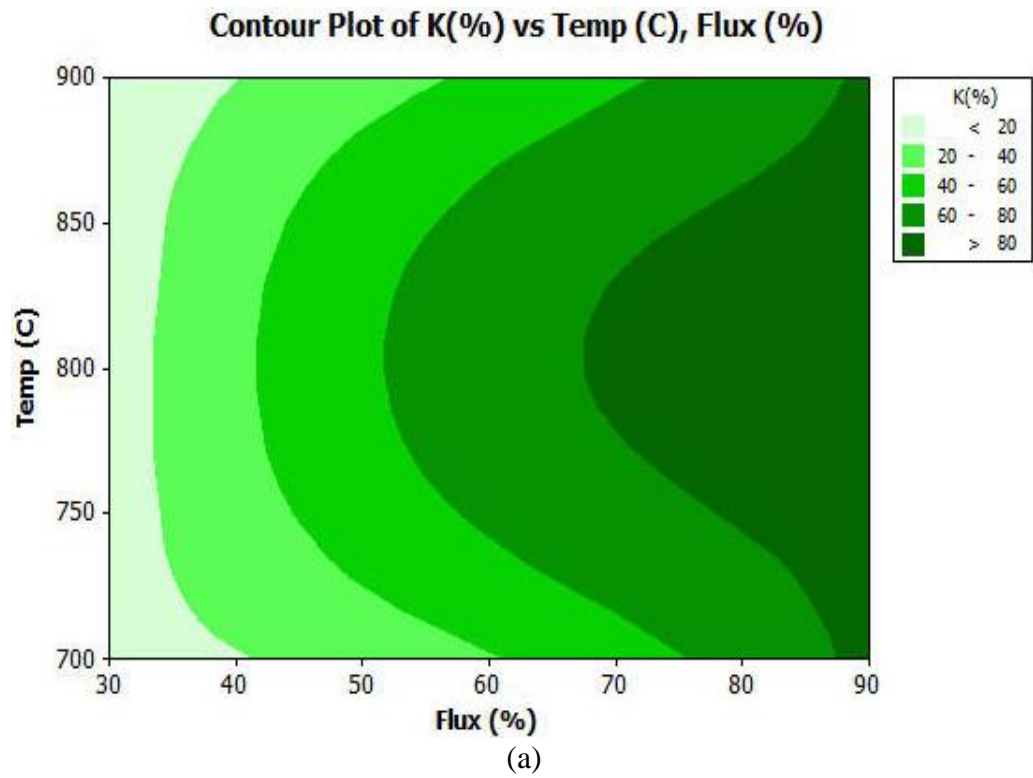


Fig. 4.28. Contour plots showing the effects of (a) Temperature and CaCl₂ (fused) (b) time and CaCl₂ (fused) on K recovery.

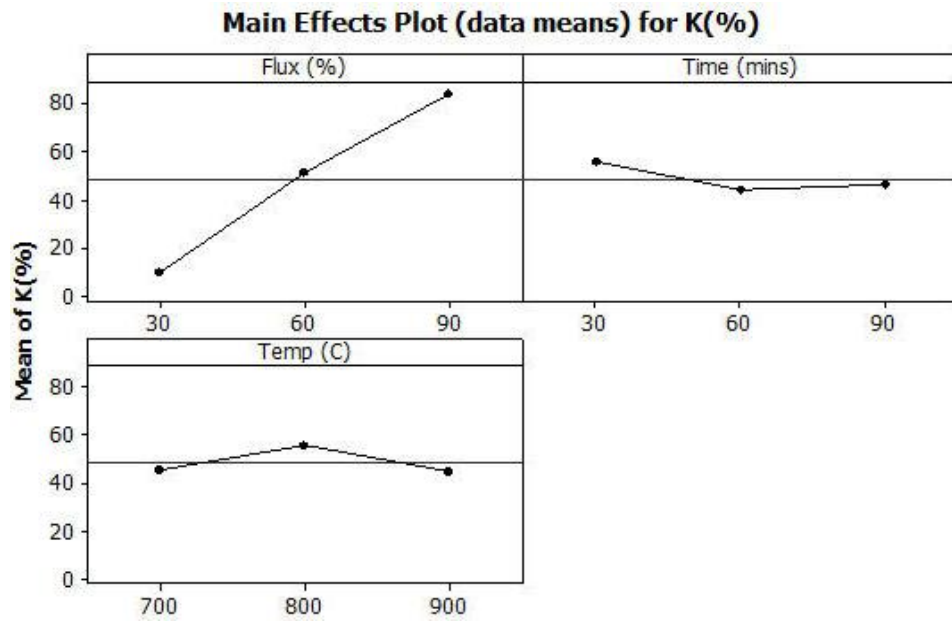


Fig. 4.29. Main effect plot for K% using mechanical activation followed by muffle furnace heat treatment.

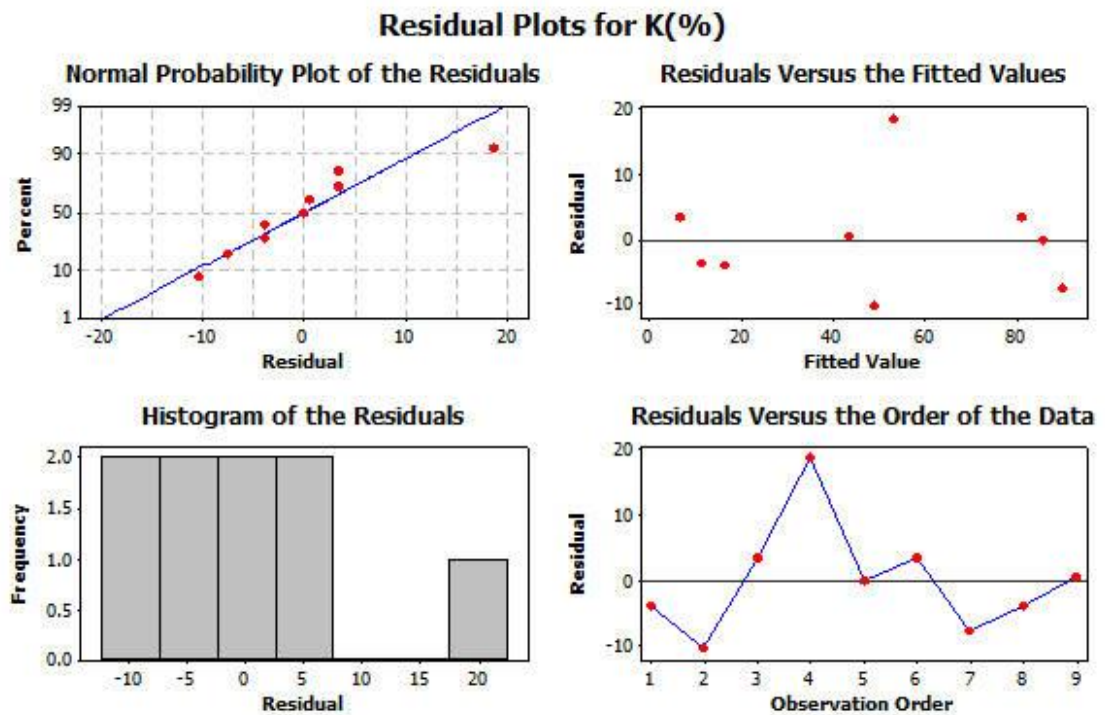


Fig. 4.30. Residual plot for K%.

The regression equation is

$$K(\%) = -13.6 + 1.23 \text{ Flux}(\%) - 0.158 \text{ Time}(\text{mins}) - 0.0028 \text{ Temp}(\text{C})$$

As using CaCl_2 (fused) as flux we achieved %K extraction up to 84.52% which is maximum till now, but to go beyond this we tried using NaOH as in muffle furnace it was successful so we tried this in MA followed by muffle furnace.

XRD analysis of CaCl_2 (fused) treated sample of all the routes explains all the formation and dissolution of phases has been given in Fig. 4.32. In all the routes of treatment we can see that sylvite phase has appeared in heat treatment, but without treating it with CaCl_2 (fused) at 900°C only peak intensity has decreased.

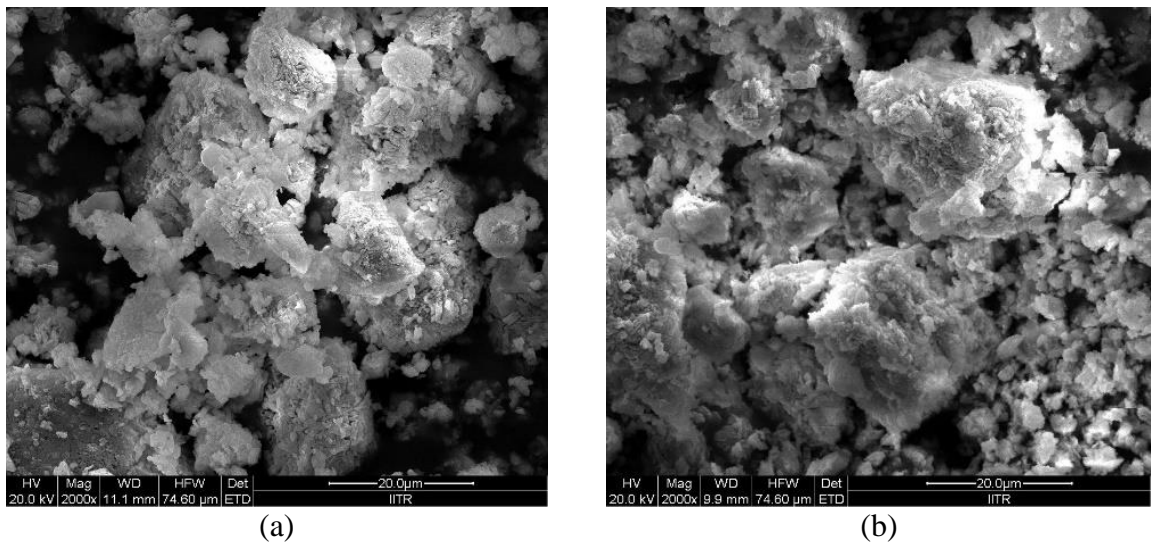


Fig. 4.31. SEM image of (a) Heat treated sample (b) leach residue sample.

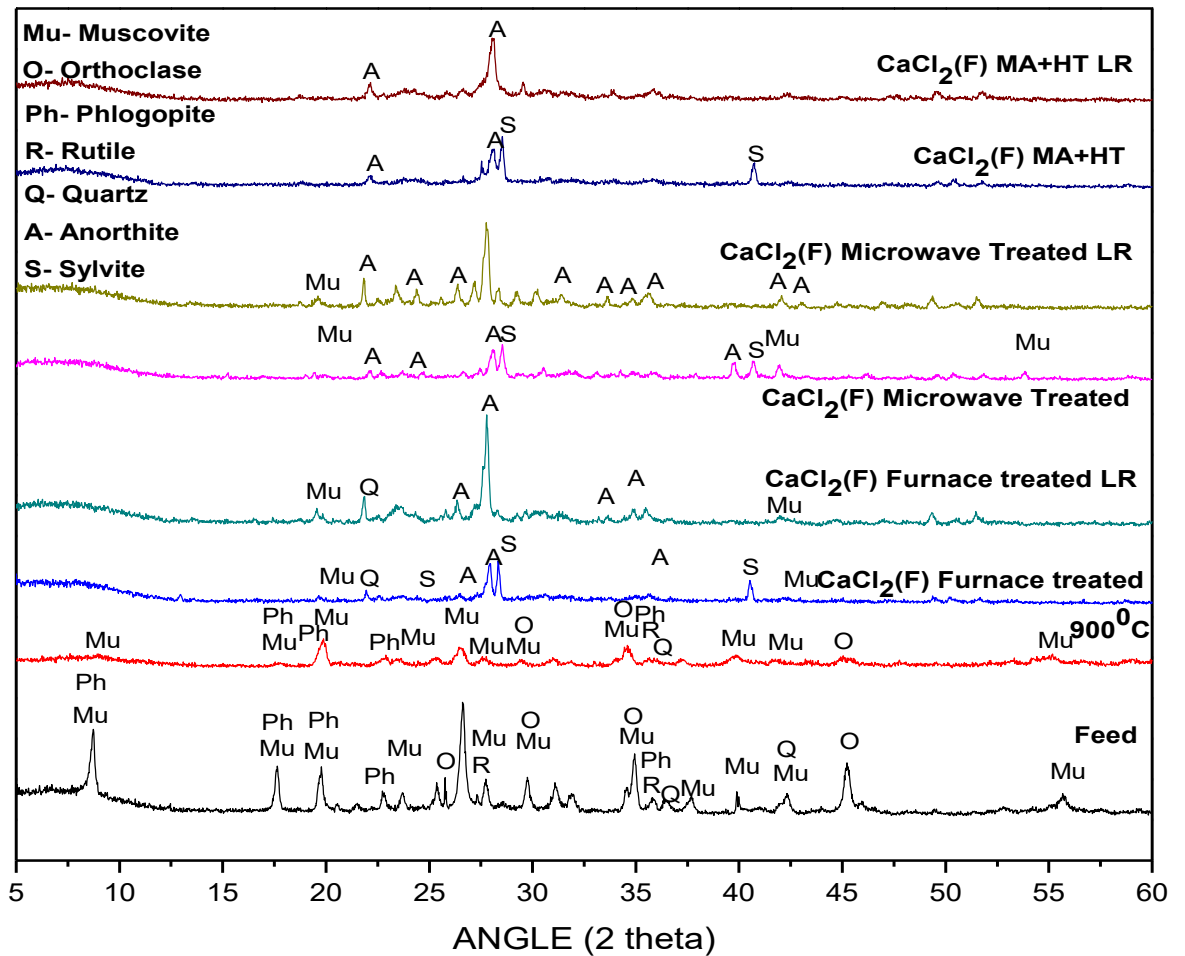


Fig. 4.32. XRD plot of CaCl_2 (fused) treated sample in all the extraction route.

First direct water leaching was tried of MA product, which gave %K extraction of 37.33%, this shows that MA is successful in the case of NaOH also. So experiment was moved forward by heating in muffle furnace of 90% NaOH MA feed at 200°C, 300°C, 400°C, 500°C and 600°C for 30 min, reason to go only up to 600°C is that without MA 600°C was best so with MA it is expected to be less than that temperature and time 30min was also chosen from previous experiment. The results are given in the Fig 4.33.

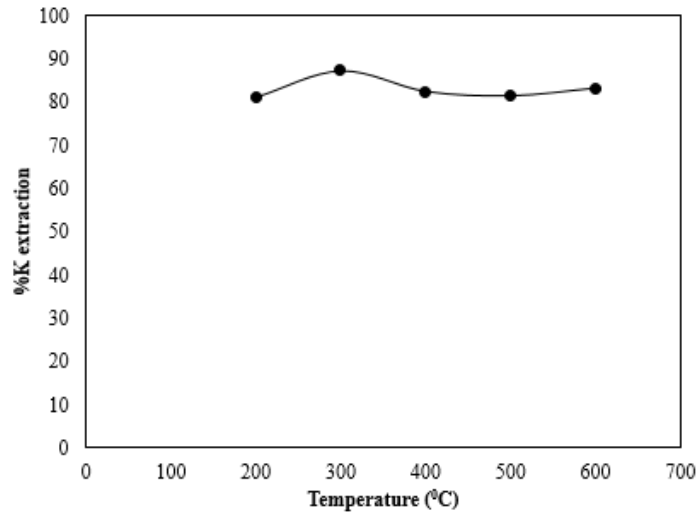


Fig. 4.33. Effect of variation of Temperature in %K extraction of 90% NaOH MA feed using muffle furnace.

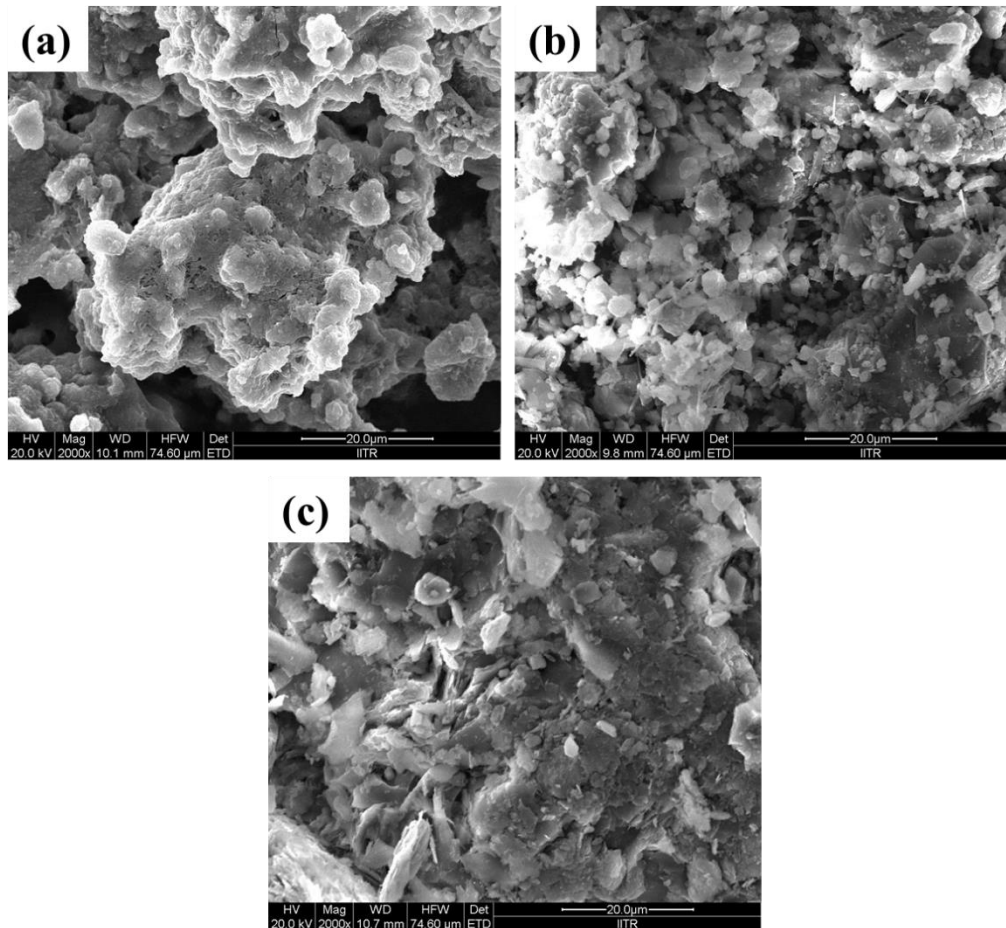


Fig. 4.34. SEM image of sample treated with 90% NaOH in MA+HT at 300°C for 30min (a) Heat treated sample (b) First leach residue (c) Second leach residue.

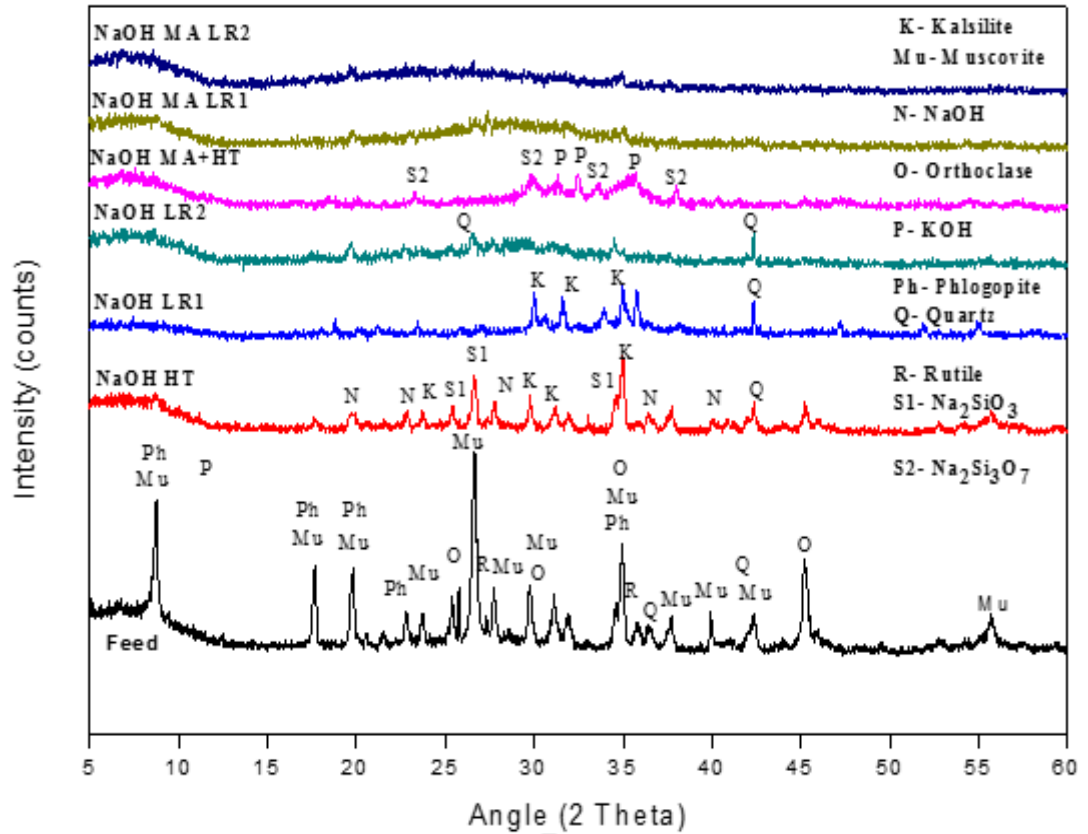


Fig. 4.35. XRD analysis of NaOH treated sample through muffle furnace and MA + muffle furnace route.

This clearly shows that % K extraction has increased from 200°C to 300°C but after heating further it has been decreased. So maximum %K extraction was 87.22% at 300°C for 30min of heat treatment. This provides a clear indication that during MA, flux and K-rock are getting completely fused in each other due to high impact.

So after using NaOH as flux we tried using calcium based fluxes using MA+ heat treatment route, we prepared 25%, 50% and 75% flux MA feed of CaCO_3 , CaSO_4 and $\text{Ca}(\text{OH})_2$. First we directly water leached it without heat treating and got the following results.

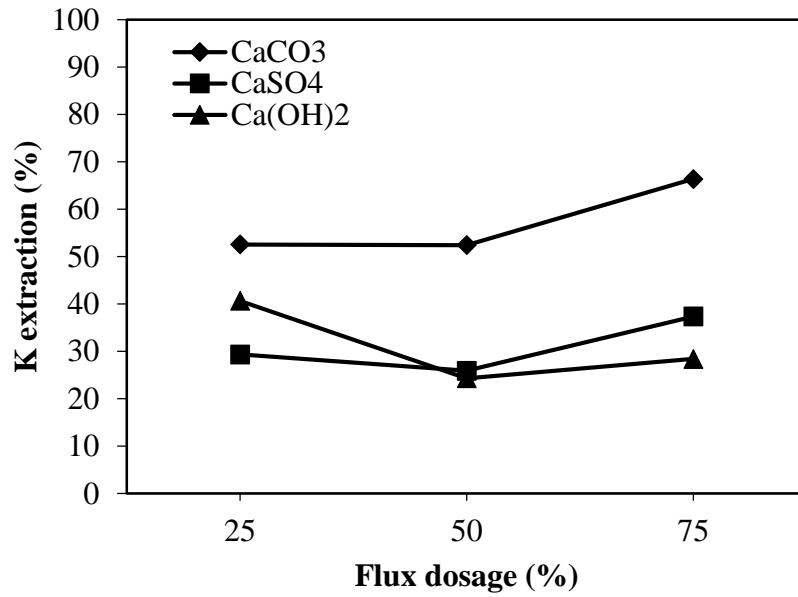


Fig. 4.36. Effect of variation in dosage% of CaCO₃, CaSO₄ and Ca(OH)₂ in %K extraction after MA without heat treatment leaching in water.

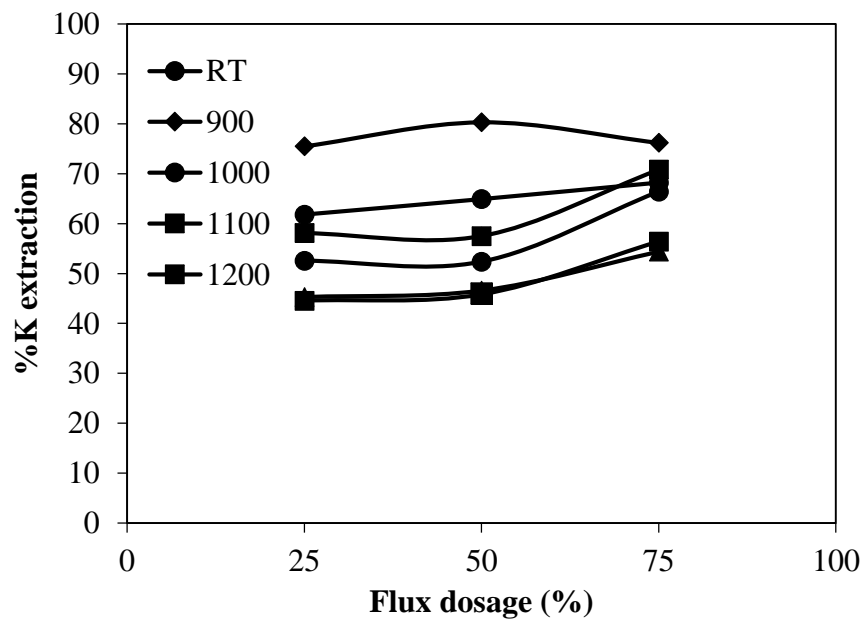


Fig. 4.37. Effect of temperature and flux dosage of CaCO₃ treated sample for 90 min.

We can see in graph that CaCO₃ as flux at 75% has leached 66.5% K, so to increase the %K extraction we started heat treating at RT, 300°C, 600°C, 900°C, 1000°C, 1100°C and 1200°C for 90min.

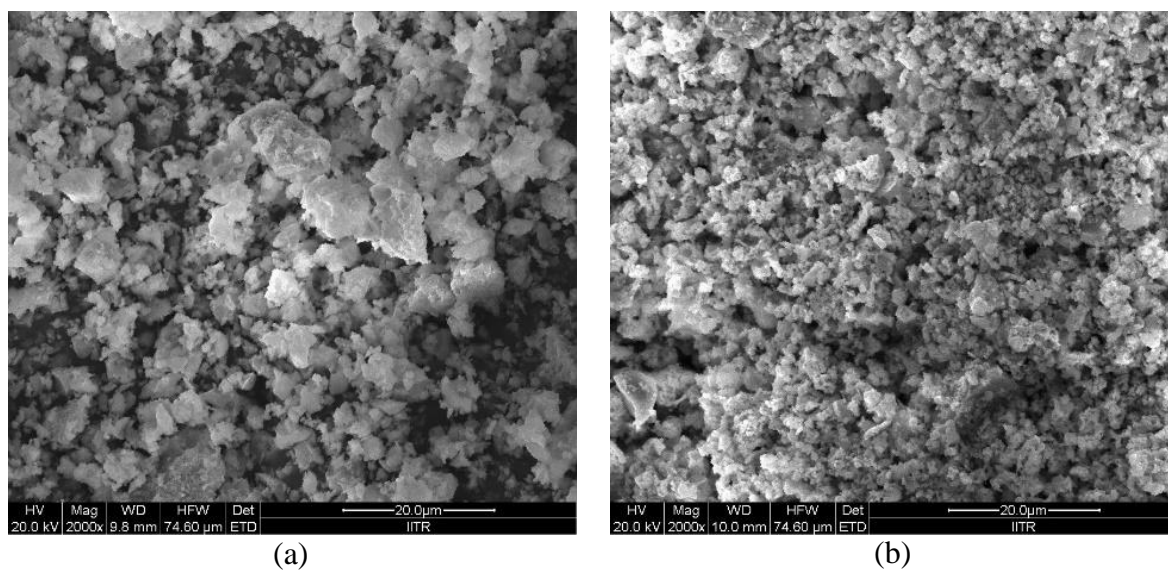


Fig. 4.38. SEM image of CaCO_3 75% treated sample for 30min (a) Heat treated (b) Leach residue.

As it can be seen that at 900°C we are getting maximum extraction by heat treating it for 90min. After getting the required temperature we optimised the heat treatment time at 900°C by heat treating it for 30, 60, 90, 120, and 150 min in muffle furnace. Effect of time in each dosage of flux is different, as dosage is increasing time to extract out maximum potassium is decreasing. Maximum %K was 87.83% at 30 min for 75% flux at 900°C .

Due to dehydration and dehydroxylation initial 11.26% mass loss can be seen from the TG curve up to 600°C . In DTA at 716°C there is an endothermic peak which is due to the decomposition of CaCO_3 , due to mechanical activation effective surface area has increased thus reactivity has also increased so decomposition temperature of CaCO_3 has decreased from 825°C to 716°C , corresponding mass loss can be seen from TG curve up to 729°C . Exothermic peak between 800°C and 900°C in DTA curve is attributed to the formation of new phase gehlenite which has been assured by XRD analysis [26].

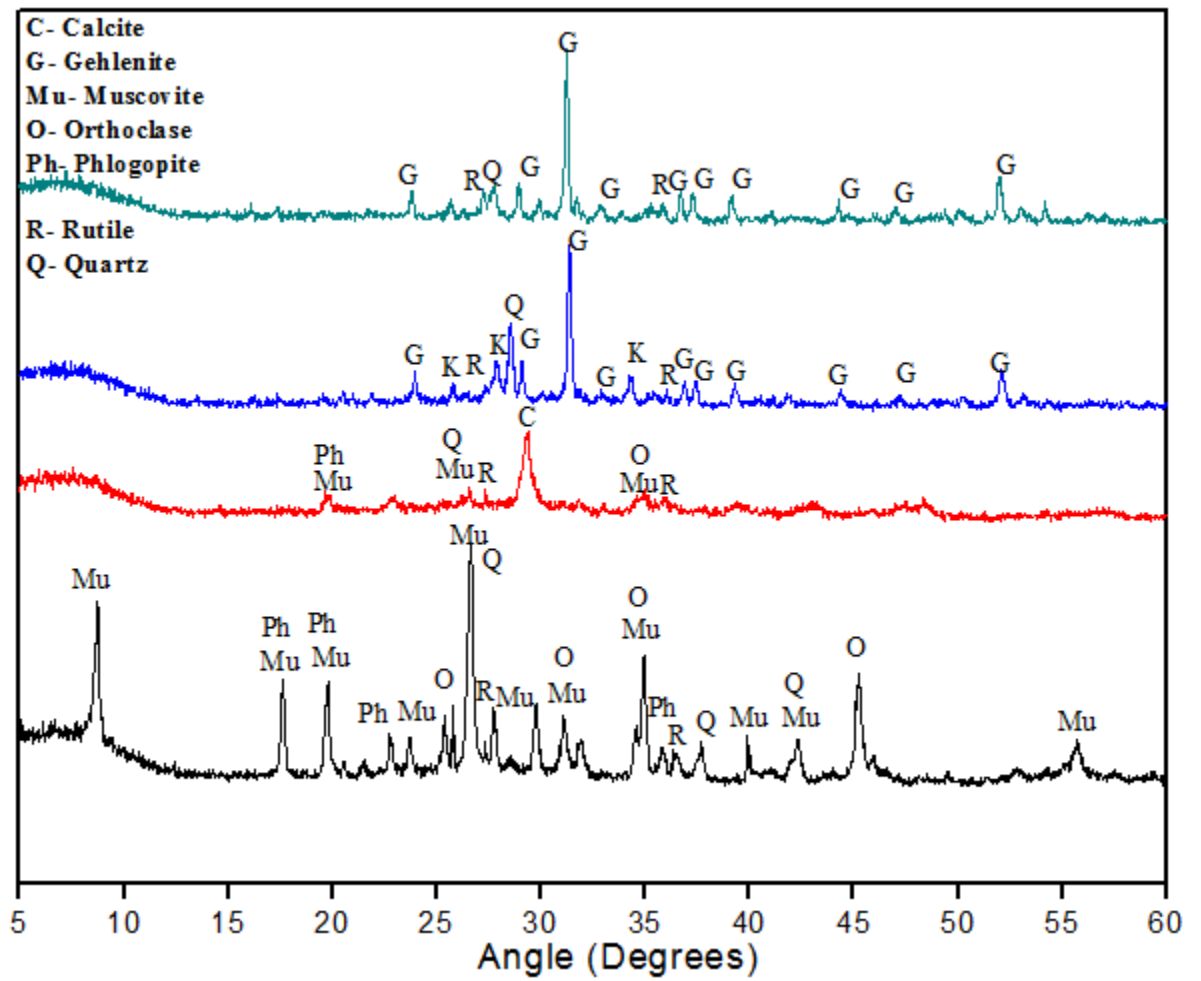


Fig. 4.39. XRD analysis of CaCO₃ treated sample.

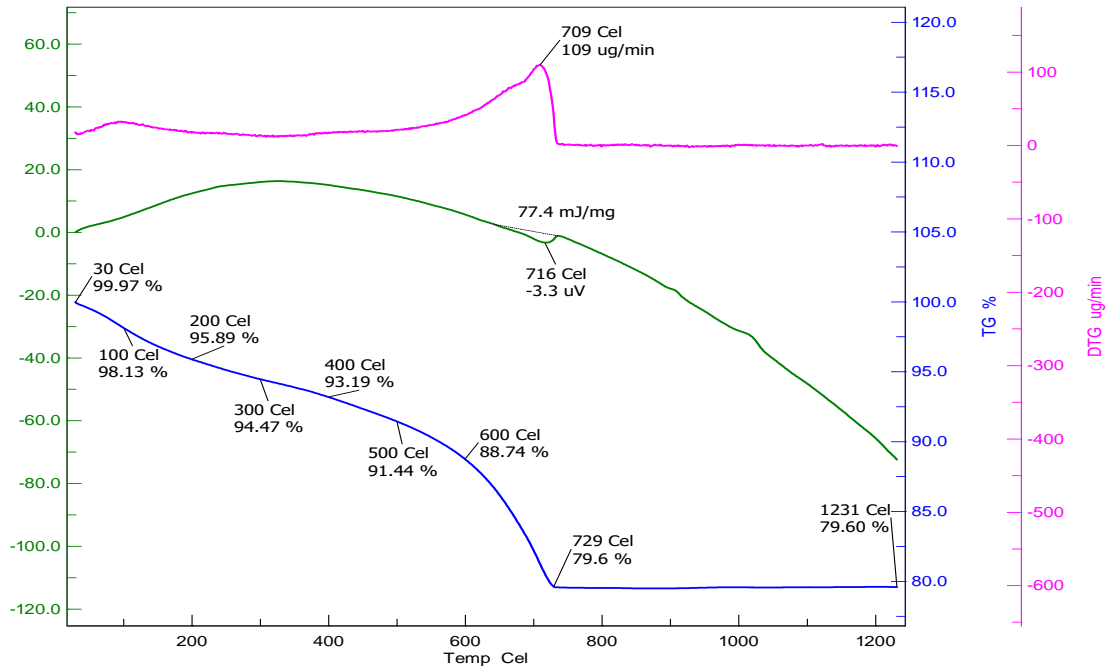


Fig. 4.40. DG/DTA analysis of 50% CaCO₃.

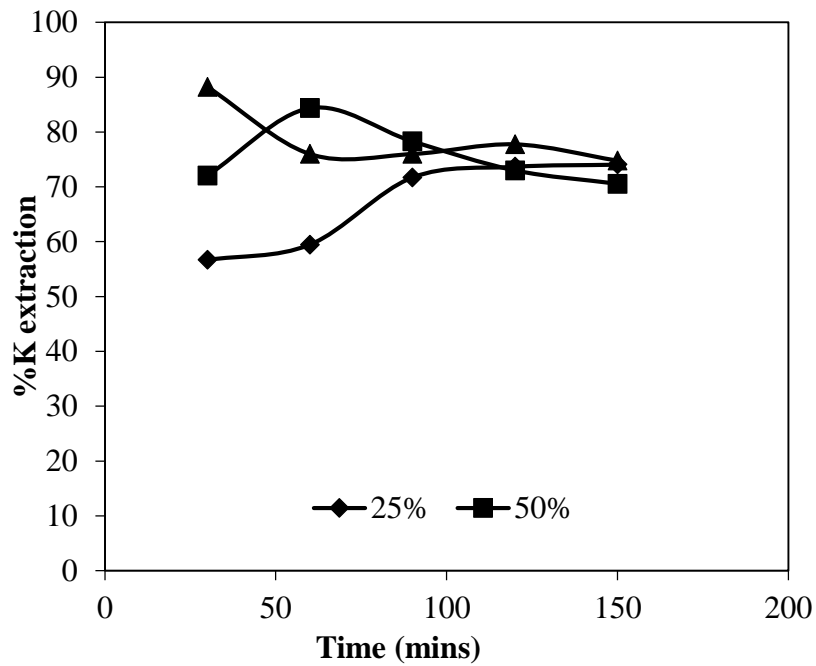


Fig. 4.41. Effect of time on CaCO₃ treated sample of 25%, 50% and 75% dosage sample.

Hence by comparing CaCl₂ (fused), NaOH and CaCO₃ as flux for treating K-rock. Comparing all this fluxes we see that NaOH has worked lot better than any other flux, %K extraction is 87% as well as heat treatment temperature is also only 300°C. Cost of fluxes are more or less same but environmental effect need to be considered.

Table 4.9. Comparison of CaCl₂ (fused), NaOH and CaCO₃ as flux in extracting K from K-rock using MA+heat treatment in muffle furnace

Parameter	Flux		
	CaCl ₂ (fused)	NaOH	CaCO ₃
K extraction (%)	84.52	87	87.83
Time (mins)	90	30	30
Temperature(°C)	800	300	900
Flux (%)	90	90	75
Cost of flux (Rs. Per Kg)	498	500	510
Medium of leaching	Water	2% Citric acid sol	2% Citric acid sol

4.6 COMPARISON OF FLUX CaCl₂ (FUSED) AND NaOH USED IN ALL THE TREATMENT PROCESS

All the three routes were able to extract K out the complex silicate structure, from muffle furnace treatment to microwave treatment to prior mechanical activation before muffle furnace treatment.

Using CaCl₂ (fused) as flux in all the three routes we got maximum %K extraction in muffle furnace treatment as well as in mechanical activation followed by muffle furnace treatment approx. same around 84%, but going through mechanical activation we have achieved in decreasing the temperature to 800°C, but 800°C is also not so worthy as prior mechanical activation also needs energy which will become overall more than only muffle furnace treatment.

Table 4.10. K extraction percentage using different routes of extraction for CaCl₂ (fused) as flux.

Route	K extraction (%)	Conditions
Muffle furnace treatment	83	1000 ⁰ C, 90 min, 60% flux
Microwave assisted heating	68.6	720W, 8 min, 90% flux
Mechanical activation followed by muffle furnace treatment	84	800 ⁰ C, 90min, 90% flux

So using CaCl₂ (fused) as flux will be kind of same for the muffle furnace treatment route and mechanical activation route. By comparing the extraction of this two route we find that %K extraction in with mechanical activation route is way higher that direct heat treatment in muffle furnace. When treated with muffle furnace only we needed 600°C to extract maximum 80.95% K whereas if prior mechanical activation has performed than extraction percentage has increased 87.22% and also temperature required for maximum extraction has also been decreased 300°C. This shows a huge breakthrough by decreasing the temperature to much low and increasing the %K extraction. Mechanical extraction has worked way lot than then just heat treating the sample.

Table 4.11. K extraction percentage using different routes of extraction for NaOH as flux.

Route	K extraction (%)	Conditions
Muffle furnace treatment	80.95	600°C, 30 min, 90% flux
Mechanical activation followed by muffle furnace treatment	87.22	300°C, 30 min, 90% flux

Outcome of the comparison is that extraction of potassium in handmix sample is good in both the fluxes but using mechanically activated sample potassium extraction has not only increased but also the temperature for maximum extraction has decreased. This shows that the effect of mechanical activation is favourable. So in the next section parameter of mechanical activation was varied and the effect was analysed.

4.7 EXPERIMENTS USING MECHANICAL ACTIVATION:

Mechanical activation of feed sample was performed by varying the milling time from 4 hr to 16 hr and leaching was done in water, 2% citric acid, HCl, HNO₃ and H₂SO₄. In the case of water leaching the potassium extraction was less than 10% as shown in Fig 4.42. Same mechanically activated feed sample was leached in 2% citric acid and the potassium extraction was 75%, which is a very good number as without flux and temperature. Not only in citric acid but in HNO₃, HCl and H₂SO₄ was also good which is shown in Fig 4.43, Fig 4.44, Fig 4.45 and 4.47.

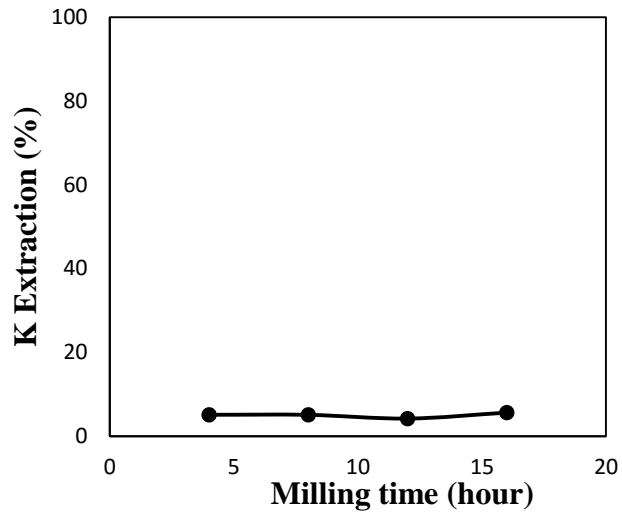


Fig. 4.42. Effect of milling time in the K extraction in water leaching of sericite feed sample.

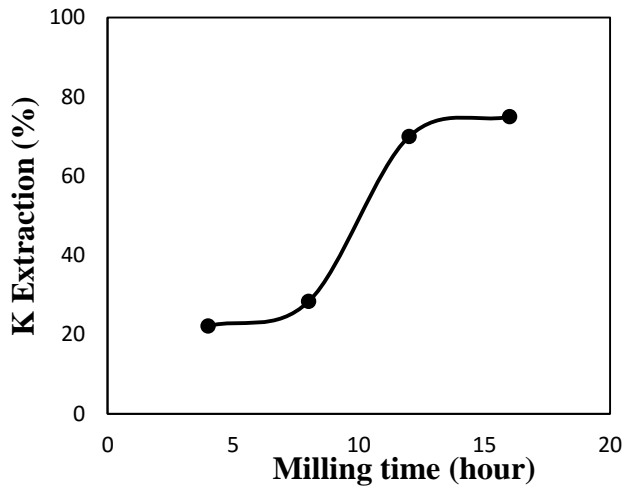


Fig. 4.43. Effect of milling time in the K extraction in 2% citric acid leaching of sericite feed sample

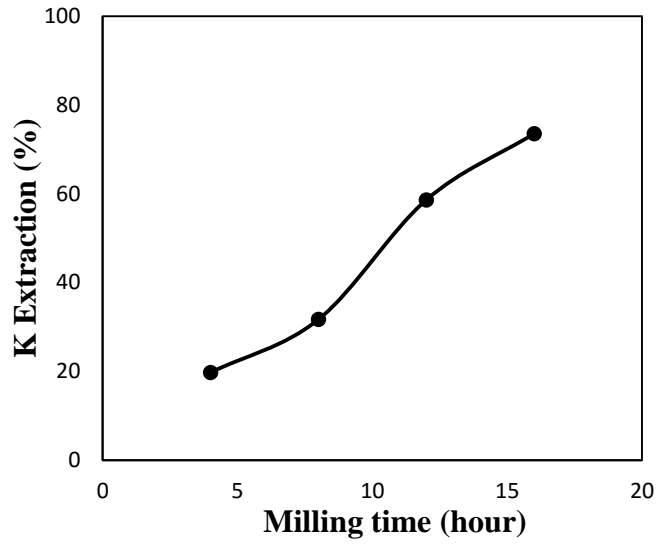


Fig. 4.44: Effect of milling time in the K extraction in HNO₃ acid leaching of sericite feed sample

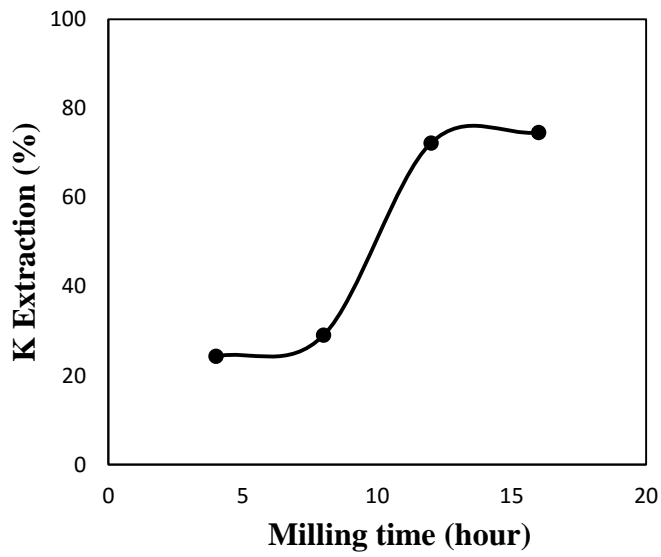


Fig. 4.45: Effect of milling time in the K extraction in HCL acid leaching of sericite feed sample

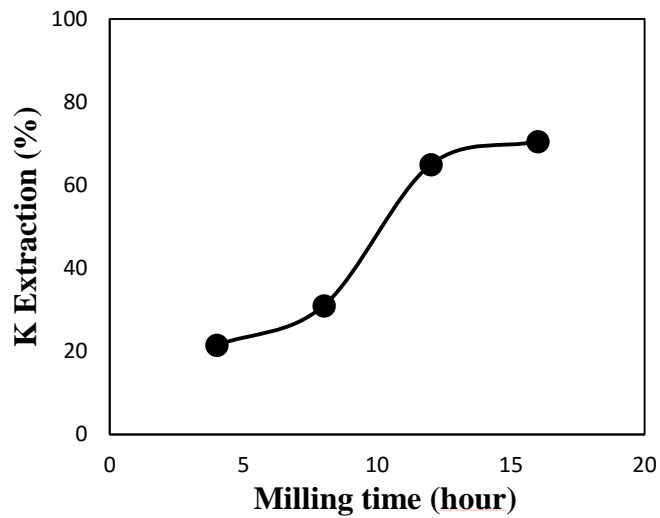


Fig. 4.46: Effect of milling time in the K extraction in H₂SO₄ acid leaching of sericite feed sample

This results shows that due to extensive milling potassium is getting liberated from the structure and without heat treatment also it is dissolving in the leach solution. So milling with flux Ca(OH)₂, CaSO₄ and CaCO₃ was also tried.

Firstly the dosage percentage was fixed by varying the dosage percentage for K extraction and the best dose for each flux was selected and mechanical activation was performed at that percentage of dose of flux.

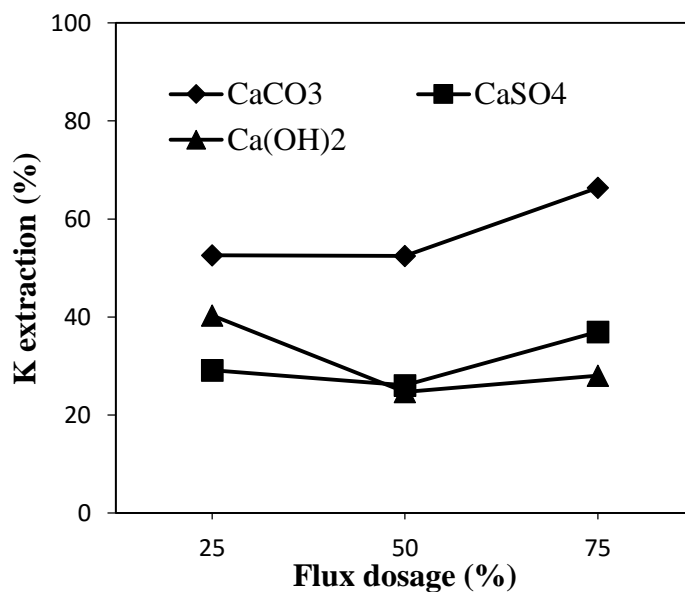


Fig. 4.47: Effect of variation of flux dosage of mechanically activated sample for the flux Ca(OH)₂, CaSO₄ and CaCO₃.

Milling time variation was performed for the selected dosage of flux. In the case of Ca(OH)_2 , CaSO_4 and CaCO_3 the best dosage was 25%, 75% and 75% shown in Fig 4.48, 4.49, and 4.50. In the case of CaCO_3 maximum K extraction of more than 90% was achieved.

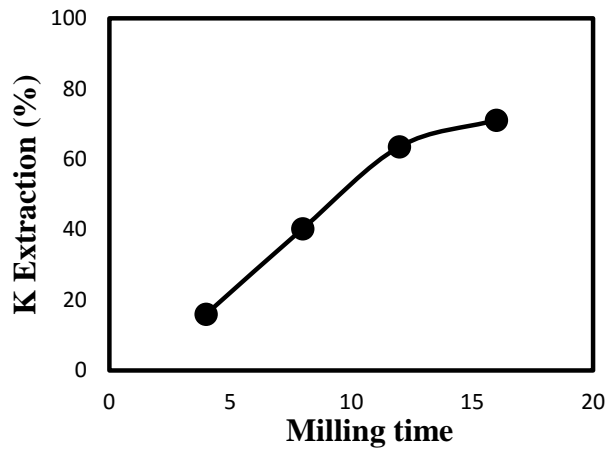


Fig. 4.48: Effect of milling time in the K extraction in 2% citric acid leaching of sericite feed mixed with 25% Ca(OH)_2 sample.

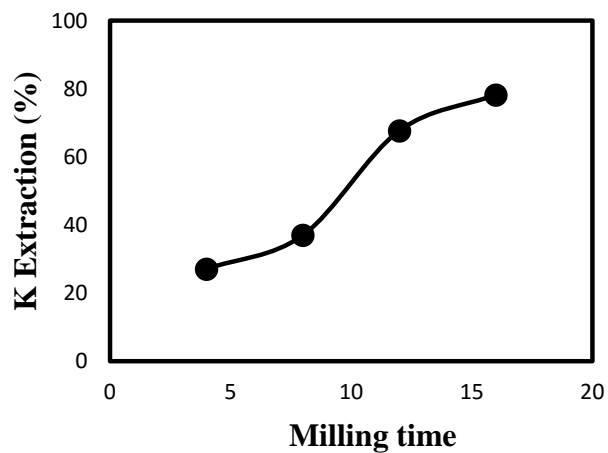


Fig. 4.49: Effect of milling time in the K extraction in 2% citric acid leaching of sericite feed mixed with 75% CaSO_4 sample.

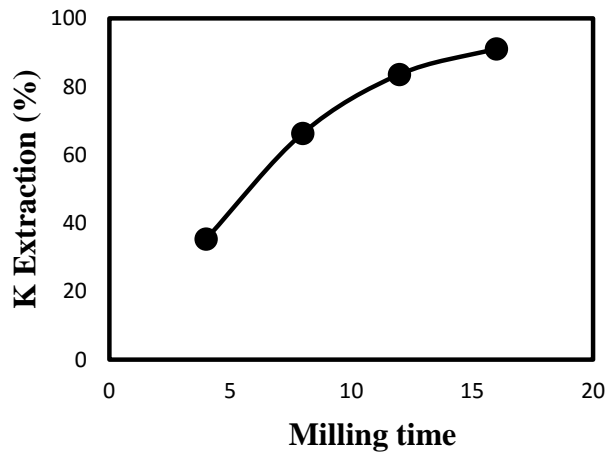


Fig. 4.50: Effect of milling time in the K extraction in 2% citric acid leaching of sericite feed mixed with 25% CaCO₃ sample.

In experiments different fluxes were tried with different process route and gives final outcome:

1. Leaching with different lixiviant without flux and heat treatment is ineffective.
2. Extraction using flux $\text{CaCl}_2(\text{F})$ and NaOH with heat treatment was limited to 80%, but in the case of mechanical activation and heat treatment it was impressive for NaOH as temperature of maximum extraction gone down to 300°C and extraction was 87%.
3. Mechanical activation played a vital role in the liberation. Leaching of feed sample in 2% citric acid was 75% without providing heat treatment.
4. Mechanical activation using CaCO_3 as flux of milling time of 16 hr was the best among all the extraction route, it gave above 90% extraction without any heat treatment.

PUBLICATIONS/ PRESENTATIONS

Journal

Yogendra Pratap Singh, **Gulshan Kumar Pradhan**, Nikhil Dhawan, COMPARISON OF EXTRACTION OF POTASH VALUES FROM DIFFERENT ALUMINO-SILICATE ROCKS, submitted to Minerals Engineering, 2016.

Conference Proceedings

Gulshan Kumar Pradhan, Yogendra Pratap Singh, Nikhil Dhawan, SILICATE ROCKS (SERICITE) - A SOURCE OF POTASH FOR FERTILIZERS, Paper ID: Material- 27, India International Science Festival (IISF), 4-8 December, Delhi.

Nikhil Dhawan, Yogendra Pratap Singh, **Gulshan Kumar Pradhan**, SILICATE ROCKS (GLAUCONITE) - A SOURCE OF POTASH FOR FERTILIZERS, Paper ID: 869, Symposium: Extractive Metallurgy: Hydro and Pyrometallurgy, IMPC 2016, Canada.

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