

DISSOLUTION BEHAVIOUR OF POTASSIUM FROM MICACEOUS MINERALS

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requirements for the award of the degree*

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(With specialization in Physical Metallurgy)

BY

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the dissertation, entitled “**DISSOLUTION BEHAVIOUR OF POTASSIUM FROM MICACEOUS MINERALS**” in partial fulfilment of the requirements for the degree of **Master of Technology** in the **Department of Metallurgical and Materials Engineering with specialization in “Physical Metallurgy”**, Indian Institute of Technology Roorkee, is an authentic record of my own work carried out during the period from May, 2015 to April, 2016 under the supervision of **Dr. Nikhil Dhawan**, Assistant Professor, Department of Metallurgical and Materials Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter embodied in the dissertation has not been submitted to any of the University/Institute for the award of any other degree.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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LIST OF ABBREVIATIONS

| | |
|----|--------------------------|
| MA | Mechanical activation |
| MW | Microwave |
| Mu | Muscovite |
| M | Microcline |
| G | Glaucosite |
| Q | Quartz |
| K | Kalsilite, Kaliophilite |
| W | Wollastonite |
| S | Sylvite, Sodium Silicate |

ABSTRACT

Potassium (K) is one of the essential elements for the growth of plants and thereby for humans. It is vital for many plant functions such as carbohydrate metabolism, enzyme activation, osmotic regulation and protein synthesis. In fertilizers, potash demand has been steadily increasing at ~3.5% annually. Water soluble potash deposits are rare and highly localized. India is neither present on the world potash production map nor it has adequate soluble potash rich deposits such as sylvite, Sylvinite, carnalite etc. The K-bearing minerals are recovered either by using conventional underground mining methods or through solution mining methods. At present, India is importing all its potash (about 2 million tons per annum) from different countries. However, India possesses a vast resource of micaceous minerals in the form of glauconite and it is mainly found in Madhya Pradesh, Gujarat, Uttar Pradesh, Rajasthan and Uttarakhand. These rocks are basically a group of alumino silicate of potassium, sodium and calcium ($K_2O\%$: 5-12, $Na_2O\%$: 0-1%, $SiO_2\%$: 52-60, $Al_2O_3\%$: 15-20, $Fe_2O_3\%$: 5-9, $MgO\%$: 1-2). The K extraction from these minerals has received little attention probably due to lack of scientific know how, economic considerations and not much awareness. It is important to exploit these resources to substitute some import of potash in the country and to provide self-dependency in potash production. The strong chemical bonding of potassium in these minerals makes the mineral dressing route futile. In present work, an attempt has been made to extract potassium in form of some soluble salt under different routes such as acid leaching, thermal treatment with and without fluxing agents followed by leaching, microwave treatment and mechanical activation. These different treatments are targeted to increase K availability/solubility which is related to the modifications in mineral structure and possible exchange reactions of the suitable ions in the system. The modifications in the feed sample and treated samples are studied through SEM-EDAX, XRD, EPMA, TGA/DTA and Optical Microscope. With the combination of suitable fluxes and treatments, it is possible to get up to 96% K dissolution.

CHAPTER 1.

INTRODUCTION

Potash is an essential nutrient for plants and crops along with phosphate and nitrogen. The potash extraction is usually carried from buried ancient evaporites by underground or solution mining, brine from landlocked water bodies such as Dead Sea. Majority (95%) of potash produced in all world is used in agriculture and remaining is used in other industrial uses such as glass manufacturing, plastics, soaps and pharmaceuticals.

Most of the potash production comes from United states, Canada, Germany, France, Belarus, Russia and Ukraine because these countries have large deposits of soluble potash in form of sylvite (KCl), Sylvinite (KCl and NaCl) or carnalite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) [1]. India is nowhere in the production map of potash because India has no deposits of potash in soluble form. India imports all of its required potash from other potash rich countries because there is no commercial production of it. The current import of potash is around 2.0 million tonne with the cost of 1836.59 crores per annum and it will projected more in coming future because consumption of potash is continuously increasing [2]. India does not possess any water soluble source but there is large source of insoluble potash in form of silicate rocks such as mica and feldspar. As per United Nation framework classification (UNFC), India has 21,816 million tonnes of potash resources [3].

1.1 World Scenario of Potash-

The world reserves of potash are estimated at approximately 3500 million tonnes of K_2O content. It is found in Canada (31%), Belarus (21%), Russia (17%), China and USA (6% each), Chile and Germany (4% each). The world potash production was 34.3 million tonnes in 2013 as against 36.3 million tonnes in 2012. Canada was leading producer of potash with dominating 30% of total potash in 2013, followed by Russia (17%), Belarus (12%), China (10%), Germany (9%), Israel (6%), and Jordan & Chile (3% each) [3].

Potash production Chart

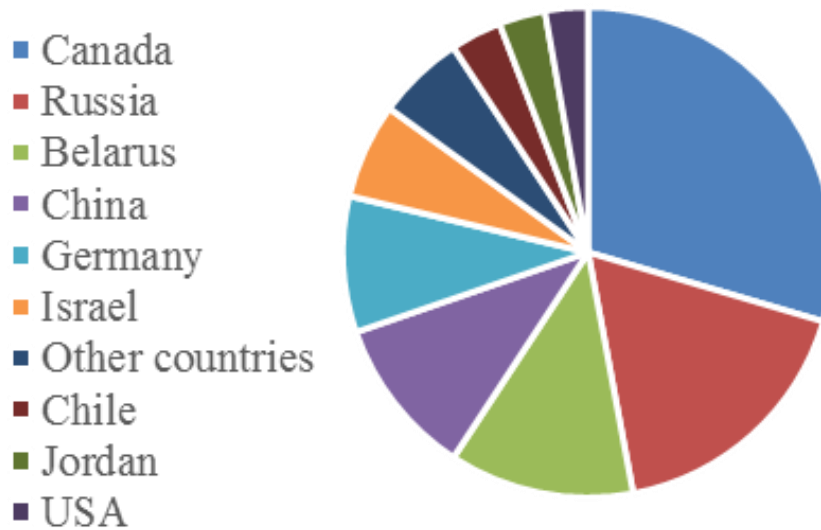


Fig. 1.2. Potash production Chart (Adapted by IBM).

1.1.1 Potash Source in India

In India, potash source exist mainly in the form of polyhalite, syloite and glauconite. However, there is no commercial exploitation of these sources in India so the entire requirement of potash for direct application and for the production of fertilizers is met through imports [3].

Rajasthan contributes 94% of total resources and Madhya Pradesh contributes 5%, followed by Uttar Pradesh 1%. Glauconitic sandstone deposits are available in plenty in India so Glauconite may be an indigenous resource of potash in India. It contains K_2O from 5.4% to 10%. Glauconite is often found in association with sand, shale, marl and sometimes with limestone also. The oldest deposit of glauconite of the country is in Madhya Pradesh and Uttar Pradesh. In Madhya Pradesh deposits are mainly in Satna and Sidhi district. The deposits of same origin are also found in Banda, Sonbhadra and Mirzapur district of Uttar Pradesh. Glauconite also found in Dehradun district, Uttarakhand. In Rajasthan glauconite deposits are present in Kota, Chittorgarh, and Jaisalmer and Barmer districts. In Gujarat, glauconite is found in Kachchh district. In Himachal Pradesh, glauconite is found in Kumla-Kathwar area of Sirmaur district [3].

Table 1.1. Potash reserves in India.

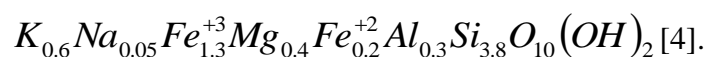
| Grade/State | Total Resources (In million tons) |
|-----------------|--------------------------------------|
| By Grade | |
| Glaucouite | 1968 |
| Sylvite | 2477 |
| Polyhalite | 16164 |
| Unclassified | 1206 |
| By State | |
| Rajasthan | 20419 |
| Madhya Pradesh | 1206 |
| Uttar Pradesh | 190 |

1.2 Mica

Micas are an important group of phyllosilicate mineral and are found in all three rock types: Igneous, Metamorphic and Sedimentary. The most common mica minerals are Muscovite, biotite, Lepidolite and less common micas are found in form of Glaucouite and phlogopite. Mica is a family of approximately 30 minerals and all are types of sheet silicate minerals. They are light, soft and heat resistant mineral. In all micas, glaucouite which is interlayer deficient mica) had been used as slow acting potash fertilizer in England, Belgium, France, USA and Western Australia during pre-world war.

1.2.1 Glaucouite

Glaucouite consists of a group of dioctahedral, potassium, iron-rich, and phyllosilicate clay type minerals. Generally, it is found in olive green to greenish black color. Glaucouite is a group of hydrous, iron, potassium sheet silicates with a compositional range between smectite type glaucouite and mica type glaucouite end members. Its empirical chemical formula is



1.2.2 Glaucouitic Sandstone Structure

Glaucouite is a dioctahedral layer potassium sheet silicate which is made of complex potassium, aluminum and iron silicates having greater than 15% iron (III) oxide. It is described as an iron-rich illite with a structure much alike muscovite and consists of dioctahedral T-O-T

sheets. The octahedral sites contain more Fe^{3+} than Al^{3+} and significant amounts of Mg^{2+} and Fe^{2+} .

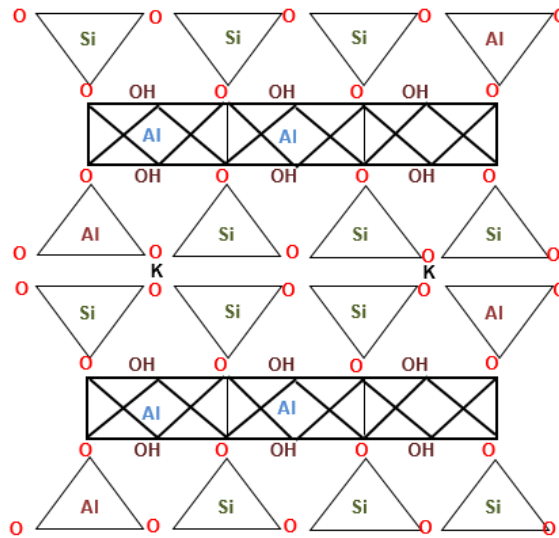


Fig.1.1. Structure of Mica.

So, the tetrahedral sites in glauconite contain lower amounts of Al^{3+} than in muscovite for compensation of the divalent cations in octahedral sites. In mica structure), the octahedral sheet is in the middle of two tetrahedral sheets and these three sheets are combined into one layer with suitable replacement of OH and O. Due to replacement of 25% Si with Al, charge deficiency in the structure is generated which is compensated by inter-layered K^+ ions. In glauconite Al can substitute for 4.2 to 17.5% of the Si in tetrahedral sheet.[4]. Glauconite structure is assumed to be similar to mica and often appears in rounded ill formed platelets, which are not similar to mica and muscovite [4].

1.2.3 Properties of Glaucosite

Table 1.2. Properties of glaucosite.

| | |
|-----------------------------|---|
| Physical Properties | Luster- Dull, Earthy |
| | Color- Blue to green |
| | Cleavage- Perfect on {001} |
| | Fracture- Micaceous |
| | Density- 2.45 to 2.95g/cm ³ |
| Chemical properties | Chemical class- Phyllosilicate |
| | Group- Mica |
| | Formula- (K, Na) (Fe ⁺³ , Al, Mg) ₂ (Si, Al) ₄ O ₁₀ (OH) ₂ |
| Crystallographic properties | Crystal system- monoclinic |
| | Cell parameters a= 5.23Å, b=9.06 Å, c=10.16 Å and β=100.5° |

1.2.4 Important Properties of Glaucosite for this study

Magnetic Susceptibility- Glaucosite has a variable paramagnetic susceptibility and therefore magnetic separation is a commonly used method for separating it from impurities [4].

Specific Gravity-The specific gravity of glaucosite ranges widely depending on the abundance of mixed layer minerals, potash content, the degree of substitution in the tetrahedral and octahedral sites and the extent of weathering. The specific gravity of glaucosite of various geologic ages ranged between 2.32 and 2.92 [4].

Thermal Characteristics- Typical thermal curves for glaucosite show weight losses between 80-255°C and between 520°-825°C. The first temperature range corresponds to dehydration, the second to actual decomposition of the mineral. Prolonged heating at 1,000°C results in the formation of maghemite which inverts into hematite [4].

CHAPTER 2.

LITERATURE REVIEW

In this study a detailed literature review was conducted prior to experimental work. The prime intention was to find the gaps in the research work. For the sake of brevity the entire literature review is shown in the following

2.1 Literature Overview

Table 2.1. Literature Review

| Sr. No | Ore Type/ Deposit | Experimental details | Key Findings | Ref |
|--------|--|--|---|-----|
| 1. | Glauconite $K_2O=6.6, SiO_2=51.8, Fe_2O_3= 17.1,$ $Al_2O_3= 6.2, CaO= 0.5, MgO=$ $3.6, Na_2O= 0.7, CO_2= 0.3, P_2O_5=$ $0.3 LOI= 9.9$ P. size: -850 μm | Roasting:500-550°C Action of mineral acids (H_2SO_4)- 40-60% with external heating. | Solubility increased with increase in temperature while roasting from 0.45% (unroasted) to 0.9% (roasted – 500-550°C).After treatment with sulfuric acid, sulfates were formed. | [5] |

| | | | | |
|----|---|--|---|------------|
| 2. | Glaucanite, Madhya Pradesh, India-SiO ₂ = 52%, Al ₂ O ₃ = 11.71%,Fe ₂ O ₃ = 15.97%,CaO= 4.21%,MgO= 1.82% K ₂ O= 5.4%,L.O.I= 7.80% P. size:-152 +125 μm | Crushing, Grinding, Acid leaching and Experiments were performed with HCl, HNO ₃ , H ₂ SO ₄ , H ₃ PO ₄ .200mL of HCl(1.5-6M)+5g of preheated glaucanitic sandstone stirred with desired speed for different time intervals (1-6hr). The same procedure was followed for other acids. | Extraction of potassium increased with increase in concentration of HCl, leaching time and temperature. Best results achieved (96% K-extraction) with 6M HCl at 378K , 3hr (450 rev/min ⁻¹) | [6] |
| 3. | Glaucanite | Mixture of 100 parts by wt. of greensand+ 50 parts of lime sand + 30 parts of CaCl ₂ was subjected to roasting (800-820 °C) | After roasting, green sand was dehydrated and CaCO ₃ decomposed to CaO. The action of CaCl ₂ on dehydrated green sand in the presence of CaO produced KCl. | [7] |
| 4. | Glaucanite ,Madhya Pradesh, India) SiO ₂ = 52wt%,Al ₂ O ₃ = 11.76%,CaO= 4.21%,Fe ₂ O ₃ = 15.97% MgO= 1.82%, K ₂ O= 5.4%L.O.I= 8.8% P.size-150μm. | Mixture of ore + CaCl ₂ .2H ₂ O [1:0.1 to 1:0.5 .] was roasted [5-180 min] at [700-850°C and leaching was done with hot water (70°C) for 10min. Leaching of glaucanite sandstone was done by :H ₂ SO ₄ , (H ₂ SO ₄ + HF (few drops)) Mixture of glaucanite, anhydrous CaCl ₂ and CaCO ₃ was subjected to thermal treatment at 1200-1300°C to extract K in form of KCl. | %K extraction increased with roasting time and temperature. And decreased with increase in particle size. No effect of leaching time was observed. 33% K extraction was observed with H ₂ SO ₄ and it increases up to 77% when few drops of HF were added. | [8] [9] |
| 5. | Glaucanite from Verdete, Brazil K ₂ O=12.5% P.size:44 μm | Mixture comprising of verdete ore + phosphate mineral + muriate of potash + dolomite + soda ash was heated at 1100°C for an hour. | Solubility of K was about 8.4% in 2% citric acid solution | [10] |
| 6. | Verdete (glaucanitic rock) Brazil P. size:-150μm | Fluxing agents -CaCl ₂ .2H ₂ O, CaCO ₃ ,CaSO ₄ ,Ca ₃ (PO ₄) ₂ , NaCl, Na ₂ CO ₃ and LiCl, Temp: 300,700,1100°C, Leaching agents: Water and 2% citric acid Chemical solubilization: Effect of acids and alkali (H ₂ SO ₄ ,HCl,H ₃ PO ₄ ,HNO ₃ and NaOH) was observed., Temp:25.8, 150,225 °C. | Almost 100% K extraction by using LiCl and CaCl ₂ .2H ₂ O as flux. Alkaline reagent (NaOH-60% solubilization H ₃ PO ₄ (42.3% solubilization) was found to be more effective than other acids. | [11] |
| 7. | Ore: K-bearing substances (K-feldspar, leucite, sericite, glaucanite, other silicate rocks) | K-bearing minerals were mixed with CaF ₂ and heated to high temperature such that all the K present was volatilized. The fumes were brought into solution and then the K salts were recovered from the solution. | Good results were obtained when quantity of CaF ₂ used was equal to quantity of potash in K bearing substance. Temp was kept high enough for volatilization of K. | [12] |

| | | | | |
|-----|---|---|---|------|
| 8. | Ore: Muscovite Yichang, China K ₂ O = 3.94 % | Muscovite mixed with BaCl ₂ . 2H ₂ O in 0.5 M HCl and kept on stirring in thermostatic water bath. Filtrate was then dried for 12 hrs. At 90°C. | 29% extraction occurred under optimum conditions. | [13] |
| 9. | Ore: K-bearing mineral | Mixture of mineral and Al ₂ (SO ₄) ₃ was heated to 100°C to form K ₂ SO ₄ thereby extracting K ₂ SO ₄ with water. | Al ₂ (SO ₄) ₃ was used slightly in excess to ensure complete conversion of K present in mineral to K ₂ SO ₄ | [14] |
| 10. | Ore: K-feldspar Baixin, China Na ₂ O = 0.08%, K ₂ O = 11.48% Al ₂ O ₃ = 15.94%, SiO ₂ = 66.88%, CaO = 0.95% Fe ₂ O ₃ = 2.56% | The ore was subjected to crushing, grinding and drying at 120°C for 24hr. Powder was mixed with CaSO ₄ and shaped into tablets then kept in furnace at 1100-1120°C for 0.5-2 hr. After treatment, the tablets were cooled and milled. The calcined powder was then dispersed in DI water (1:3) and kept in autoclave filled with CO ₂ (0.3-4.0 MPa, T= 50-150°C, t=2hr). Then, the slurry was filtered to separate K-rich filtrate and CaCO ₃ rich slag. | Under optimum condition, 87% K extraction was observed. The reaction of K-feldspar with CaSO ₄ is a solid-solid reaction and reaction depends on ion diffusion and solid reaction activity. Solid state reactions can be sharply accelerated at temp near m.p. of reactants. | [15] |
| 11. | Ore: K-Feldspar Location: Shandong Province, China P. size: 45µm | K-feldspar and CaCl ₂ .6H ₂ O were mixed and calcined to 800°C to form Ca silicates. The calcined sample was cooled and washed by distilled hot water (80°C) | At 800 °C, conversion of K-feldspar reached 84.7%. | [16] |
| 12. | Ore: Nepheline syenite Location: Odisha, India Composition: Fe ₂ O ₃ = 2.8%, Al ₂ O ₃ = 19.9% SiO ₂ = 55.5% K ₂ O = 5.4% Na ₂ O = 11.1% CaO = 3.8% LOI = 5.3% | Mixture of nepheline syenite and CaCl ₂ was roasted at 900°C for 30min. Leaching was done with water for 15min | Extraction of 99.6% K ₂ O was observed at 900°C | [17] |
| 13. | Ore: K-feldspar Location: Shaanxi province, China, Composition: SiO ₂ = 65 % Al ₂ O ₃ = 17.26% Fe ₂ O ₃ = 1.20% , MgO = 0.84 %, CaO = 0.61%, Na ₂ O = 1.09%, K ₂ O = 13.92% P.size: < 75µm | Alkaline solution comprising of KOH, NaOH, distilled water was prepared. K-feldspar was mixed with the alkaline solution and then kept on stirring in Ni hydrothermal stirring reactor at 240-280°C for 3hr. | Kalsilite and hydroxyl cancrinite were the products obtained after breaking of crystal structure of K-feldspar due to alkaline-hydrothermal process. | [18] |

| | | | | |
|-----|---|--|---|------|
| 14. | Phonolitic rock powder, Brazil 6.1% K ⁺ , 5.3% Na ⁺ Mineral -Microcline, Orthoclase, Sanidine, Nepheline, Analcime, Aegirine P. size: <0.15mm | Calcination of samples at 300-1200°C for 4hr. Samples were subjected to slow cooling (air) and rapid cooling (iced water bath). After cooling, samples along with extraction solution (0.01 mol/L citric acid) were subjected to shaking for 4hrs at 300rpm. The filtrate obtained was analyzed. | Up to 400°C no change At 600°C- Analcime decomposed. At 1200 °C- glassy phase forms due to migration of K ⁺ from crystalline to glassy phases (mixed alkali effect). | [19] |
| 15. | Orthoclase | Powdered ore was treated with HF. After stirring and mixing, the solution was cooled and insoluble (K ₂ SiF ₆) was filtered out. Then, K ₂ SiF ₆ was treated with conc. H ₂ SO ₄ to form K ₂ SO ₄ . | | [20] |
| 16. | Feldspar or other alumina and potash bearing silicate minerals. | Dry mixture of ore and caustic alkali was prepared under atmospheric pressure and temp within 185-350°C. New basic silicates were formed which separated water soluble and water insoluble products which were further treated with acids to get desired compound. | | [21] |
| 17. | Feldspar or other potash bearing rocks. | The rock powder was mixed with suitable quantity of (borax + alkali carbonate + water) then mixture was placed in retort under heat and pressure and CO ₂ was passed into the mixture. | Borax breaks up the alkali aluminum silicate into alkali silicate + aluminum silicate. Alkali carbonate or hydrate dissolves alkali silicate. | [22] |
| 18. | Potassium bearing silicate rocks | The rock sample was finely divided and mixed with suitable quantity of finely divided carbon (ground coke, coal dust etc.). The mixture was heated to temperature of 1200-1400°C. Decomposition products formed were K ₂ C ₂ , Al ₄ C ₂ which were further treated with superheated steam to form respective oxides. | | [23] |
| 19. | Feldspar or other potash bearing rock | The method involved recovering potash by mixing and heating the sample with alkali metal acid sulphate, alkali metal chloride and a reducing agent (coke) to bright red heat for 1-2 hrs. Reducing agent used in such quantity such that it reduced only a part of the sulphate | | [24] |
| 20. | Potassium, shale, SiO ₂ -60.11, K ₂ O-10.72 Al ₂ O ₃ - 15.11 Na ₂ O- 0.22 Fe ₂ O ₃ - 5.94, MnO ₂ - 0.14 TiO ₂ -0.65 LOI-3.83 | Flux NaOH is used with the shale and heating temperature- 400 to 800°C. Leaching solution 34% H ₂ SO ₄ and temperature- 80°C. Liquid to solid ratio- 4.75 | K extraction increases with roasting temperature. Roasting temperature 600°C time 2hr and NaOH dosage 70% is optimum for K extraction. | [25] |
| 21. | Ore -Biotite, muscovite, microcline, orthoclase. Particle size -20 to 50 microns | 200 mg of each sample in 20 ml water, citric acid or oxalic acid (0.01 M) was kept in centrifuge tubes for various time and at the temperature of 298 K. rate constant for releasing K is studied for each sample. | Rate constant for K release in citric and oxalic acid was found in following order- Biotite > K feldspar > muscovite. | [26] |

| | | | | |
|-----|---|---|--|------|
| 22. | <p>Ore- K-feldspar, Composition- SiO₂-65, K₂O- 13.92%, Al₂O₃-17.26, Na₂O- 1.09%, Fe₂O₃- 1.20% MgO- 0.84%, CaO-0.61% P. Size- 75microns</p> | 150 g of feldspar was mixed with 540 ml of prepared alkaline solution made by using KOH ($\geq 85\%$), NaOH ($\geq 96\%$) and distilled water. This slurry was discharged into a nickel hydro- thermal stirring reactor (200 r/min) and heated at 240–280 °C for 3hr. | Metastable Kalsilite was formed at 240°C when mole fractions of KOH were 1.0 and 0.9 and it becomes Kalsilite when mole fraction of KOH is 0.3 to 0.9. Increment in temperature from 240 to 280 is disadvantageous for metastable Kalsilite. This behavior shows that feldspar structure is destroyed with hydrothermal alkaline treatment. | [27] |
| 23. | <p>Biotite (from Ajmer, Rajasthan, India. P. Size- 80-150 mesh Si- 16.67, Al-9.67, Fe-19.24, Ti- 3.35, Ca-0.23, Mg-2.60 Na- 0.26, K- 7.75, adsorbed water, structural water- 0. 1.20)</p> | Biotite and HCl(11.55 N) was put in the ratio of (100:0, 90:10, 80:20, and 75: 25) and the container was covered with Parafilm and kept for 48, 96, 144, 192, 240, and 312hr. K ⁺ is determined by flame photometry. | Rates of release of K ⁺ from biotite increase with increasing concentrations of HCl. By increasing temperature up to 100°C all K ⁺ released within 90 minutes. Diffusion of H ⁺ into interlayer occur by release of K ⁺ . This H ⁺ migrates into the octahedral and tetrahedral positions occupied by Al ⁺³ , Mg ⁺² , Fe ³⁺ , and Fe ⁺³ , thereby solubilizing these cations. | [28] |
| 24. | <p>Ore- Potassium feldspar(China) SiO₂-65% Al₂O₃-16.38% Fe₂O₃- 1.19% MgO-0.96% Na₂O- 0.79% K₂O- 13.66% P. Size- 75 μm</p> | Ore: NaOH=0.6:1.4, 10 mL water, at 200°C, react for 60 min, 90 min, 120 min, and 150 min, 180 min in a kettle. | K extraction was increased by increasing reaction time, temperature and NaOH dosage. Ore: NaOH=0.6:1.4 with 10 ml of water at temperature of 200°C was used then K extraction of 75.39% was obtained. | [29] |
| 25. | <p>Ore: K-bearing minerals (K-feldspar and illite)</p> | Aspergillus fumigatus was cultured with K-bearing minerals and then kept in incubation for 30 days. | The K solubilization increased steadily with time and is approx. 400-500% from day 2 to 30. K dissolution in this method is higher than any separation method. | [30] |

2.2 Summary of Literature review-

Various methods of K extraction from micaceous mineral, feldspar group minerals or from any silicate rock having potassium in insoluble form, have been used which are summarized below-

1. Mineral processing route to improve K dissolution.
2. Leaching of ground rock in acids at ambient and at elevated temperature.
3. Roasting of Potassic rocks with different fluxes followed by leaching in different media.
4. Bacterial leaching of Potassic rock.

2.3 Literature Gap and Problem Formulation

This study was carried out to provide solution of following problems in context of potassium dissolution-

1. **Better flux-** In this study most of the sodium bearing as well as calcium bearing flux was tried. Also, an optimization study for all fluxes will be conducted to pick best flux.
2. **Process without heat treatment-** Roasting at higher temperature is not always economically feasible and reliable technique in context of K extraction. Therefore, it is tedious task to find process without thermal treatment. In this lieu the method of mechanical activation is used in this study.
3. **Method for faster recovery-** Roasting in muffle furnace followed by leaching is a time consuming process to extract potassium from minerals. Due to low potassium concentration it is very difficult to apply these laboratory scale methods on pilot scale/ plant scale. So it is necessary to find a method which can recover potassium from minerals in faster mode. In this context microwave assisted heating was studied in this work.

Application of mechanical activation and microwave processing to improve dissolution of potassium values-

1. **Mechanical activation-** Mechano-chemistry deals with physicochemical and chemical transformations of substances in all states of aggregation produced by the effect of mechanical energy. The main effect of mechanical activation is size reduction of mineral particles that results in changes in a great number of physicochemical properties of a system. This disintegration by high-energy grinding is accompanied by an increase in the surface area of particles and by generation of fresh, previously unexposed surface. Mechanical activation is one of the effective methods of increase leaching rate which is attributed to the following

aspects: (i) the decrease of particle size and increase in specific surface area; (ii) changes and the disorder of crystalline structure and (iii) the occurrence of chemical reaction. The mechanical activation of minerals makes it possible to reduce their decomposition temperature or causes such a degree of disordering that the thermal activation may be omitted entirely.

Microwave assisted heating-Microwave energy is based on non-ionizing electromagnetic radiation with frequencies range of 0.3 GHz to 300 GHz is an alternative source of heating. Microwaves generate molecular motion by migration of ionic species and rotation of dipolar species. Microwave heating is material specific which depends on the dissipation factor which is ratio of the dielectric loss and the dielectric constant. The major advantage in microwave treatment energy transfer without making contact compared to heat transfer in conventional heating. The other benefits of this method are rapid and selective heating that can be absorbed, reflected and transmitted depending on the nature of the material. Major advantage of microwave heating is faster heating of material as comparison to heating in conventional process. In microwave, heating start from center of the sample which is in reverse direction as observed in conventional heating. The efficiency of microwave treatment is dependent on the microwave power and time of heating. Considering the abovementioned wide applications of microwave energy, a dedicated effort has been made in this thesis to extract potassium values from micaceous mineral by microwave assisted heat treatment. The purpose of using microwave in place of the conventional process of muffle furnace is that, it is eco-friendly and less time consuming process.

2.4 Basic theory used in this study

2.4.1 Difficulties in K release from micaceous mineral-

K^+ ions are always found in the interlayer position of T-O-T structure and it compensates the charge deficiency generated in the structure due to replacement of Si with Al (shown in Fig. 1.1). The presence of K^+ ion in interlayer position bonds with tetrahedral oxygen prevents the separation of layers and does not allow the expansion of minerals [31].

2.4.2 Role of flux in the study

The silica (m.p.-1713°C) and alumina (m.p.-2072°C) content in the micaceous minerals are always high so the melting point of micaceous minerals are quite high. Fluxing agent must fulfill some of the following requirements to release interlayer layer K from the minerals by pyro metallurgical route [32, 33].

- (a.) These fluxing agents form eutectic in the system and create miscibility gap with the silicate so the temperature of the system is decreased and K dissolution becomes easy.
- (b.) Calcium bearing and sodium bearing fluxes are mostly used to extract K from the system because there is always swap between calcium and sodium with potassium to form silicate structure. By providing sufficient time and thermal energy reaction promotes the formation of calcium or sodium silicate due to higher stability of both in comparison to potassium silicate and by these reactions potassium release becomes easy from the complex structure.

2.4.3 Leaching

Leaching is a process in which metallic values of an ore are selectively dissolved using a suitable liquid reagent. The selectivity of dissolution depends mainly on the nature of the solvent. Rate of leaching depends on various factors such as temperature, pressure, the ore particle size, the liquid to solid ratio, the concentration and composition of the reagent and leaching time.

2.4.4 Role of leaching solvent in the study

Acidity of the leaching medium plays a vital role in the extraction of potassium. At pH 3 the H^+ ions behaves as a strong interlayer cation exchanger in micaceous mineral. It is noticed that with increase in pH mostly above 8.5 silicate activity is increased and K may be dissolved by the attack of OH^- group in the structure [28].

CHAPTER 3.

MATERIAL AND METHOD

3.1 Material

3.1.1 Sample

A glauconite sandstone sample was procured from Satna district Madhya Pradesh was used in this study. The sample was crushed in roll crusher and ground in ball mills and sieved by 200 mesh sieve. The complete chemical analysis of the bulk sample such as CaO, MgO, Na₂O, Fe₂O₃, TiO₂, Al₂O₃, SiO₂, and LOI was carried out by standard wet chemical methods. The complete chemical analysis of the sample is shown in Table 3.1. The sample was also characterized by electron probe micro analyzer (EPMA) for chemical analysis. The sample contains 10% K₂O and 15.37% Al₂O₃, 54.34% SiO₂ and 8.67% Fe₂O₃ as the major valuable sources. The other constituents such as and CaO, Na₂O and MgO are also present in minor quantity.

Table 3.1. Chemical analysis of sample

| Elemental oxides | EPMA results | Chemical analysis |
|--------------------------------|--------------|-------------------|
| SiO ₂ | 55.27 | 54.34 |
| Al ₂ O ₃ | 22.95 | 15.37 |
| K ₂ O | 11.33 | 10.54 |
| Fe ₂ O ₃ | 3.20 | 8.67 |
| Na ₂ O | 0.18 | 0.05 |
| MgO | 0.30 | 1.01 |
| TiO ₂ | - | 1.03 |
| LOI | 6.77 | 5.49 |

3.1.2 Reagents

The chemicals used in this study were fused calcium chloride, calcium chloride dihydrate, calcium oxide, calcium hydroxide, calcium carbonate, calcium sulfate, calcium phosphate, sodium chloride, sodium hydroxide, sodium carbonate and barium chloride dihydrate. All these chemicals were of high grade purity and supplied/ marketed by Merck Millipore Company.

Acids used in this study were hydrochloric acid, hydrofluoric acid, sulphuric acid, nitric acid and citric acid. All these acids were of emplura grade and these were also marketed from Merck Millipore. Acetone was also used before pulverizing to avoid any contamination to the sample.

3.2 Instruments used in the study

In this study lot of facilities and machines were used which are described below.

3.2.1 Ball mill

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.

3.2.2 Muffle Furnace

A Proportional Integral Derivative controlled muffle furnace was used in this study as shown in Fig.3.1 furnace was of outer dimensions of 24'' x 16'' x 14''.



Fig.3.1. Photograph of Muffle furnace.

The furnace consisted of heating zone of dimensions of 9'' x 6'' x 6'' and the heating temperature range was from room temperature to 1200°C. The furnace was well insulated in and there was no loss of heat during heating. Heating rate of the furnace was 20°C/minute.

3.2.3 Domestic Microwave-

A domestic microwave (LG Company) having capacity of 21 liter was used in this study. This microwave has the power range of 180W to 900W and has dual heating mode i.e. convection

mode and micro mode. Micro mode was mostly used in this study. Different time intervals were used throughout the experiments.



Fig.3.2. Photograph of Domestic Microwave.

3.2.4 Planetary ball mill-

A RETSCH PM 400/2 planetary mill having agate bowl and balls was used for the mechanical activation of the sample. The machine has milling speed of maximum 400 RPM. In this milling machine two jars can be used simultaneously.



Fig.3.3. Photograph of Planetary Ball mill.

For mechanical activation balls of different sizes (4, 6, 8 mm diameters) were used. The samples about 45 g in each stage were subjected to dry milling in ambient atmosphere. The milling was carried out in following conditions: sample to ball ratio - 1:10(by weight); speed – 200 rpm; and milling time – 120 minutes. After completion of experiment, the whole content of the bowl was removed and was thoroughly cleaned and dried before the next experiment to avoid any contamination.

3.2.5 Glass wares

The beakers of 250 ml, measuring cylinders of various volumes (10 ml, 25ml, and 100ml), conical flask of 250ml, funnel of 40 mm diameter, and culture tubes of 15 ml used in this study were made up of borosilicate glass. These beakers could sustain the temperature up to 250°C and were used mainly for leaching of the samples. Conical flasks were used for the filtration after leaching. Glass funnel was used for filtration and culture tubes were used for keeping the prepared solution after dilution for flame photometer analysis.

3.2.6 Magnetic stirrer, filter paper and Parafilm-

Magnetic stirrers with ceramic hotplate (Cole Parmer) were used throughout study. These stirrers have the stirring speed of maximum 1500 RPM and temperature up to 250°C.



Fig.3.4. Photograph of Leaching setup.

Parafilm was always used for covering the beaker during leaching to avoid any material loss during leaching. Whatman filter paper grade 1 having 110 mm diameter was used to filter the solution after leaching. All the leaching experiments were carried out in a 250 ml glass beaker placed on a magnetic stirrer with controlled temperature environment. All leaching experiments were carried out at atmospheric pressure with appropriate leaching media under continuous stirring at 900 rpm.

3.2.7 Flame Photometer-

Flame photometer is often used to analyze the elements which are sensitive to flame color. These elements are Ca, Li, Na, K and their presence in the sample changes flame color. The systronic flame photometer with compressor was used in this study. The instruments have two modes of analysis i.e., high concentration mode and low concentration mode. In high concentration mode the standard solution of concentration should be in between 10- 100ppm whereas in case of low concentration mode standard solution should be in between 1-10 ppm for calibration. The high concentration mode was mostly used in this study to analyze the potassium content in the sample.



Fig.3.5. Photograph of Flame Photometer.

3.2.8 Scanning electron microscope-

The morphology, chemical composition, structural alteration of feed , heat treated and of leach residue sample was studied by scanning electron microscopy attached with Electron dispersive X-ray technique (FE-SEM Quanta 200 FEG).

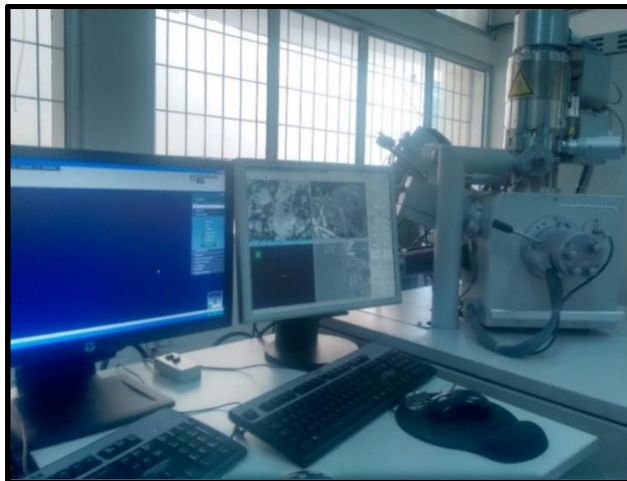


Fig.3.6. Photograph of FEI Scanning electron microscope.

3.2.9 X-Ray diffractometer-

The X-ray diffraction study of the powdered sample was carried out using a RIGAKU Smart Lab X-ray diffractometer using CuK_α radiation.



Fig.3.7. Photograph of X-Ray diffractometer.

The diffraction peaks were recorded from 10 to 60° with a rate of 2°/minute to identify different mineral phases present in the sample at each stage of the treatment.

3.3 Methodology-

The experimental procedure of this study was divided into two parts one was preliminary experiments and other one was final experiments. The whole methodology was shown by the flow sheet in Fig.3.8.

Heat treatment studies of samples with different fluxes were carried out in refractory crucibles using a laboratory muffle furnace. The experiments were carried out at different temperatures and different residence time followed by water leaching for 30 minutes. Powdered sample and flux were uniformly mixed for the heat treatment studies. Immediately after the heat treatment the crucible was air cooled. Subsequently, the heated sample was subjected to water leaching. The leached solution was then subjected to filtration and the filtrate was analyzed for potassium using a flame photometer.

3.3.1 Preliminary experiments-

Some primary experiments were performed on the sample. In all leaching experiments solid to liquid ratio was maintained 1:50 means 50 ml leachant was used per gram of a sample. All Preliminary experiments include-

(a) **Feed Leaching-** The feed sample of less than 100 micrometer was leached in water, citric acid (2, 5 and 10%), hydrochloric acid (1M-6M), sulfuric acid (1M), nitric acid (1M), hydrochloric acid with few drops of hydrofluoric acid. After leaching, leached sample was filtered and collected in culture tube for flame photometer analysis.

(b) **Heat treatment of feed without flux followed by leaching-** The feed sample was heated in a muffle furnace at 600°C and 900°C. After heat treatment sample was air cooled and re-grinded into pestle mortar then this grinded sample was leached into water, citric acid, and hydrochloric acid. After leaching filtration and flame photometer analysis was done on the sample.

(c) **Heat treatment of feed with flux followed by leaching-** the feed sample was mixed with appropriate flux such as calcium chloride fused, calcium chloride dihydrate, calcium carbonate, calcium oxide, calcium sulphate dihydrate, calcium phosphate, calcium hydroxide, sodium chloride, sodium hydroxide, sodium carbonate, sodium sulphate, barium chloride dihydrate in appropriate proportion and heat treated in the muffle furnace for sufficient time. After heat treatment samples were air cooled and this fused mass was grinded in pestle mortar and leached in water. After leaching, filtration and flame photometer analysis was done.

3.3.2 Final experiments-

After preliminary experiments, some flux was chosen such as calcium chloride, sodium hydroxide, sodium carbonate and some regular experiments were performed on the sample.

(a) **Heat treatment with flux in muffle furnace-** By the preliminary experiments, it was concluded that calcium chloride was best flux to treat the sample and then leaching out in water. So the optimization of parameter such as temperature, flux dosage, residence time was done by some experiments and also by Taguchi L9 design. In Taguchi L9 design 9 experiments were performed to maximize the K extraction. Sodium hydroxide and sodium carbonate were also proved to a better flux provided that the grinded fused mass was leached out in 2% citric acid.

(b) **Microwave assisted heating followed by leaching-** After deciding calcium chloride fused as a better flux choice some of the experiments were performed in domestic microwave. Due to unavailability of high temperature in microwave system some amount of charcoal was also used because charcoal works as microwave absorbent material and it increases the temperature of the system till desired level. The Taguchi L9 design was used to optimize parameters such as flux dosage, power of the microwave, time of heating and amount of

charcoal used. After heat treatment leaching was done in water and after filtration solutions were analyzed in flame photometry test.

(c) **Mechanical activation followed by thermal treatment and leaching-** Both types of fluxes one which was proved better for K extraction in case of hand mixing followed by roasting and other one which was proved ineffective for K extraction in a similar way was tried in planetary ball mill to activate the powder and then heat treated in the muffle furnace then leached in appropriate media. In this method feed sample with some fluxes such as calcium chloride dihydrate, sodium hydroxide, calcium carbonate, ($\text{CaCO}_3 + \text{CaCl}_2$ fused) and ($\text{NaCl} + \text{CaCO}_3$) was mixed in appropriate proportion and grinded in planetary ball mill for 8hr at the speed of 200 rpm then heat treated in muffle furnace and leached in water (in case of chloride fluxes), or in 2% citric acid (in case of NaOH, CaCO_3) after leaching filtration was done and then solution was analyzed in flame photometry.

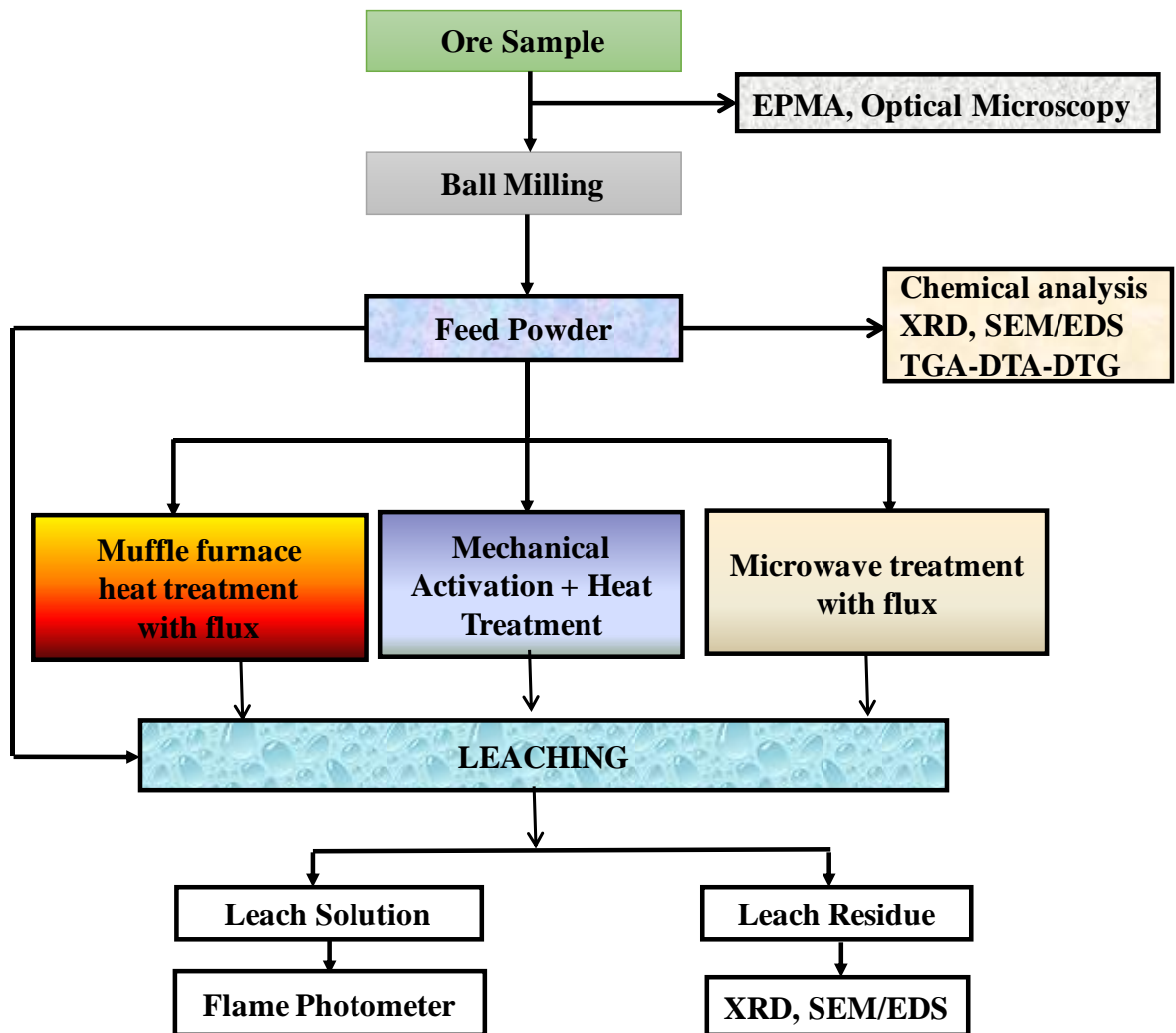


Fig.3.8. Flow diagram of experimental path followed in this study.

CHAPTER 4.

RESULTS AND DISCUSSION

4.1 Characterization of Feed sample

Feed sample was characterized by optical microscopy, Scanning electron microscopy, Electron probe micro analyses and by X-ray diffraction analysis.

4.1.1 Scanning Electron microscopy/Electron dispersive X-ray Analysis of sample

SEM image in Fig.4.1 shows that particles are dispersed throughout the matrix. Corresponding EDX spectra tells about the elemental analysis of the sample.

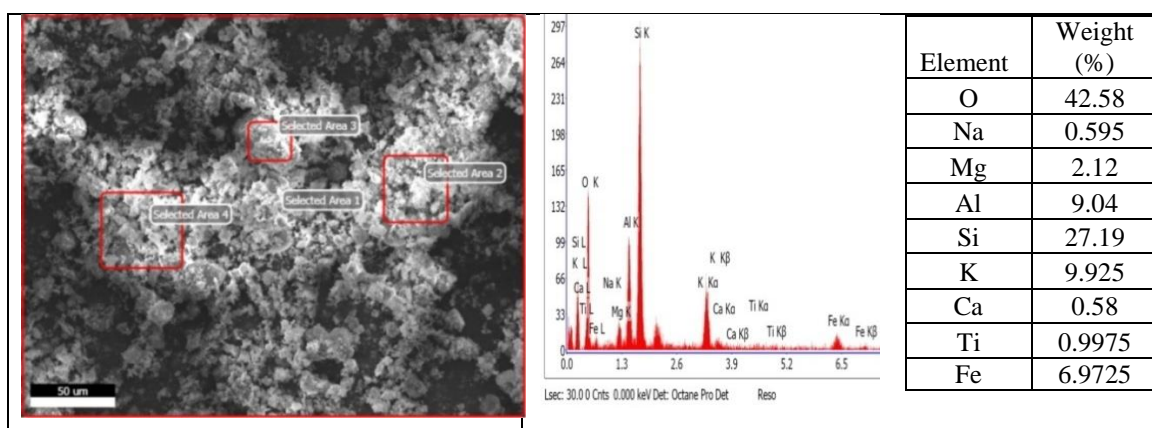


Fig.4.1. SEM/EDX spectra of Feed sample.

4.1.2 Electron probe micro analysis

Electron probe analysis technique is a reliable technique in case of geological samples rather than any other method of chemical analysis because it uses very small probe size to detect the element in the sample. Here EPMA was done on the sample and analysis is shown in Fig.4.2.

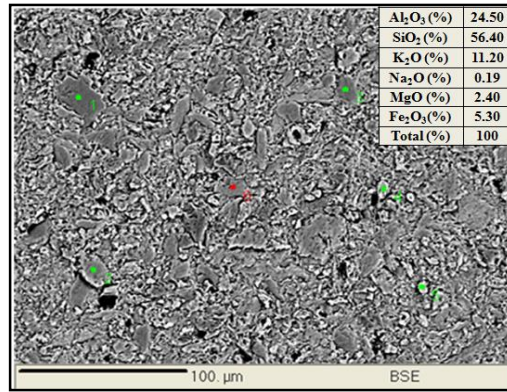


Fig.4.2. Electron probe micro analysis of feed sample.

4.1.3 X-Ray diffraction analysis

XRD of the feed sample was done using RIGAKU, CuK_α diffractometer. Scan angle was 5 to 60° and the scan rate was used 2° per minute. XRD analysis shown in Fig.4.3 reveals that main phases in the feed sample are Muscovite, microcline, Glauconite and quartz. The main K bearing phases are muscovite, microcline and Glauconite. A quantitative analysis of the sample by XRD was also done in this study.

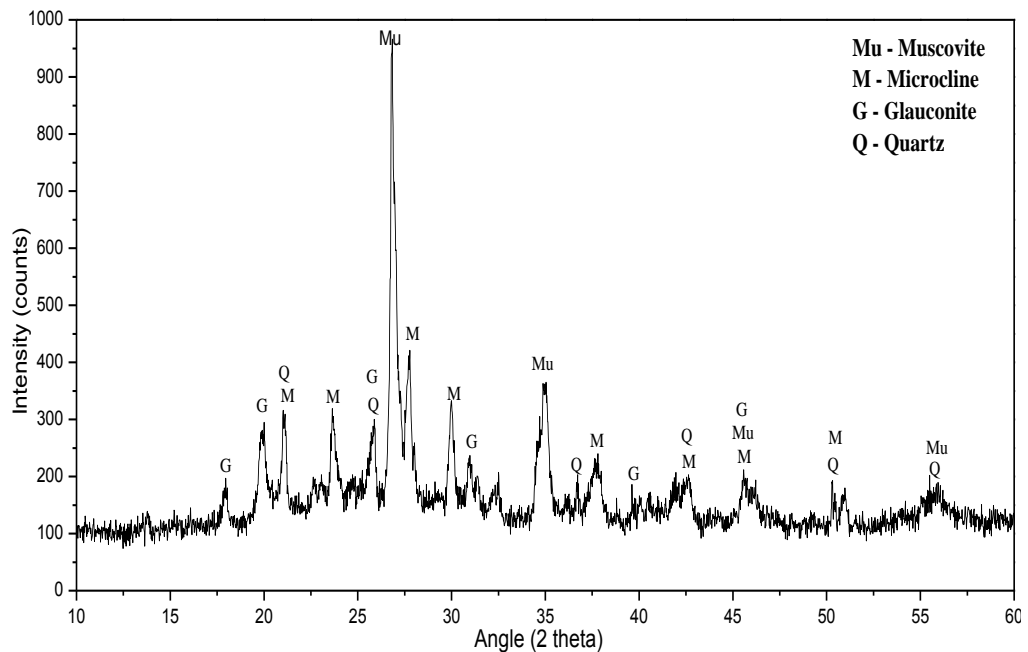


Fig.4.3. XRD analysis of feed sample.

Assumptions made during quantitative XRD analysis are:-

1. All peaks are assumed to be a triangle.

2. Peak area is the reflection of the amount of phase present in it means if peak area of some phase is high then it is present in greater amount in feed and vice versa.

3. All peaks can be extrapolated up to the common base.

Amount of any phase (i) can be calculated by formula % of phase = $\frac{A_i}{A}$

Where,

A_i = Area of all peaks of some phase i, A = Total area of all peaks present in XRD curve.

From XRD analysis of feed the amount of phases present are as follows -

Muscovite = 33% Quartz = 15.17%

Microcline = 30.25% Glauconite = 21%

Total K in Feed by XRD = $K_{Mu} + K_{Mi} + K_G$

Stoichiometric amount of K in muscovite, microcline and in glauconite is 11.33%, 14.075% and 0.55% respectively.

Total K in feed by XRD = $33 \times 0.1133 + 30.25 \times 0.14075 + 21 \times 0.055$

Total K in Feed by XRD = 9.15%

4.1.4 TGA/DTA analysis of the sample-

Thermogravimetric analysis and differential thermal analysis of the feed sample was done using EXTAR TG/DTA 6300 machine and alumina pan was used as reference material, heating rate was maintained at 10°/ minute, air rate of 200ml/minute and temperature range from room temperature to 1200°C.

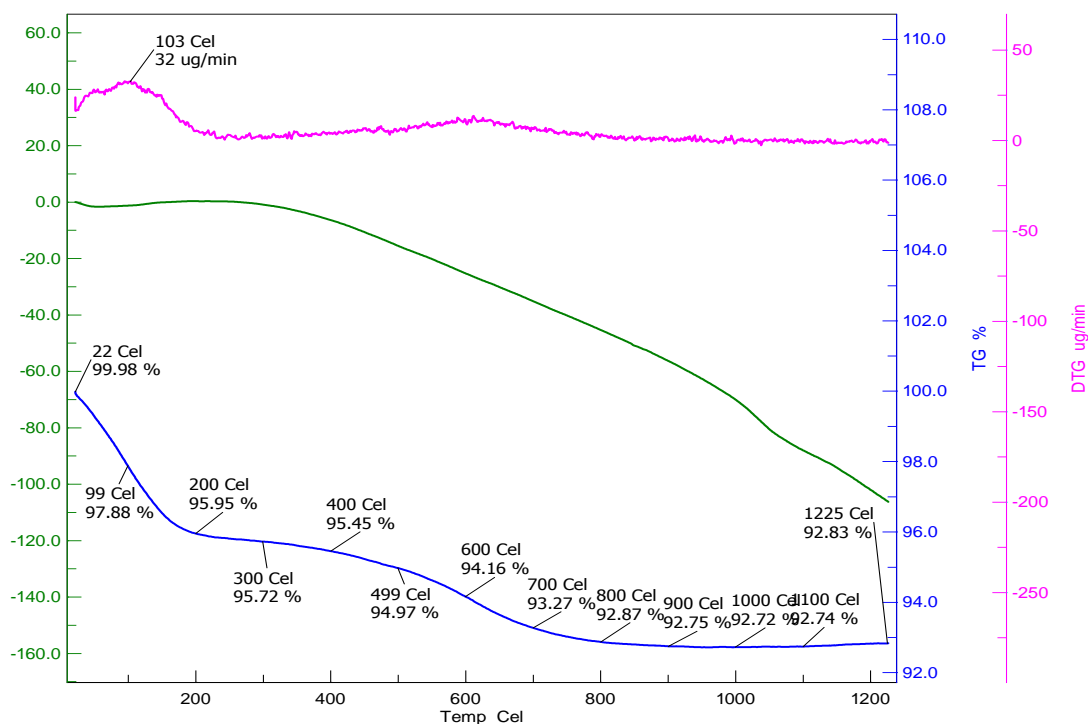


Fig.4.4. TGA/DTA Analysis of sample.

It can be concluded from the Fig.4.4 that rapid mass loss of 4.05% was observed up to 200°C temperature, this was due to dehydration of water a) attached to surface by Vander-wall force and (b) present in interlayer position. From 430°C to 700°C 1.43% mass loss was due to dehydroxylation of OH-group present in octahedral position. And above 900°C there is thermal stability up to 1200°C, although material has gone melted which is reflected from the endothermic peak in DTA curve.

4.1.5 Optical metallography of feed sample under plane polarized light and under reflected light-

The sample investigated consists of dark green color grains and golden appearance grains in a uniform texture. It is evident that there is the presence of distinct colored minerals in the sample. The sample was seen under plane polarized light and reflected light microscopy and it reveals that the material is a fine grained and elements are distributed uniformly throughout the matrix. Due to very fine grained texture of the rocks, sometimes it is difficult to identify the mineralogy, especially when forming an aggregate of clay minerals and it also reveals that material is a combination of two or more minerals. Overall with hand specimen photograph and optical microscopic images, it can be concluded that the rock is a green slate, formed by metamorphism of sedimentary rocks composed of quartz, feldspar, muscovite, and microcline. In general, Glauconitic meta-argillite is a pelitic metasedimentary rock which is weakly

deformed and metamorphosed to lower green schist facies. Glauconitic meta-argillite displays a lepidoblastic texture, and preserves relict textures from its original clastic origin.

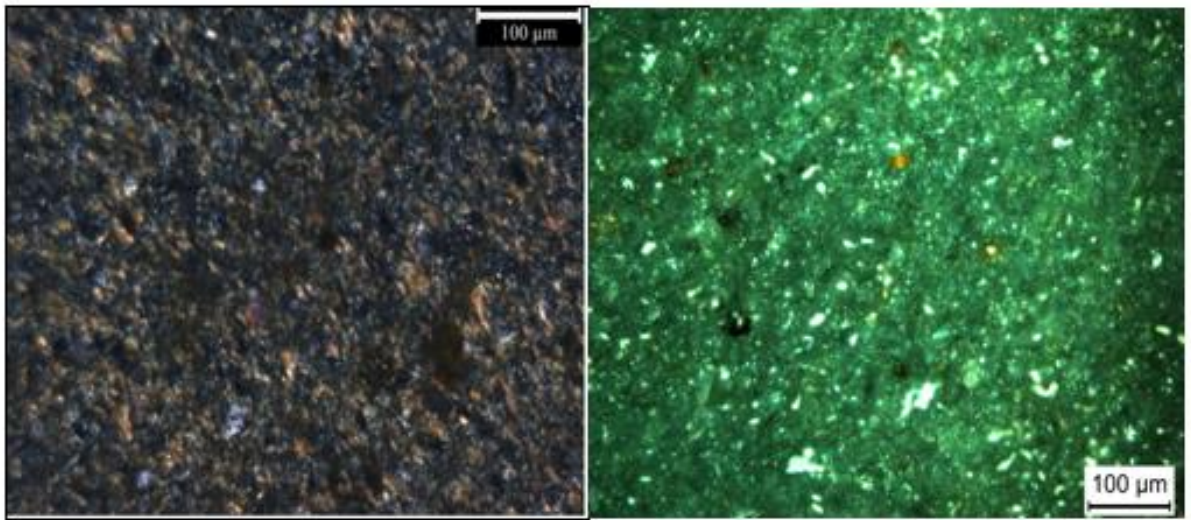


Fig.4.5. Optical image at 20X (a) under plane polarized light (b) Under reflected light microscopy.

4.2 Preliminary Results

In the preliminary experiments as shown in Table 4.1 initially, the sample was subjected to water leaching. It was observed that the potassium extraction was only 1%. It indicates that the potassium is locked in the silicate matrix and needs either acid or alkali treatment to release the potassium values. The potassium extraction from samples using different inorganic acids at different concentrations resulted in 1-5% only. The leaching conditions maintained during the experiment were: room temperature, time 30 min, solid/liquid ratio 1:50, and stirring speed 900 rpm.

In the preliminary experiments according to the Table 4.1 feed and flux are mixed in the ratio of 2:1 then heat treated in muffle furnace for 60 minutes residence time and leaching was carried out in water or citric acid solution, then filtered solution was analyzed in flame photometer and it is concluded that $\text{CaCl}_2(\text{fused})$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl was effective flux for K dissolution if leaching was carried out in water and the fluxes such as Na_2CO_3 , NaOH were effective flux for K dissolution if leaching was carried out in 2% citric acid solution.

It is inferred from the Table 4.1 that leaching of feed in water, Citric acid of different concentration (2, 5, and 10%), hydrochloric acid of different molarity, combination of

hydrochloric acid and hydrofluoric acid, sulphuric acid and nitric acid could not release K more than 2%. So water and acid leaching of feed was found to be ineffective route for K dissolution.

It is also clear from the Table 4.1 that fluxes such as CaCO_3 , Ca(OH)_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_3(\text{PO}_4)_2$, CaO were ineffective flux in case of water as well as citric acid leaching. It could release only up to 6% K from the feed sample.

It is also clearly understood from the Table 4.1 that CaCO_3 was ineffective if sample and flux was hand mixed, heat treated and leached in water or citric acid but it become effective if sample and flux was mechanically activated in planetary ball mill then heat treated and leached in citric acid solution. So it might be an effective flux if pretreatment of high intensive grinding was done on sample instead of hand mixing.

Table 4.1. Preliminary results

| Flux (%) | Temp.(°C) | Leachant | K (%) |
|---|-----------|---------------------|---------|
| Feed | 25 | HCl(1-6 M) | 0.2-0.6 |
| Feed | 25 | Citric acid(2,5,10) | 1.2 |
| Feed | 25 | HCl (6M) +HF (2%) | 2.2 |
| $\text{CaCl}_2(\text{fused})(50)$ | 900 | Water | 45.1 |
| $\text{CaCl}_2(\text{Di})(50)$ | 900 | Water | 29.0 |
| $\text{CaCl}_2(30)+\text{NaCl}(30)$ | 900 | Water | 62.6 |
| $\text{CaCl}_2(40)+\text{NaCl}(20)$ | 900 | Water | 62 |
| $\text{CaCl}_2(20)+\text{NaCl}(40)$ | 900 | Water | 42 |
| $\text{CaCl}_2(60)+\text{Charcoal}(10)$ | 900 | Water | 67.7 |
| $\text{CaCl}_2(60)+\text{Charcoal}(20)$ | 900 | Water | 67.7 |
| $\text{CaCl}_2(30)+\text{Charcoal}(10)$ | 900 | Water | 17.2 |
| $\text{CaCl}_2(30)+\text{Charcoal}(10)$ | 900 | Water | 26.8 |
| $\text{CaCO}_3(50)$ | 1200 | Water | 0.2 |
| $\text{CaO}(50)$ | 1200 | Water | 3.5 |
| $\text{CaSO}_4(50)$ | 1200 | Water | 25.4 |
| $\text{Ca(OH)}_2(50)$ | 1200 | Water | 0.5 |
| $\text{Ca}_3(\text{PO}_4)_2(50)$ | 1200 | Water | 0.8 |
| $\text{CaCO}_3(50)$ | 900 | Citric acid (2%) | 7.7 |
| $\text{CaSO}_4(50)$ | 900 | Citric acid (2%) | 5.2 |
| $\text{Ca(OH)}_2(50)$ | 900 | Citric acid (2%) | 6.0 |
| $\text{Na}_2\text{SO}_4(50)$ | 900 | Water | 22.7 |
| $\text{NH}_4\text{Cl}(50)$ | 900 | Water | 0.4 |
| $\text{NaCl}(50)$ | 900 | Water | 31.4 |
| $\text{Na}_2\text{CO}_3(50)$ | 900 | Citric acid (2%) | 69.5 |
| $\text{Na}_2\text{SO}_4(50)$ | 900 | Citric acid (2%) | 37.1 |
| $\text{NaOH}(60)$ | 600 | Water +citric acid | 70.32 |
| $\text{MA(G+CaCO}_3)$ | 600 | Citric acid (2%) | 47.1 |

It was observed that verification takes place on heating to a temperature above 1000° C with Na₂CO₃. The ignited mass remains in the form of a powder, and consequently the soluble material present can be readily leached out without the necessity of any previous grinding of the mass.

The melting point of the additives appears to be an important factor in dissolution of K from silicates. Glaucosite is K dominating silicate member in this rock. Additives which have lower or near temperature than the sample such as CaCl₂ (m.p. = 775 °C), NaCl (m.p. = 800.7 °C) and Na₂CO₃ (m.p = 856 °C) may form soluble K salts easily after reaction with additives.[31].

CaCO₃, Ca₃(PO₄)₂ and CaSO₄ proved ineffective due to their high melting point. Due to high melting point these additives may not make proper interaction with rock. These all salts give CaO as product after decomposition and it has melting point of around 2613°C which is quite high than the temperature used in the experiments this may be a valid reason for failure of these salts in context to K solubilization. (1100 °C)[31].

Chloride based reagents have higher thermal conductivity than that of the salts such as phosphate, carbonates, and sulphate. Due to high thermal conductivity chloride based reagents are more effective in transfer of thermal energy so these flux are proved more efficient than others. The other possible reason for higher efficiency of chloride flux than others may be the need of lower activation energy for formation of KCl as compared to formation of other potassium salts such as K₂CO₃, K₂SO₄, and K₃PO₄ etc. The thermodynamic properties such as thermal diffusivity, thermal conductivity, melting points, and calorific capacity play vital role to determine better flux. The calcium bearing and sodium bearing flux are most effective to form soluble potassium salts because Ca⁺² and Na⁺ ions ionically bond to oxygen at the time of melting of silicates and disrupt the silicate structure. NaOH is proved to effective flux because K-feldspar decomposes into soluble K-salts in NaOH-H₂O system. It is found that in alkaline media Al-O bond is broken more easily in comparison to Si-O bond during dissolution of K-feldspar. During dissolution the metal atoms (Ca, Na, K) on the surface of feldspar react with hydroxide ion and form hydrolyzed cation at the same time Al atoms of feldspar react with hydroxide ion and form Al(OH)⁴⁻ due to this silicate tetrahedral is broken. However Al(OH)⁺²(aq) and Si₃O₈⁴⁻ are not final product they react to form Al(OH)⁴⁻ and Si(OH)⁴⁻. When concentration of these product increases with decomposition product of feldspar then the ions K⁺, Al(OH)⁴⁻ and H₂SiO₄²⁻ reacted to form Kalsilite (KAlSiO₄)[32].

The chemical stability of the silicate during acid dissolution is determined by the perfect combination of properties and structural factors of the metallic cations in the silicates. The type of anions in the acid and the type of compound it forms with the metal of the rock are highly influencing factors in acid dissolution of minerals[33].

4.2.1 Dosage variation of selected fluxes

The behavior of fluxes such as CaCl_2 (fused), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl and CaCO_3 was recorded by variation in dosage of flux in

Fig.4.6. From this it can be easily concluded that Chloride based flux is better than Calcium carbonate in the context of K dissolution in water leachant. In case of all fluxes tried, except calcium carbonate it is quite clear that K dissolution is increasing continuously with increasing flux dosage, but the rate of K dissolution (slope of the curve) decreases after 75% of the flux dosage so further experiment are restricted to 90% flux dosage. And experiments were done by taking calcium chloride as best flux.

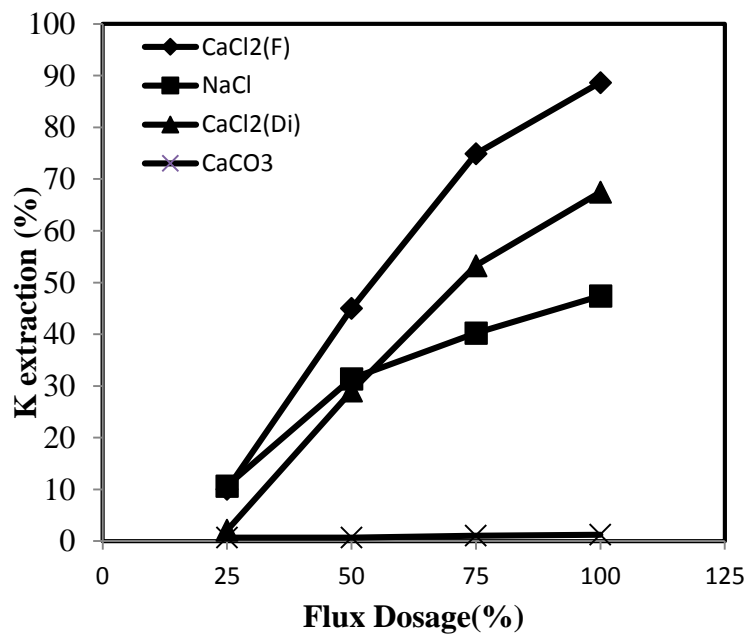


Fig.4.6. Effect of dosage of different fluxes on K extraction (temp-900°C, residence time-60min, leachant- water).

4.2.2 XRD analysis of sample after treating with chloride fluxes-

XRD analysis of the sample when it was treated with chloride flux was presented in Fig.4.7. The predominant potash minerals are muscovite and microcline. The following conclusions were made:

1. In the feed sample (heat treated at 600°C) there were no significant changes in phases, in this treatment only peak height was decreased in comparison to feed thereby indicating that crystallinity of all phases decreases.
2. When the feed sample (heat treated at 900°C) without flux was analyzed, crystallinity of all peaks further decrease and some peaks which were of very low intensity disappeared which means due to high temperature some phases may dissociate.
3. On the other hand, in the roasted sample (all of three chloride flux) sylvite form this means that there is exchange between interlayer K^+ and Ca in the structure.

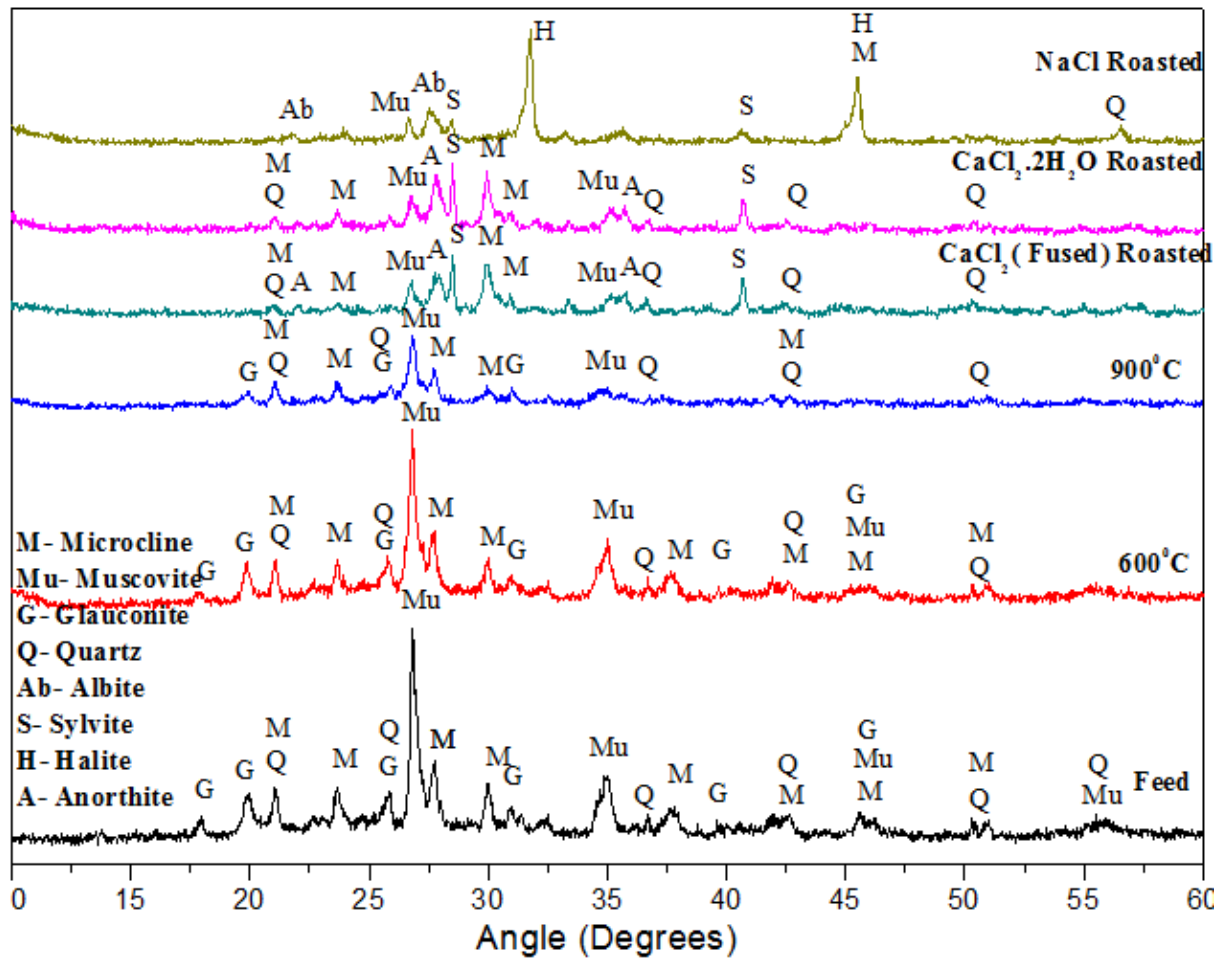


Fig.4.7. XRD analysis of sample treated with chloride flux.

4.3 Final experiments

After preliminary experiments the CaCl_2 (fused) was chosen as effective flux for K release in case of water leaching and NaOH, Na_2CO_3 were chosen as effective flux in case of citric acid solution leaching. CaCO_3 was also chosen as effective flux in case of citric acid (2%) leaching if only if mixing of feed and flux was done by milling machine. Final experiments were divided into three sections which are described below.

4.3.1 Muffle furnace treatment followed by leaching

In this section feed was mixed in appropriate proportion with fluxes such as CaCl_2 fused, Na_2CO_3 and NaOH and heat treated in a muffle furnace at temperature decided by preliminary experiments, for a given time, then leached out into the water or citric acid solution and flame photometry of filtered solution was done. This section was subdivided in following parts.

Treatment of feed with CaCl₂ fused:

After preliminary experiments, some regular experiments were done on the sample to optimize the thermal parameters such as flux dosage, temperature, residence time and some leaching parameters such as leaching time, etc. Taguchi L9 design was also used to optimize the thermal parameter and to improve K dissolution.

1. Effect of temperature on K extraction in (G+CaCl₂(F)) system

When the sample was tried with two flux dosage (60% and 90%) of calcium chloride and the effect of temperature (600°C to 900°C) on K dissolution was plotted then it can be seen in Fig.4.8 that when temperature increases from 600°C the K dissolution increases continuously till 900°C surprisingly K dissolution started decreasing after 900°C and it was almost 0.5% at 1200°C. The reason behind this discrepancy is the formation of the eutectic between KCl-CaCl₂ system, due to eutectic formation the liquid phase appears below 900°C and loss of KCl occurred due to evaporation at much higher temperature than 900°C. Almost all KCl is evaporated till 1200°C[34].

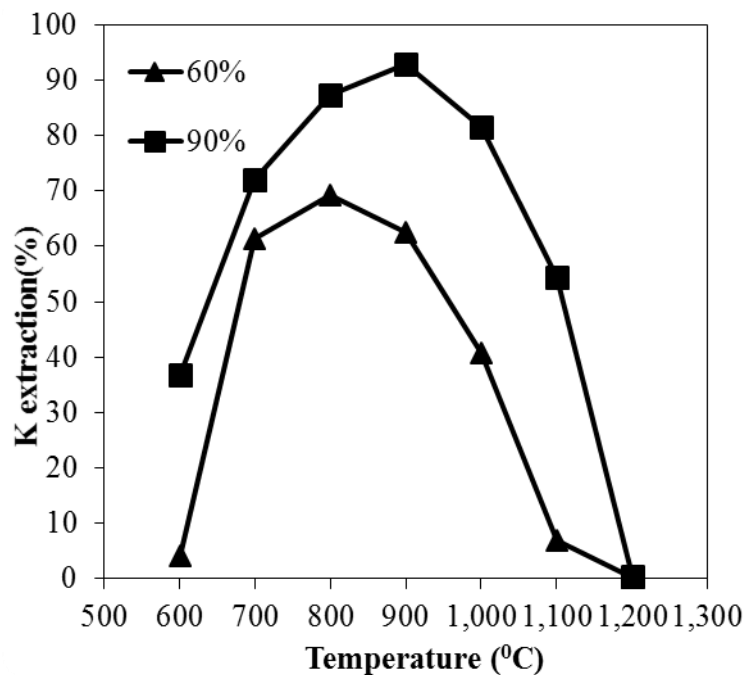


Fig.4.8. Effect of temperature on K extraction (Residence time- 60 mins, Flux- 60% and 90%).

According to the literature the potassium content in fused mass is almost equal to the potassium in reactant (glaucanite sandstone) till 900°C but this difference is started increasing after 900°C and it becomes 41% at 1100°C and quite high at 1200°C[35].

The vapor pressure of potassium chloride at 900°C and 1200°C is 0.51 kPa and 19.42 kPa respectively[36]. On account of such large increment in vapor pressure of potassium chloride on increasing temperature, almost all KCl is evaporated at 1200°C which is a potential reason of decreasing K dissolution at such higher temperature. Therefore, it is important to mention that almost all potassium chloride vaporize at 1200°C. Hence, it can be clearly concluded that 900°C is the optimum temperature to release K from micaceous mineral.

2. Effect of residence time on K extraction in case of (G+CaCl₂(F)) system

After selecting optimum temperature for K dissolution the effect of residence time at constant temperature was studied for two flux dosage (60% and 90%) with the help of Fig.4.9. It can be concluded from the Fig.4.9 that when the residence time increases from 30 to 90 minutes the K dissolution is more or less constant, but after 90 minutes, K dissolution started decreasing significantly at a much higher residence time.

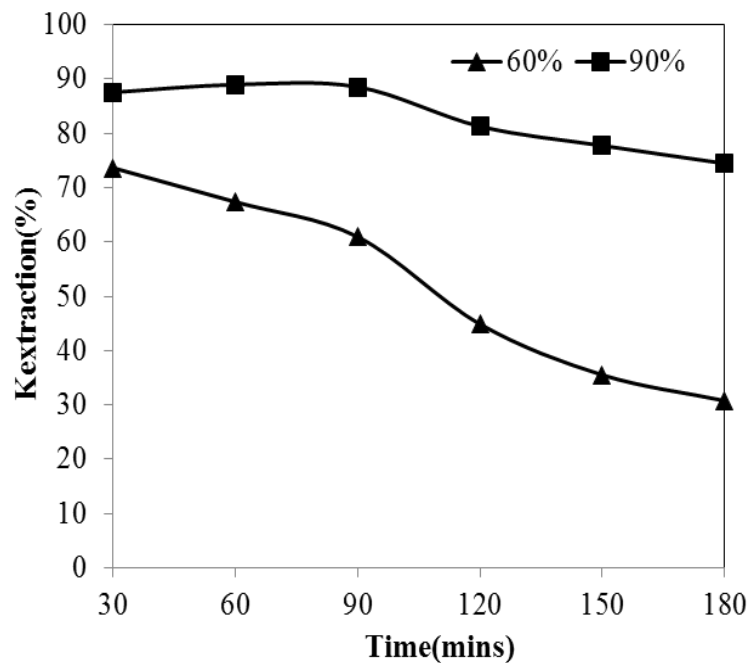


Fig.4.9. Effect of Residence time on K extraction (Residence time-60 mins, Temperature-900°C, flux- 60%).

This unusual behavior tells that the exchange reaction of interlayer cation K with Ca ion is completed within 30 minutes residence time and on increasing further time the liquid phase formed by eutectic of KCl-CaCl₂ start evaporating due to remaining in liquid state for prolonged period. Due to this some mass of KCl may be lost by volatilization. So it can be easily concluded that the optimum residence time for K dissolution is 30 minutes.

3. Effect of leaching time on K extraction in (G+CaCl₂(F)) system

One of the most important leaching parameter, leaching time at optimum conditions of thermal parameters and flux dosage was studied in Fig.4.10. The few drops of sample were collected during leaching at different intervals of time and diluted to desired level and tested in flame photometer. It can be inferred from the Fig.4.10 that there is no effect of leaching time on K dissolution. This behavior shows that KCl is readily soluble in water and it dissolved appropriately within 15 minutes of time.

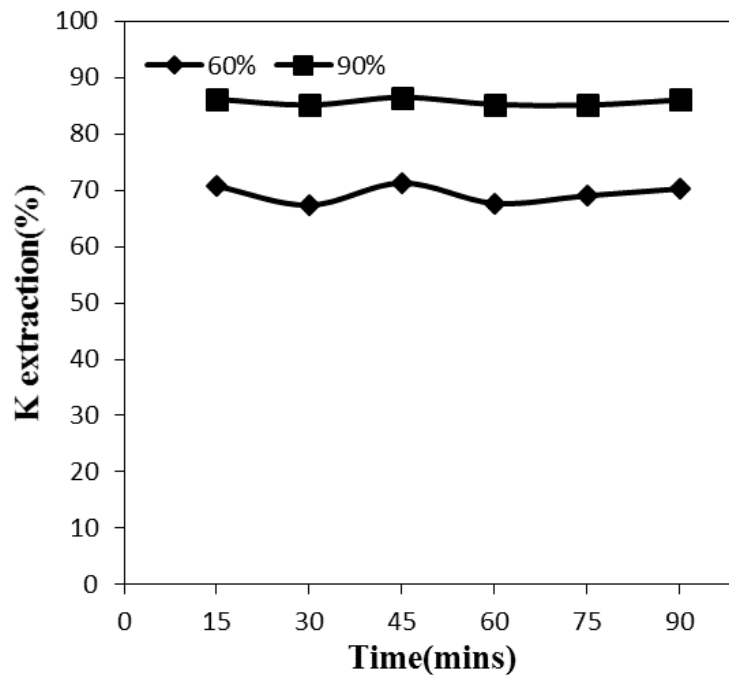


Fig.4.10. Effect of leaching time on K extraction (Residence time-60 mins, Temp. - 900°C, flux- 60%, 90%).

4. Taguchi L9 design of (G+CaCl₂(Fused)) system

After regular experiments, a statistical design of experiments was followed, i.e., Taguchi L9. Taguchi Orthogonal arrays are subsets of the full factorial experiments, which are balanced in such a way that each variable parameter occurs the same number of times and no two

experiments are the same. The experimental conditions under statistical design are shown in Table 4.2. The signature plots of Taguchi L9 design are generally shown in the form of main effect plots as shown in Fig. 4.11. It is relatively easy to see the effect of different factors on process response. The K dissolution obtained in the experimental design is shown in Table 4.2. It is evident from the table that the maximum potassium extraction is around 85%, whereas the minimum is 30% only. Fig.4.11 clearly shows the effects of all three variables on average K dissolution one at a time. With increase in flux dosage, K dissolution increases sharply whereas there is slow increase with time. The maximum K dissolution was achieved at 30 min time; 900°C temperature and 90% flux dosage. Based on ANOVA analysis, the order of significant factors for all variables are as follows: Flux dosage, heat treatment time and temperature. Also it is observed that both time and temperature have insignificant effects on the K dissolution for the given set of experiments. This indicates that the flux dosage has the most significant effect on K dissolution among all the factors. This is expected since preliminary experiments also indicated flux dosage in this range (60-90%). Based on ANOVA results, a contour plot for the two most significant factors, i.e., flux dosage and temperature, is shown in Fig.4.12 It represents the areas for maximum K dissolution which includes higher flux dosage and higher temperature.

Table 4.2. Taguchi statistical design K dissolution results with calcium chloride flux.

| Time (mins) | Temp (°C) | Flux (%) | %K |
|--------------------|------------------|-----------------|-----------|
| 30 | 700 | 30 | 30.43 |
| 30 | 800 | 60 | 59.45 |
| 30 | 900 | 90 | 85.15 |
| 60 | 700 | 60 | 51.05 |
| 60 | 800 | 90 | 77.33 |
| 60 | 900 | 30 | 24.06 |
| 90 | 700 | 90 | 68.78 |
| 90 | 800 | 30 | 28.31 |
| 90 | 900 | 60 | 60.55 |

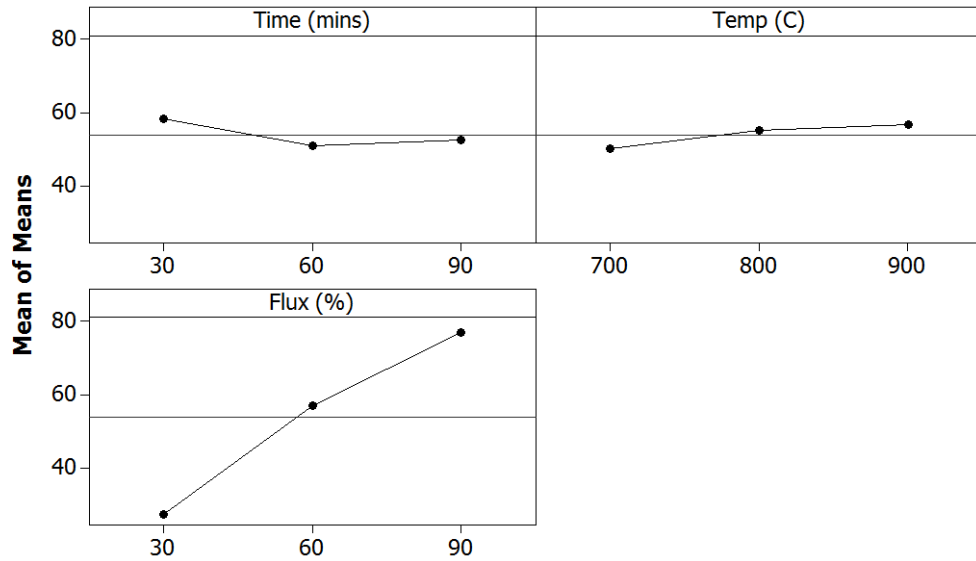


Fig.4.11. Main effects plot of average K dissolution.

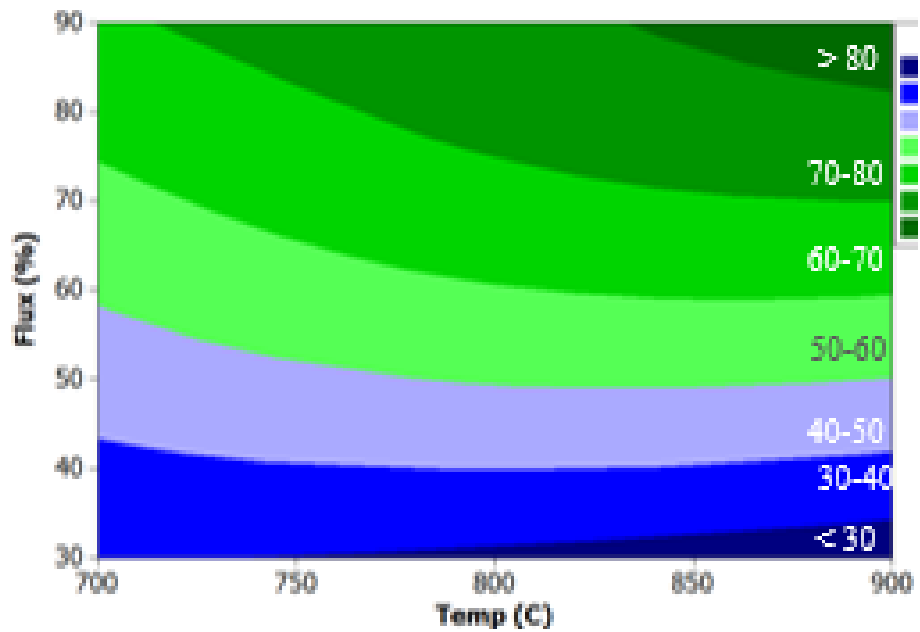


Fig.4.12. Contour plot of K dissolution vs. flux dosage and temperature

Treatment of feed with NaOH:

Feed was mixed with a certain amount of NaOH and heat treated in a muffle furnace. After thermal treatment leaching of fused mass or clinker was done in two steps, first one was water

leaching, then second one was in citric acid (2%) leaching. After grinding fused mass in mortar pestle, some amount of this powder was leached in water for 30 minutes the liquid to solid ratio was maintained 50:1, after leaching filtration was done then residue was dried in oven at temperature of 100°C. After drying, this residue is re-leached in 2% citric acid solution. Both the solutions were tested in flame photometer for obtaining dissolved K. Some regular experiments were performed to optimize the parameter such as temperature, residence time, flux dosage etc., in context to K dissolution.

1. Optimization of flux dosage

To optimize NaOH dosage the experiments were performed on different dosage at a fixed temperature (600°C) and residence time (150 minutes). It is worthwhile to mention from Fig.4.13 that on the increasing NaOH dosage the K dissolution increases continuously, but at the same time the dissolution kinetics become slower at much higher dosage so to avoid the use of more amount of flux, the flux dosage is restricted to 60%. And all further experiment was performed on 60% NaOH.

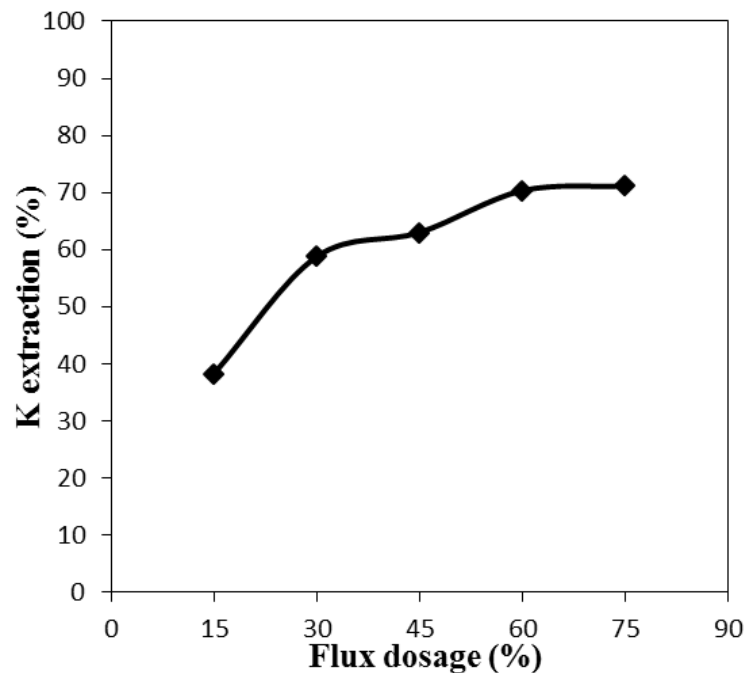


Fig.4.13. Effect of NaOH dosage on K extraction (Residence time-150 mins, Temperature-600°C).

2. Optimization of residence time:

To optimize the residence time experiments were performed at different residence time for a fixed amount of flux (60%) and temperature (600°C). It is observed from the Fig.4.14 that on increasing residence time from 30 minutes to 180 minutes the K extraction decreases significantly it indicates that the reactions are completed within 30 minutes of time and on further increasing time there might be some loss of potassic values in the system due to prolonged heating.

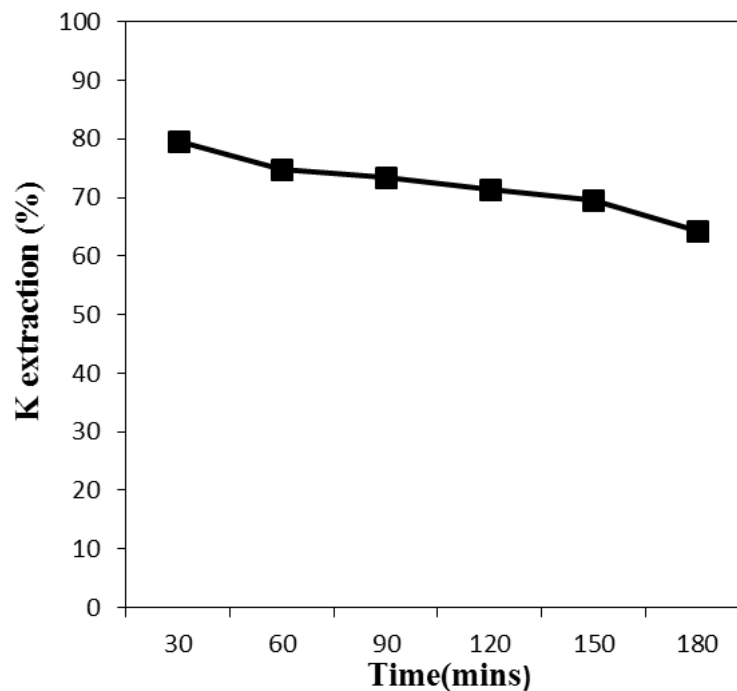


Fig.4.14. Effect of residence time on K extraction (Temperature-600°C, Flux- 60%).

3. Optimization of temperature:

To optimize the temperature of treatment experiments were performed at different temperature at the fix residence time(30 minutes) and flux dosage (60%).The Fig.4.15 shows that on increasing temperature from 200°C to 800°C the K dissolution increased continuously but at the same time the rate of increment (slope of curve decreases) means reaction kinetics become slower and the K dissolution between 600°C to 800°C was more or less constant so the temperature was fixed at 600°C to perform further experiments.

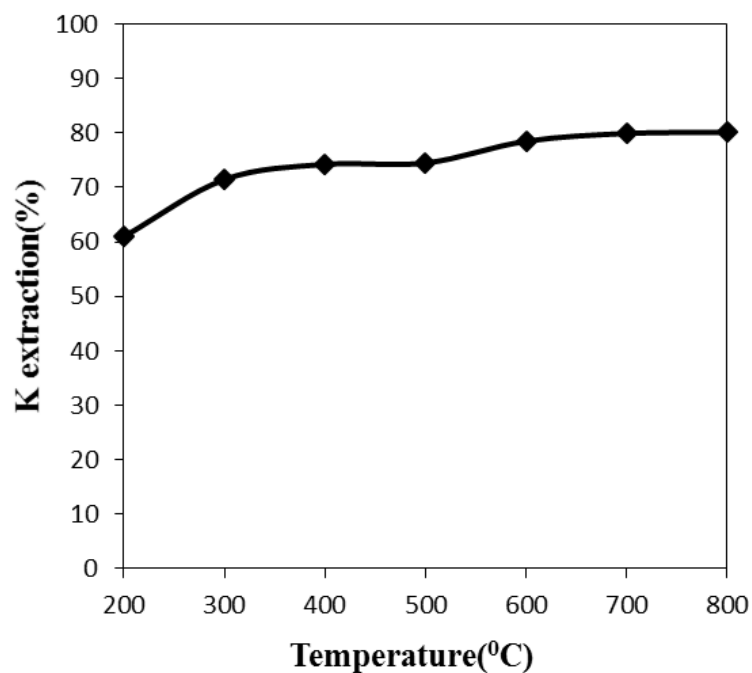


Fig.4.15. Effect of Temperature on K extraction (Residence time 30 mins, Flux dosage (60%).

Treatment of feed with Na_2CO_3

Feed was mixed with a certain amount of Na_2CO_3 and heat treated in a muffle furnace. After thermal treatment fused mass was grinded in pestle mortar and then leached in citric acid 2% solution with liquid to solid ratio of 50:1, for 30 minutes. After leaching filtration was done and leached solution was tested in flame photometer. Some regular experiments were performed to optimize the parameters such as temperature, residence time, and flux dosage.

1. Optimization of Na_2CO_3 dosage in context to K dissolution

Effect of flux dosage was studied at fixed temperature of 800°C and 900°C in Fig.4.16. It was clearly understood from the Figure that the K dissolution increases continuously with increasing flux dosage from 30% to 100%. To avoid using much amount of flux the flux dosage was restricted to 90%.

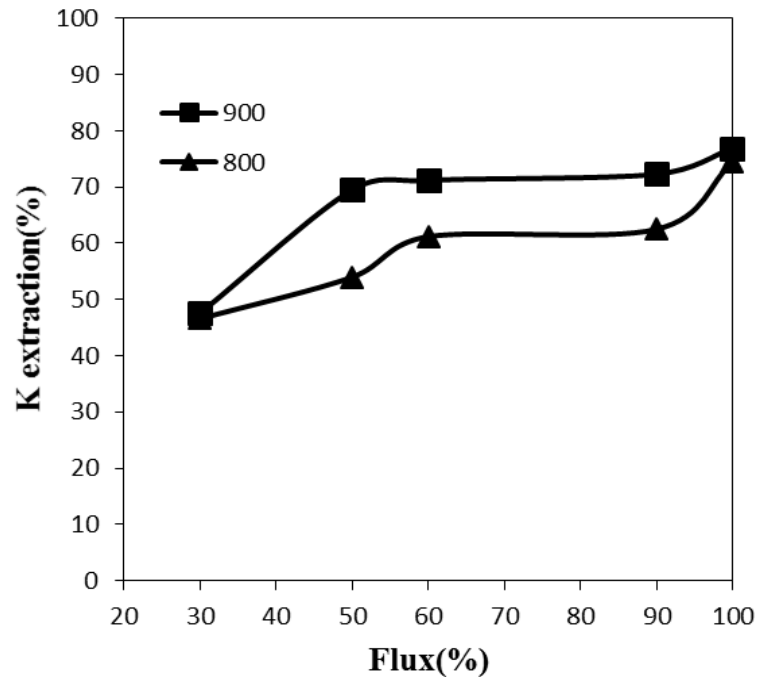


Fig.4.16. Effect of flux dosage on K extraction (Residence time 60 mins, Temp. 900°C 800°C).

Optimization of residence time

The effect of residence time was studied at constant temperature (900°C) and at constant flux dosage (90%).

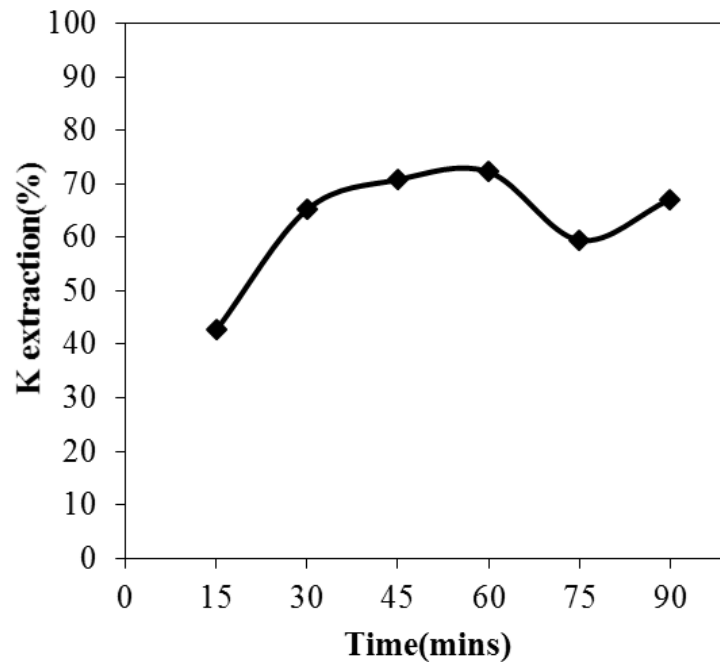


Fig.4.17. Effect of residence time on K extraction (Temperature-900, Flux dosage-90%).

It was clearly concluded from the Fig.4.17 that the K extraction increases continuously when time was increased from 15 minutes to 60 minutes but suddenly on further increasing time K dissolution decreases.

4.3.2 Microwave assisted heating followed by leaching-

Flux CaCl_2 fused was tried with feed glauconite in this method to study the K dissolution performance of the feed material. The Taguchi L9 design was tried to optimize the experimental parameters and to minimize the experiments.

Taguchi experimental design with CaCl_2 (fused)

The design of experiments was carried out by using a statistical design based on Taguchi methodology. In order to optimize the conditions for microwave roasting of Glauconite, experiments were carried out as per the L₉ orthogonal design. Experiments of design along with corresponding results are shown in Table 4.3.

The data displayed in Table 4.3 was further analyzed and shown in terms of contour plots of K extraction as a function of two variables at a time. Fig.4.18 shows the effect of time and flux dosage on K dissolution and it indicates that it is possible to obtain high K recovery (above 70%) with the flux greater than ~80% at the time range of 7 to 8 minutes. This orthogonal design array analyzed that the rank of flux is 1 it means it is most dominating factor in this design, after that time, power and the last one is charcoal. Probability plot shown in Fig.4.19 indicates that p value is 0.055 which means that the model is significant. The model indicates that the value of R square is 89.7%. This value indicates that the model is quite appropriate for these experiments. The main effect plot is shown in Fig.4.20 and it can be easily concluded from these plots that all four factors are dominating for K dissolution and it increases at faster rate with flux dosage and charcoal in comparison to power and time.

The regression equation of the model is given by-

$$K (\%) = - 56.3 + 0.750 \text{ Flux } (\%) + 1.01 \text{ Charcoal } (\%) + 3.37 \text{ Time (mins)} + 0.0364 \text{ Power (W)}$$

Table 4.3. Experimental Taguchi L9 design

| S. No. | Charcoal (%) | Calcium chloride (%) | Time(mins) | Power (Watts) | K (%) |
|--------|--------------|----------------------|------------|---------------|-------|
| 1 | 10 | 30 | 4 | 540 | 2.6 |
| 2 | 15 | 30 | 6 | 720 | 27.7 |
| 3 | 20 | 30 | 8 | 900 | 39.3 |
| 4 | 10 | 60 | 6 | 900 | 62.1 |
| 5 | 15 | 60 | 8 | 540 | 57.7 |
| 6 | 20 | 60 | 4 | 720 | 58.8 |
| 7 | 10 | 90 | 8 | 720 | 70.8 |
| 8 | 15 | 90 | 4 | 900 | 66.0 |
| 9 | 20 | 90 | 6 | 540 | 67.8 |
| 10 | 20 | 90 | 8 | 900 | 54.6 |

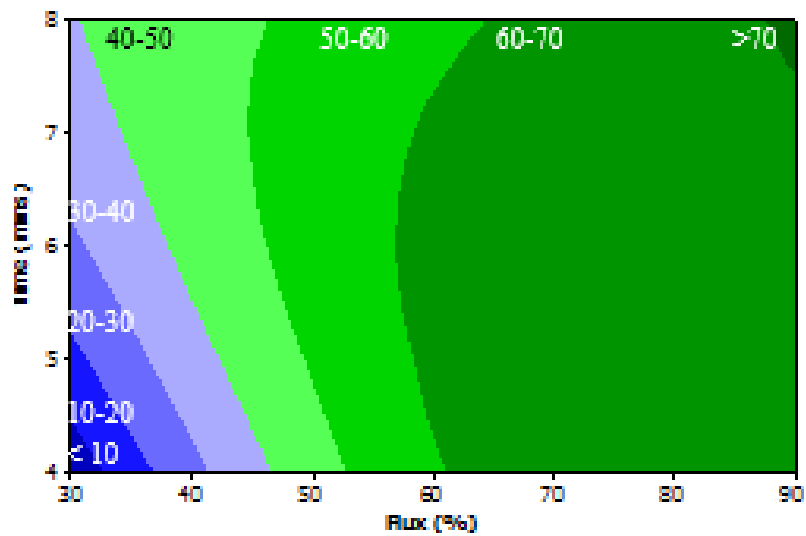


Fig.4.18. Contour plot for K dissolution vs Time, Flux.

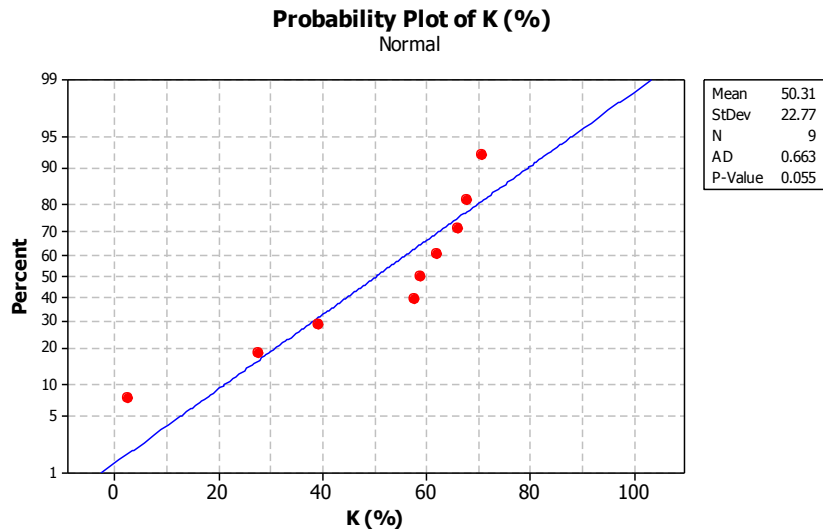


Fig.4.19. Probability plot for K dissolution.

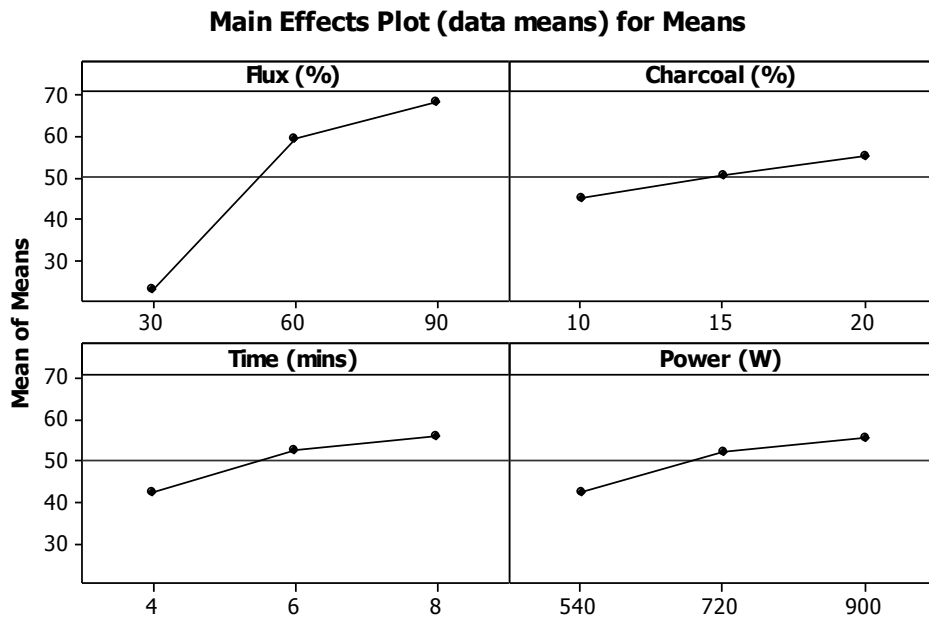


Fig.4.20. Main effect plots for K dissolution.

4.3.3 Mechanical activation followed by roasting and leaching

In this method three fluxes CaCl_2 (fused), NaOH and CaCO_3 was tried. In this method feed and flux was mixed in predefined amount and mechanically activated in the planetary ball mill for 8hrs at the speed of 200 RPM. After milling grinded mass was thermally treated in muffle furnace then fused mass was re-grinded in pestle mortar and leached in water or citric acid solution according to the flux used. In case of CaCl_2 (fused) water leaching was carried out and in case of NaOH and CaCO_3 citric acid (2% solution) leaching was done. In case of CaCl_2

(fused) flux optimization of parameters was done by using the Taguchi L9 experimental model. In case of CaCO₃ optimization was done by using the response surface box behnkem design. But in case of NaOH optimization was done by using some regular experiments.

Treatment of feed with CaCl₂ fused:

In this case feed was mixed with CaCl₂ (fused) and mechanically activated in the planetary ball mill for 8hr at the speed of 200 RPM. After preparing a mixture of feed and flux in different proportion Taguchi L9 experimental design of the same orthogonal array that was studied in the case of hand mixed feed and CaCl₂ (fused), was performed to study the effect of mechanical activation in context to K dissolution.

1. Taguchi Statistical design

This design used to optimize the parameters in context to K dissolution. It is the same model presented in section 3.4. Design experiments are shown in Table 4.4. The contour plot of K vs temp, flux as shown in Fig.4.21 indicates that the K dissolution can be achieved above 75% when flux was greater than 80% at temperature ranging from 700°C to 900°C. The main effect plot was shown in Fig.4.22 and these plots indicate that the most important factor for this model is flux then temperature and last one is time. The probability plot was shown in Fig.4.23 and this plot indicates that the model used in this study is significant and the regression equation for this model is given by-

$$K (\%) = 93.6 - 0.304 \text{ Time} - 0.116 \text{ Temp} + 1.11 \text{ Flux}$$

Table 4.4. Taguchi L9 experimental design

| Time(min) | Temp(°C) | Flux (%) | K (%) |
|-----------|----------|----------|-------|
| 30 | 700 | 30 | 28.23 |
| 30 | 800 | 60 | 66.41 |
| 30 | 900 | 90 | 81.9 |
| 60 | 700 | 60 | 57.3 |
| 60 | 800 | 90 | 82.03 |
| 60 | 900 | 30 | 1.13 |
| 90 | 700 | 90 | 84.59 |
| 90 | 800 | 30 | 19.85 |
| 90 | 900 | 60 | 17.31 |

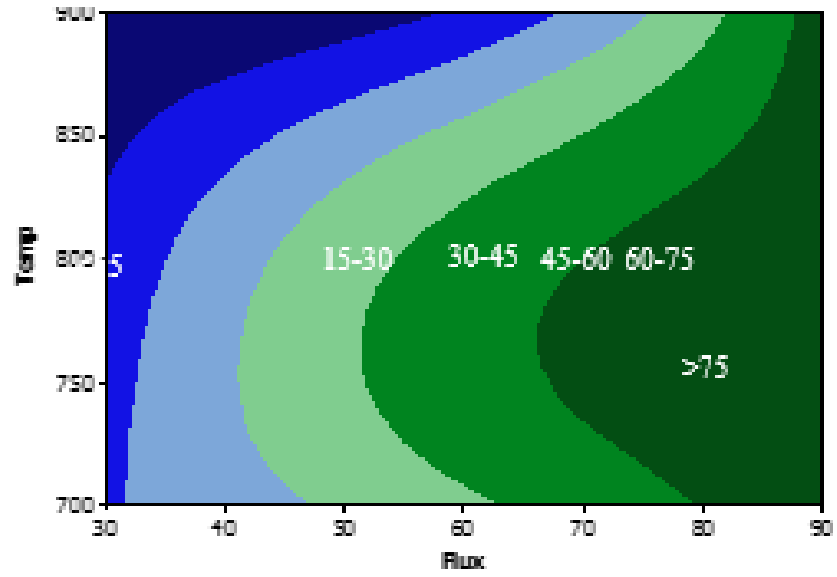


Fig.4.21. Contour plot of K vs temp, flux.

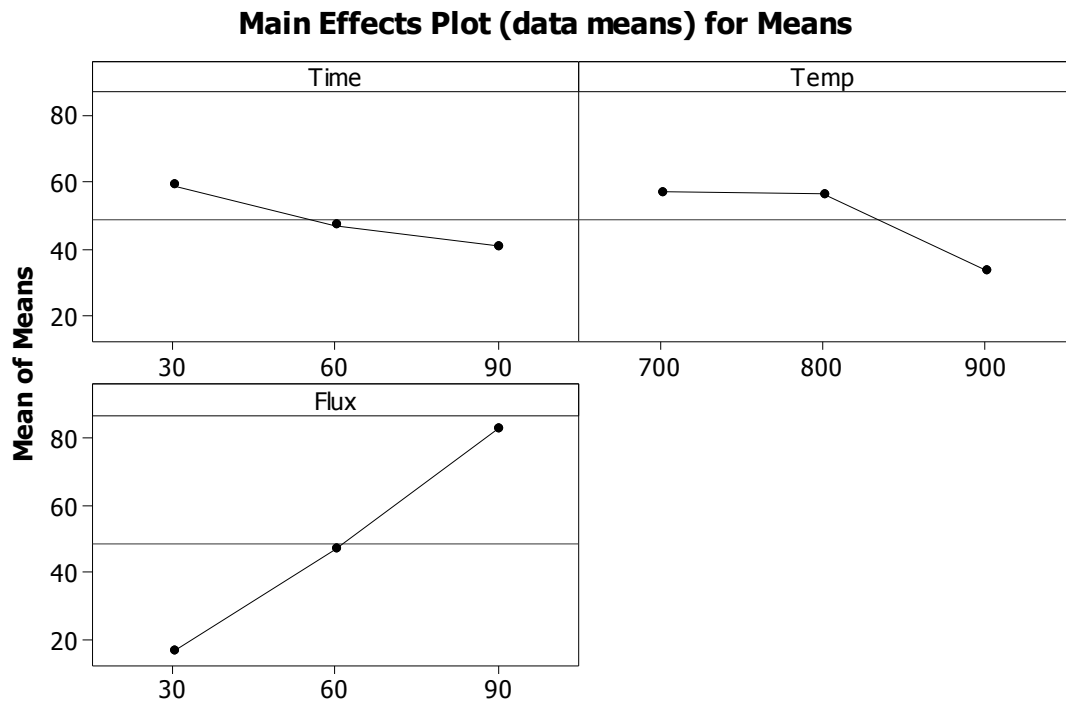


Fig.4.22. Main effect plot for K dissolution.

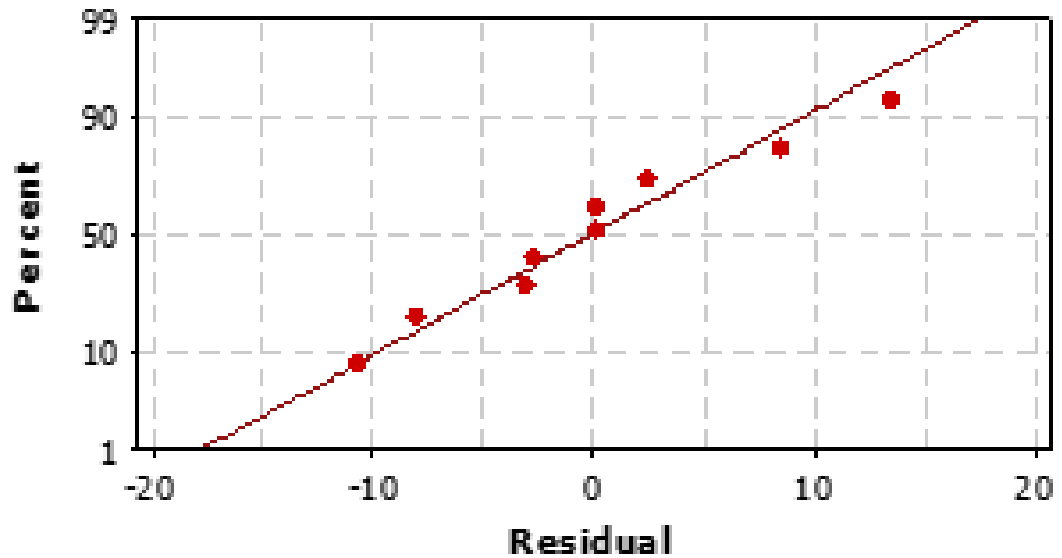


Fig.4.23. Probability plot for design.

Treatment of feed with NaOH

The feed and NaOH was mixed in the same proportion which was studied in case of muffle furnace treatment, and grinded in planetary ball mill for 8hrs at the speed of 200 rpm. One solution is prepared by direct leaching of this milled sample without giving any treatment and other solutions were prepared by heat treatment at various temperatures for the optimum time previously decided in case of muffle furnace treatment. After thermal treatment the two step leaching was performed on the samples. After leaching and filtration, solutions were checked in flame photometer to see the effect of mechanical activation on the sample. The effect of mechanical activation on the sample can be clearly seen in Fig.4.24. This shows that at all temperatures, mechanical activated (feed + NaOH) gives more K dissolution as compared to the samples without mechanical activation. In case of mechanical activation almost all K can be released from the feed material. In case of mechanical activation followed by direct leaching as much as 47% K can be released. It means in mechanical activation the complex silicate network has broken and the release of interlayer cation becomes easy.

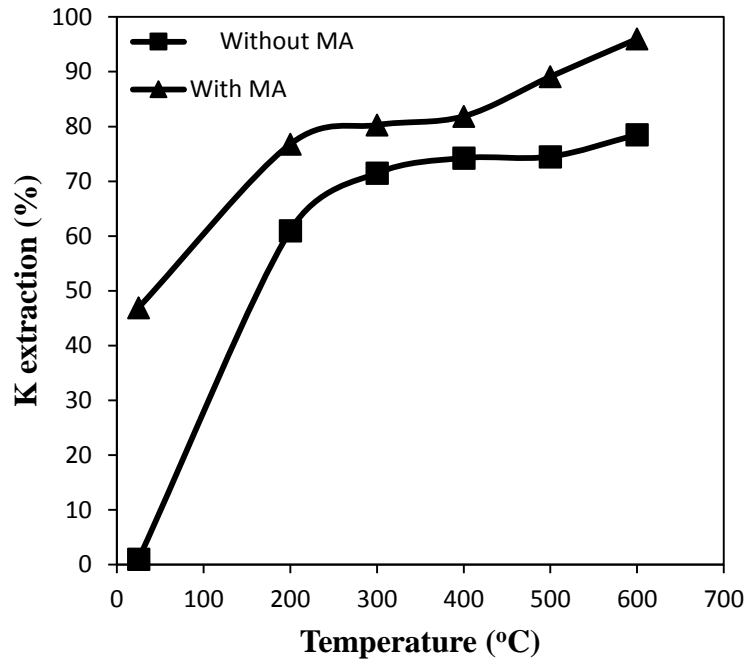


Fig.4.24. Effect of mechanical activation on (G + NaOH) system.

And when this mechanical activated powder was heat treated at temperature of 200°C and leached K dissolution was found to be almost equal to that one in the sample of (G + NaOH) hand mixed and treated at 600°C. This indicates that after mechanical activation surface area of particles become more exposed. On account of increased surface area the reaction kinetics become faster so the mechanism which happens in hand mixed sample at 600°C, occur readily at lower temperature with the same mechanical activated sample.

And when MA sample was treated at 600°C and leached almost all K was released from the sample. It indicates that mechanical activation before heat treatment may be a promising technique to increase K dissolution.

Treatment of feed with CaCO₃, CaSO₄, Ca (OH)₂

The feed sample was mixed with CaSO₄.2H₂O, CaCO₃ and Ca (OH)₂ in appropriate proportion and grinded in a planetary ball mill for 8hrs at the speed of 200rpm. Some amount of this milled sample was direct leached with citric acid, and some was heat treated in muffle furnace at different temperatures and then leached in citric acid solution. After leaching and filtration samples were tested in flame photometer analysis. And it was concluded that the fluxes such as CaSO₄ and Ca (OH)₂ were ineffective and flux CaSO₄ was effective in context to K dissolution. So the optimization of parameters was done in case of (G+CaCO₃) system by Box behken design.

Direct leaching of (feed + flux) mixture without any treatment-

It is clearly shown by the Fig. that in case of CaCO_3 the K dissolution is more than that in case of other two fluxes. At all flux dosage (40, 70,100%). This behavior indicates that CaCO_3 is more effective as compared to other two in the context of K dissolution. In case of CaCO_3 maximum K dissolution is achieved at 70% flux dosage and in another two fluxes K dissolution is maximum at 40% flux dosage.

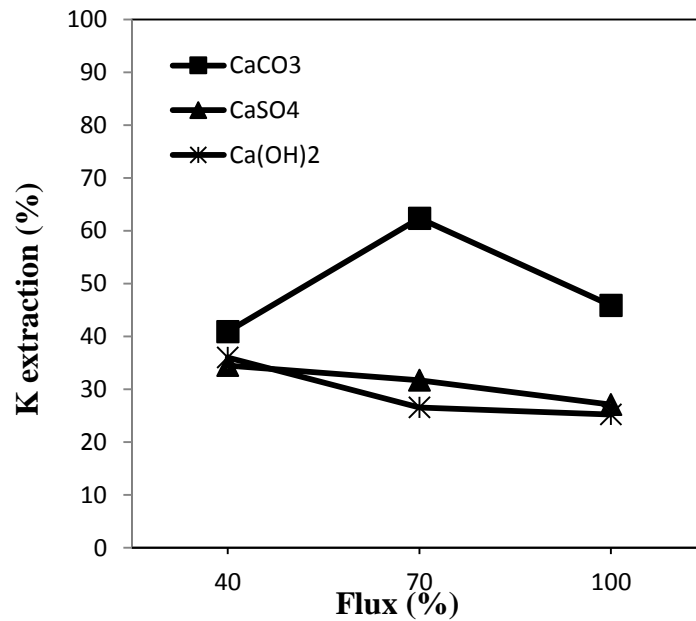


Fig.4.25. Effect of dosage of different fluxes on K extraction of Glauconite (Leachant- citric acid).

Box behnken design of thermal treatment of MA ($\text{G}+\text{CaCO}_3$) followed by leaching-

The parameters of the experiments performed with CaCO_3 were optimized using Box behnken design. In this statistical design total 15 experiments were done by taking three same experiments at the central point. The total statistical model experiments were presented in Table 4.5. The R- square value for this model was 90.9% it shows that the model is significant.

The probability plot for model as shown in Fig.4.26 tells that the experiments were quite close to the predicted actual line of the model it means that model is significant. The contour plot of K dissolution vs temperature, flux was represented in Fig.4.27 which shows that the K dissolution was above 80% if the flux was used above 80% in the temperature range of 1025 to 1100°C. The another contour plot was shown in Fig.4.28 was plotted in between K dissolution

vs time, flux It shows the K dissolution is above 80% at flux above 70% and at times in between 100 to 120 minutes. The regression equation for this model was given by-

$$K=74.62+13.47*\text{Flux}+2.24*\text{temp}+3.20*\text{time}+7.17*\text{flux}*\text{temp}.-1.59*\text{flux}*\text{time}-6.90*\text{temp}.*\text{time}-10.55*\text{flux}^2-7.49*\text{teme}^2 + 0.47*\text{time}^2$$

The main effect plot was shown in Fig.4.29 which tells how temperature, time and flux affects K dissolution individually. This plot shows that on increasing flux K dissolution increased continuously but the rate of increment decreases after 70% flux. The K dissolution increases with temperature up to 1000°C and after 1000°C K dissolution decreases. K dissolution increases with increasing time from 60 minutes to 120 minutes.

Table 4.5. Experiments of the model

| Flux (%) | Temp.(°C) | Time(min) | K (%) |
|----------|-----------|-----------|-------|
| 40 | 1000 | 120 | 54.27 |
| 70 | 1000 | 90 | 74.4 |
| 40 | 1000 | 60 | 51.5 |
| 70 | 1000 | 90 | 74.4 |
| 70 | 1100 | 60 | 74.3 |
| 40 | 900 | 90 | 50.4 |
| 70 | 900 | 60 | 47.7 |
| 100 | 1000 | 60 | 78 |
| 40 | 1100 | 90 | 32.2 |
| 70 | 1000 | 90 | 75.0 |
| 70 | 1100 | 120 | 73.7 |
| 70 | 900 | 120 | 74.7 |
| 100 | 1100 | 90 | 77.1 |
| 100 | 1000 | 120 | 74.4 |

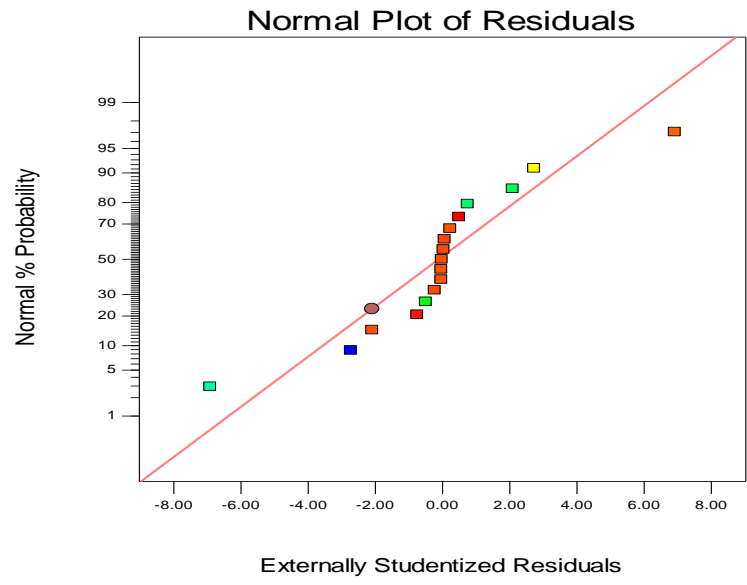


Fig.4.26. Probability plot for model.

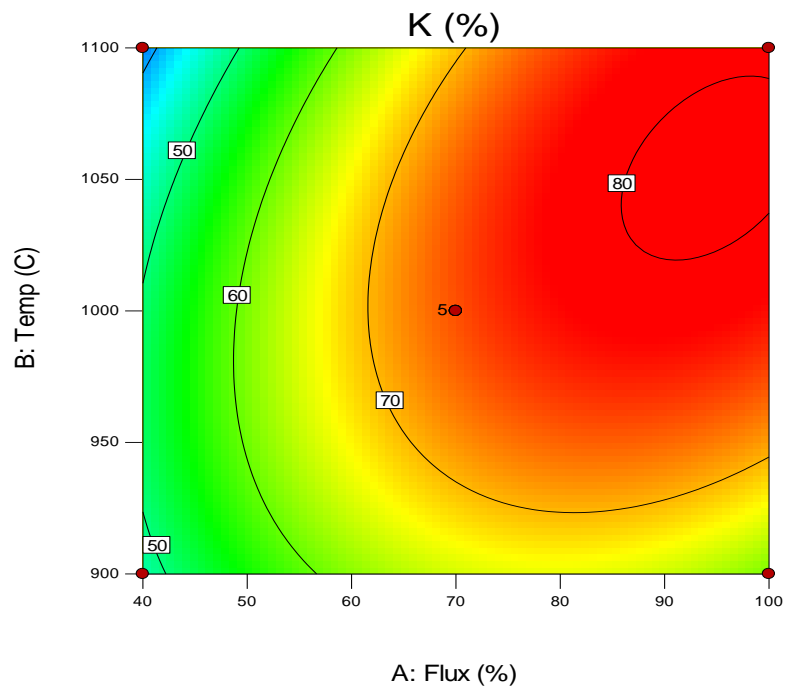


Fig.4.27. Contour plot of K vs temp, flux.

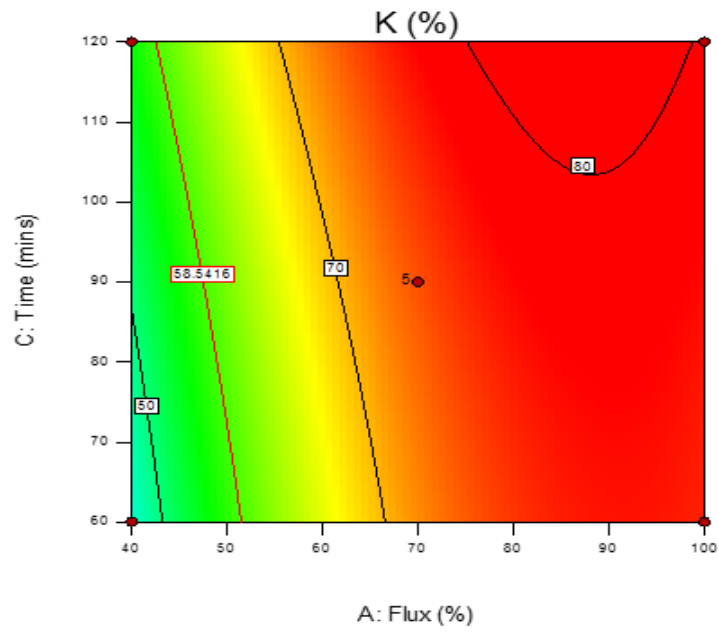


Fig.4.28. Contour plot of K vs time, flux.

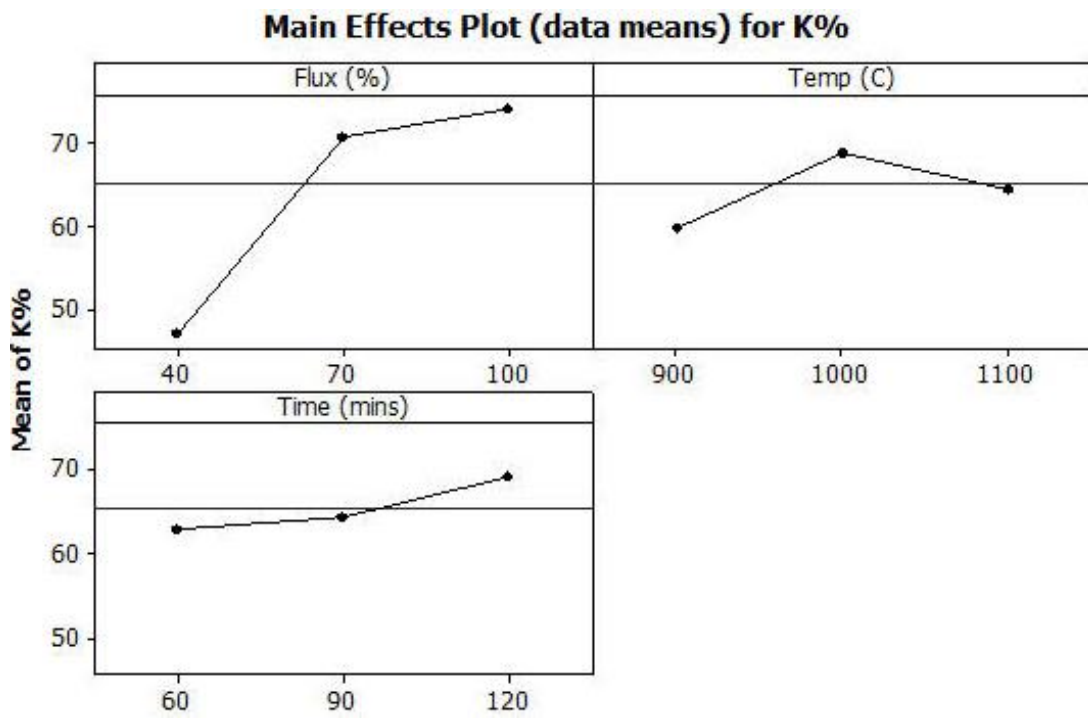


Fig.4.29. Main effect plots for model.

4.4 Characterization of heat treated samples and leach residue-

In this section characterization of feed with different fluxes is presented. This section covers characterization of heat treated sample and characterization of leach residue which was obtained after filtration. This section is also subdivided into sections according to main fluxes such as CaCl₂, NaOH, CaCO₃ and Na₂CO₃.

4.4.1 In case of feed treated with CaCl₂ (fused)-

The feed sample was treated with CaCl₂ (fused) in muffle furnace, microwave, MA then muffle furnace, the behavior of the sample at each stage was recorded by XRD, FESEM and TGA/DTA.

X-Ray diffraction analysis of sample

X-ray diffraction curve of feed treated with CaCl₂ (fused) is represented in Fig.4.30. From this Fig. it is clear that when the sample was treated at 900°C without flux, then the crystallinity of phases decreased and some phases are disappeared. When sample was treated with CaCl₂ (fused) the new phases formed such as sylvite, anorthite and wollastonite and the parent phases of muscovite, microcline, and glauconite disappeared. So it confirms that these main phases react with CaCl₂ and form sylvite, anorthite and wollastonite. When XRD curves of leach residues are plotted then it is observed that sylvite peaks disappeared. So it can be easily concluded sylvite phase is readily soluble in water. In the leach residue XRD the main phases are anorthite and wollastonite.

From XRD it is revealed that possible reaction in the system is-



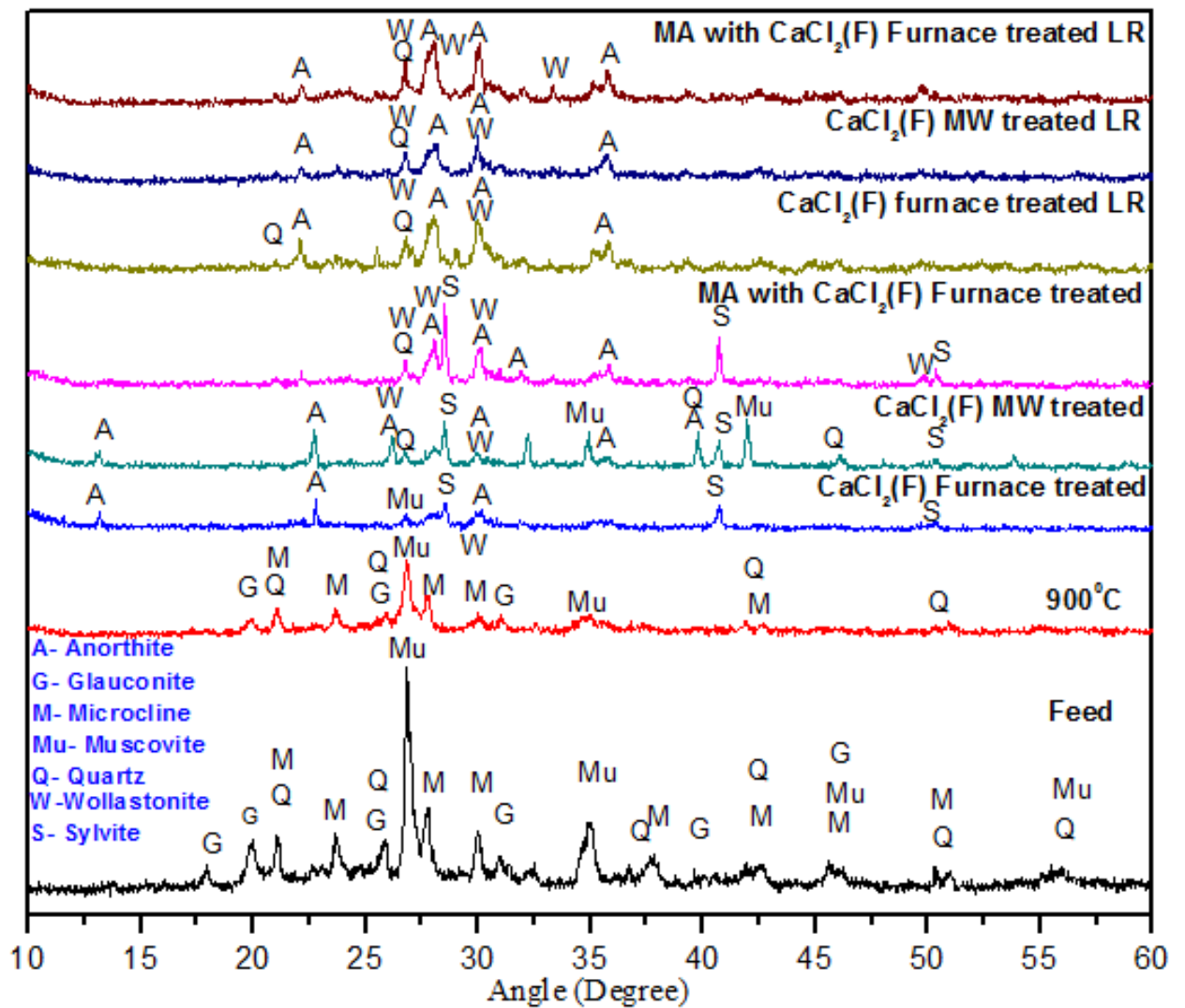


Fig.4.30. XRD analysis of (G+CaCl₂) at all stages.

Scanning electron microscopy/Electron dispersive X- ray studies-The SEM images of heat treated samples (furnace treated, microwave treated and MA + furnace treated samples) and corresponding leach residues images are presented in Fig. 4.31. The 1st image shows that during roasting all mass become fused and agglomerated and corresponding leach residue in image 2nd shows that after leaching size of particles decreased and texture become rough and particles are dispersed thoroughly. In the 3rd image particles want to form agglomerates and some cubic morphology appear which is attributed to the formation of sylvite corresponding leach residue in image 4th shows that after leaching cubic shapes disappears and texture become disperse.

EDX analysis of LR after each treatment (MF treated, MW treated, (MA+MF) treated) is presented in Fig.4.32. It shows that the K amount is only about less than 1% which was 8.71% in feed material. It shows that almost all K has been released during leaching of samples.

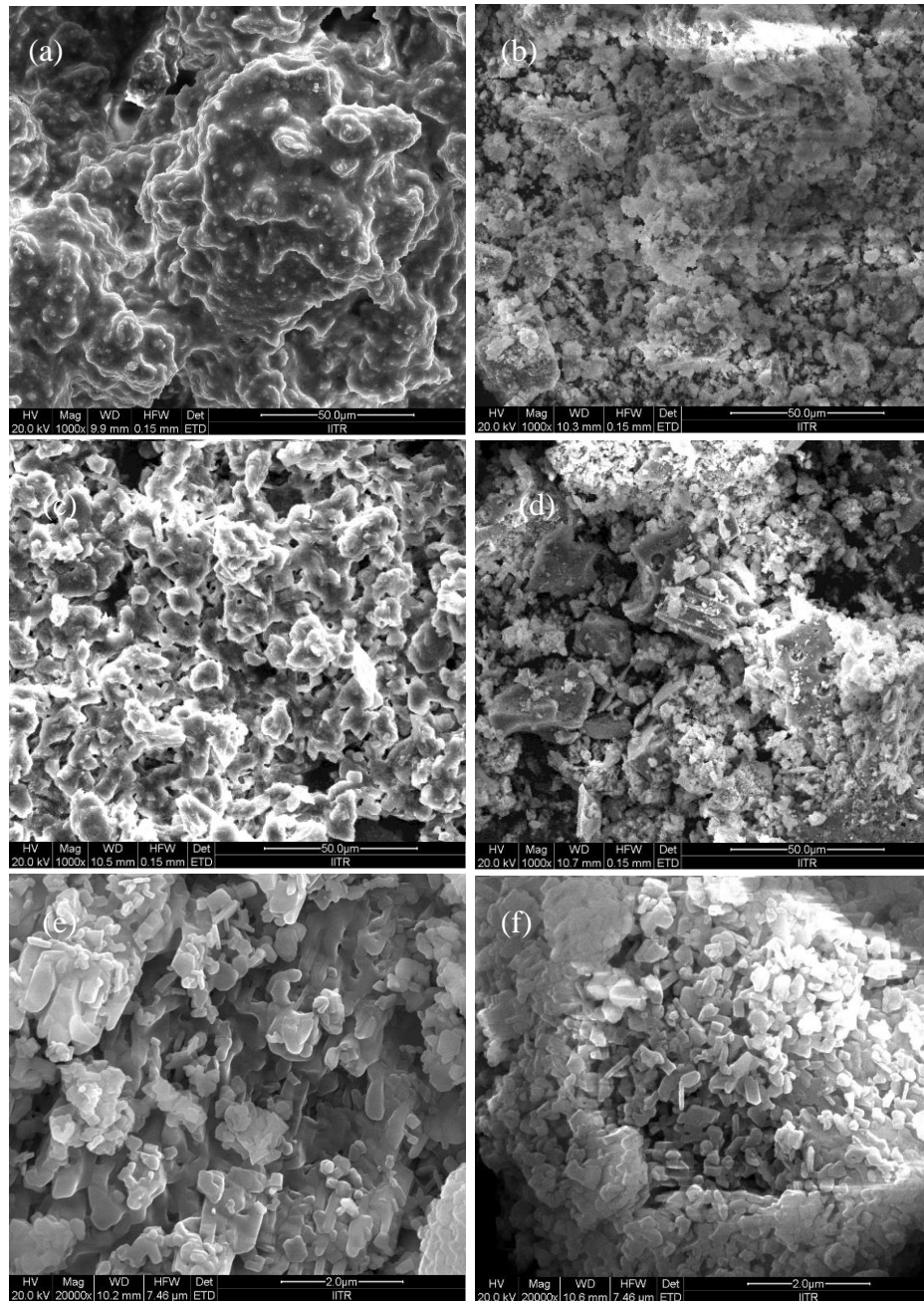


Fig. 4.31. ((a, b) furnace HT and LR at 1000X) (c, d) MW HT and LR at 1000X) (e, f) MA + Furnace HT and LR at 20000X).

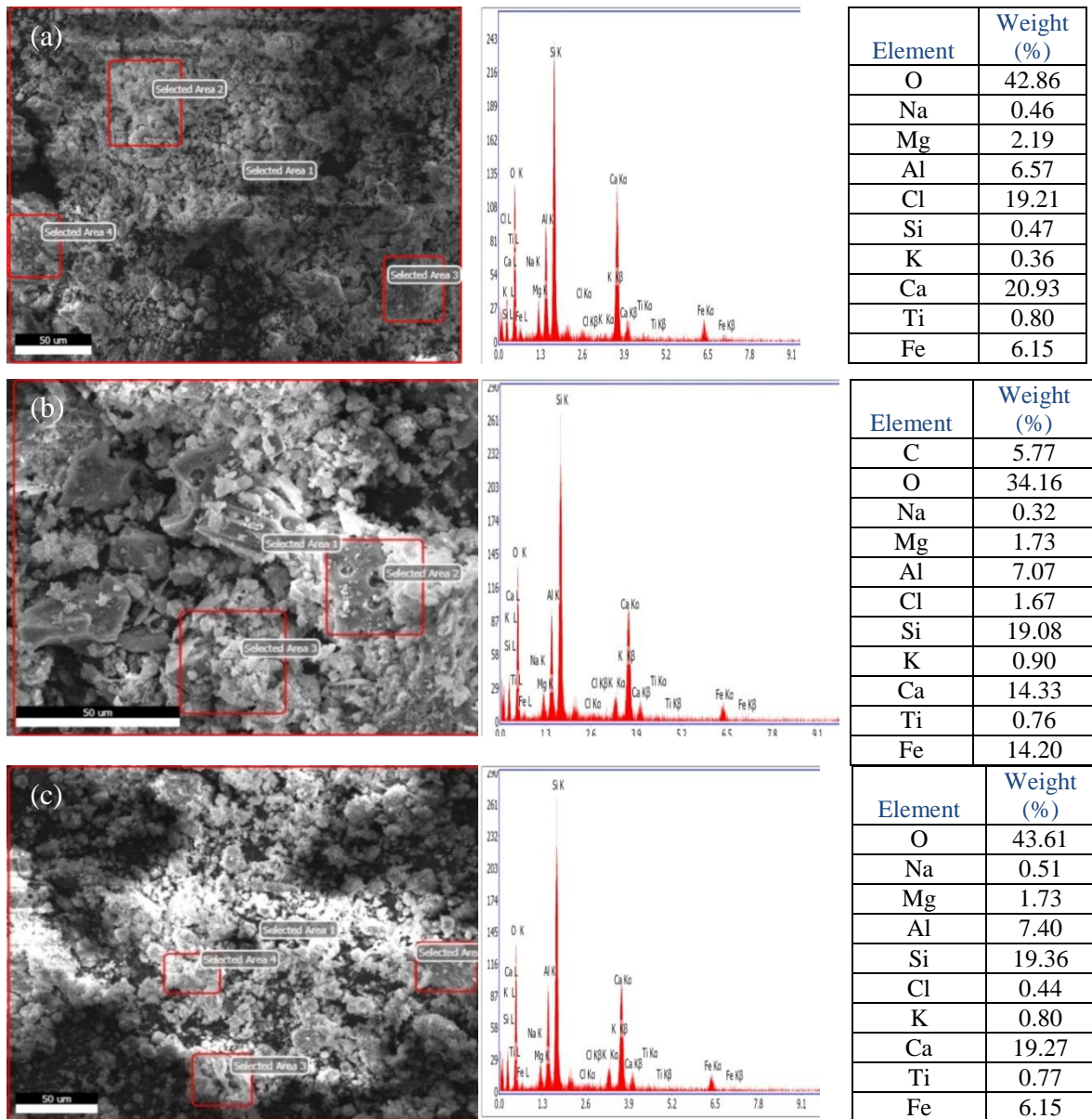


Fig.4.32. EDX analysis of leach residue (a) MF treated (b) MW treated (c) MA+ MF treated.

TGA/DTA analysis of (G+CaCl₂) system

In TGA/DTA analysis of the sample which is presented in the Fig.4.33, mass loss is observed as in feed but in this (G+CaCl₂) hand mix sample, mass loss is 16.9% reaching to 151°C. This mass loss is due to dehydration and dehydroxylation. Above the temperature up to 650°C there is a thermal stability in the sample but as further increase in the temperature there is an endothermic peak in the DTA curve at around 710°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

is due to evaporation of sylvite phase, though the evaporation temperature is above 1400°C but due to formation of CaCl₂-KCl eutectic system evaporation of KCl started at 900°C.

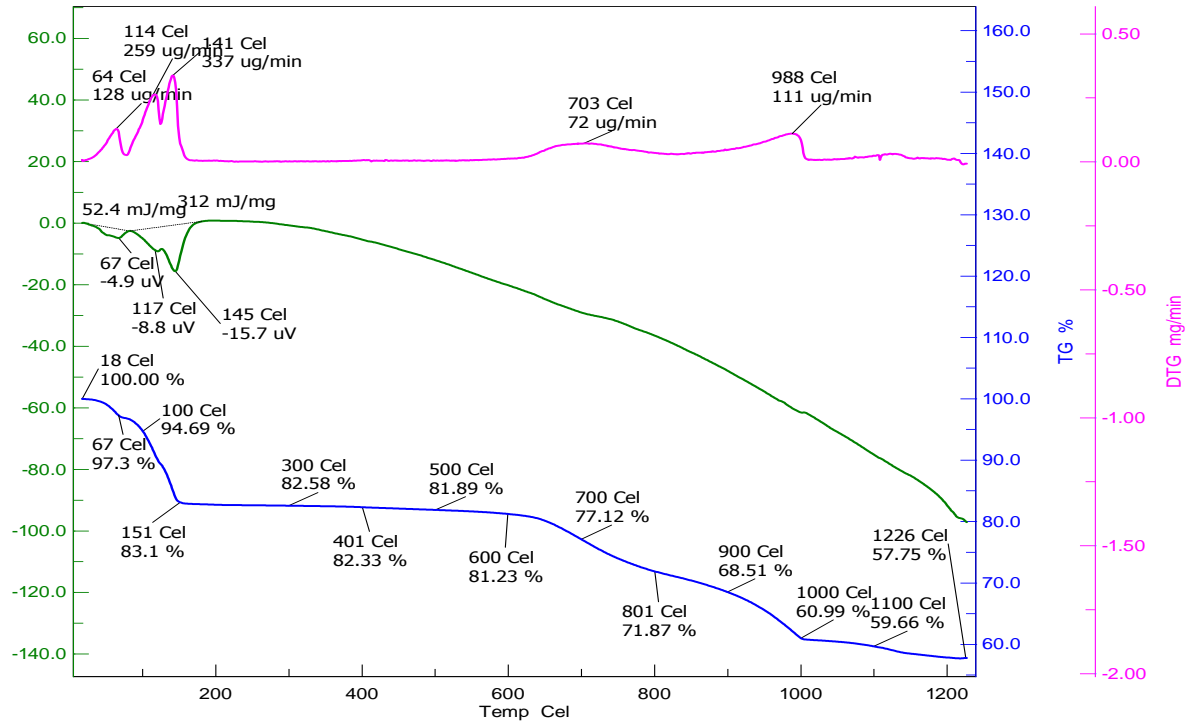


Fig.4.33. TGA/DTA analysis of (G+CaCl₂) mixture.

4.4.2 In case of feed treated with NaOH

The feed sample was treated with NaOH in muffle furnace, MA then muffle furnace, the behavior of sample at each stages was studied by XRD, FESEM and TGA/DTA.

X-Ray diffraction analysis of sample

It is clearly seen from Fig.4.34 that when without mechanical activated (feed+ flux) was heat treated at 600°C and analyzed in XRD, then the parent phases of feed which were muscovite, microcline, and glauconite disappeared and formation of some new phases such as sodium silicate, Kalsilite takes place. When this heat treated sample was leached into water and leach residue was studied in XRD then it was found that the peaks of sodium silicate which were present in heat treated sample were disappeared and Kalsilite became the main phase along with some amount of quartz. This behavior of diffractogram clearly justifies that sodium silicate was dissolved in water during leaching.

When the leach residue of water leaching was re-leached in citric acid solution and XRD analysis of second leach residue was done then it is quite clear from Fig.4.34 that Kalsilite phase disappeared and quartz became the main phase.

When the XRD analysis of the mechanical activated (feed + flux) followed by roasting at 600°C, leach residue 1(LR 1) and of leach residue 2(LR 2) was performed then this shows that sodium silicate and Kalsilite form in heat treated sample which was disappeared from the diffractogram of LR 1 and in case of LR 2 Kalsilite was also disappeared and quartz became the main phase of the sample. According to XRD analysis possible reactions are as follows-

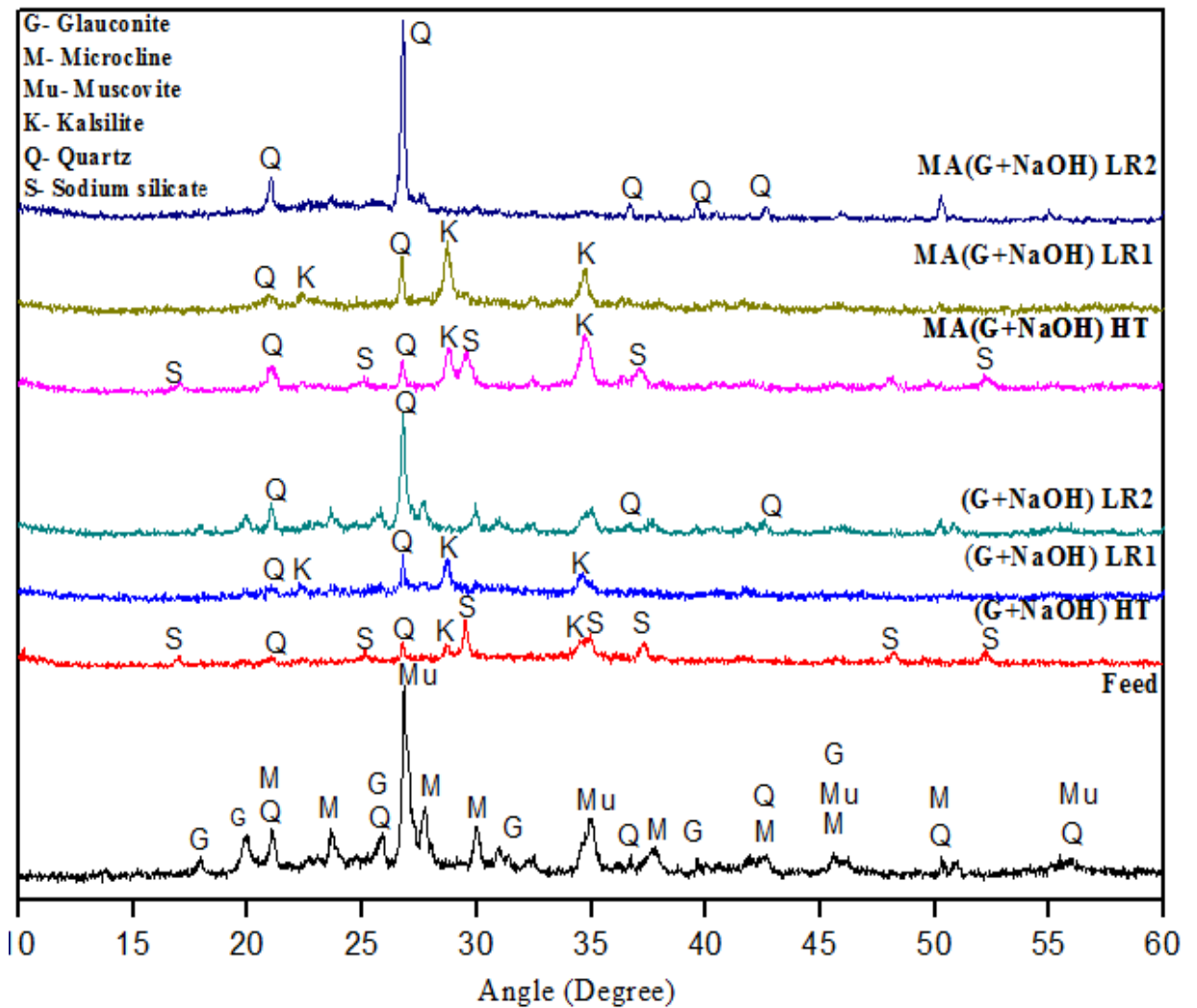
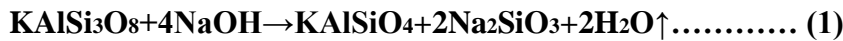


Fig.4.34. XRD analysis of (G+ NaOH) system at all stages.

Scanning electron microscopy/Electron dispersive X- ray studies

The SEM images of heat treated samples and corresponding leach residues LR1 and LR2 are presented in Figure 4.35. The 1st image shows that during roasting the reaction between NaOH and K bearing phases present in the structure takes place and the some hexagonal crystal appeared. Corresponding leach residue in 2nd image shows that after first leaching the particle become dispersed throughout in the matrix. In third image it can be clearly seen that after 2nd leaching particles of only one type is observed. The same behavior of heat treated sample and corresponding leach residue in the 4th, 5th and in 6th image. Only difference is that in case of mechanically activated samples particles was fragmented and become of less size.

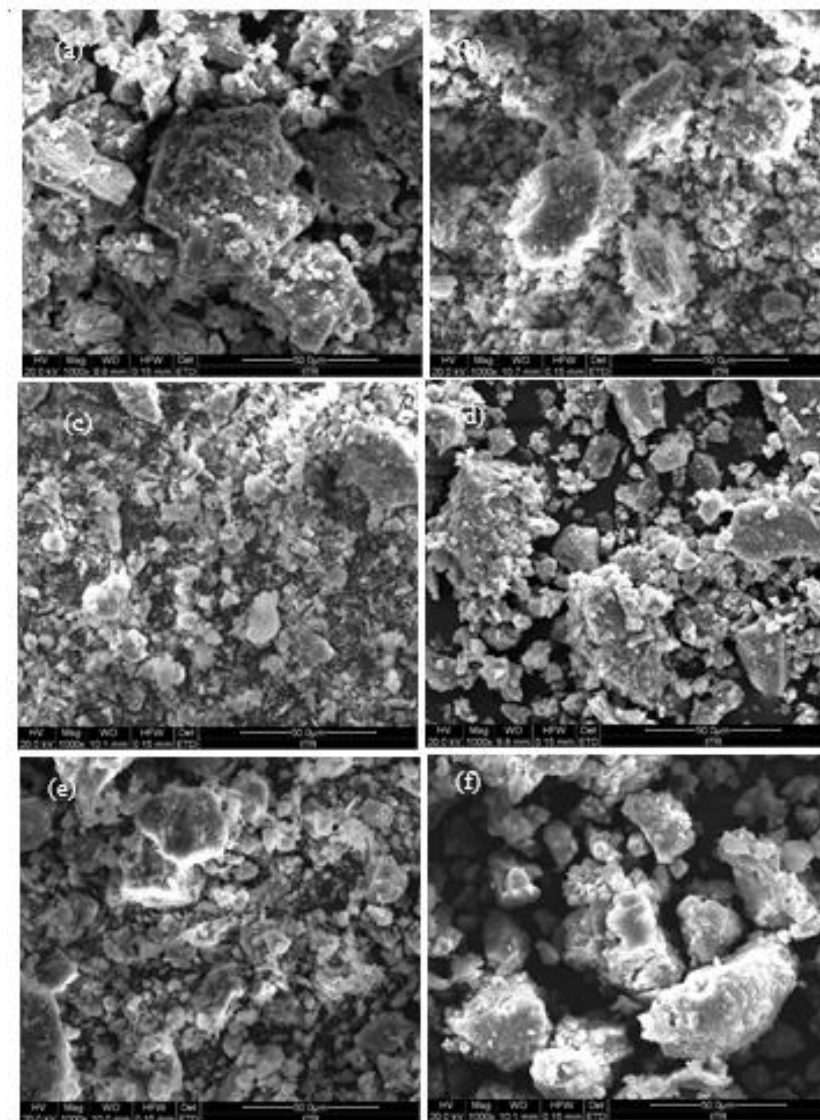


Figure 4.35. (G + NaOH) at 1000X (a) HT (b) LR1 (c) LR2 (d) MA+HT(e) MA LR1 (f) MA LR2.

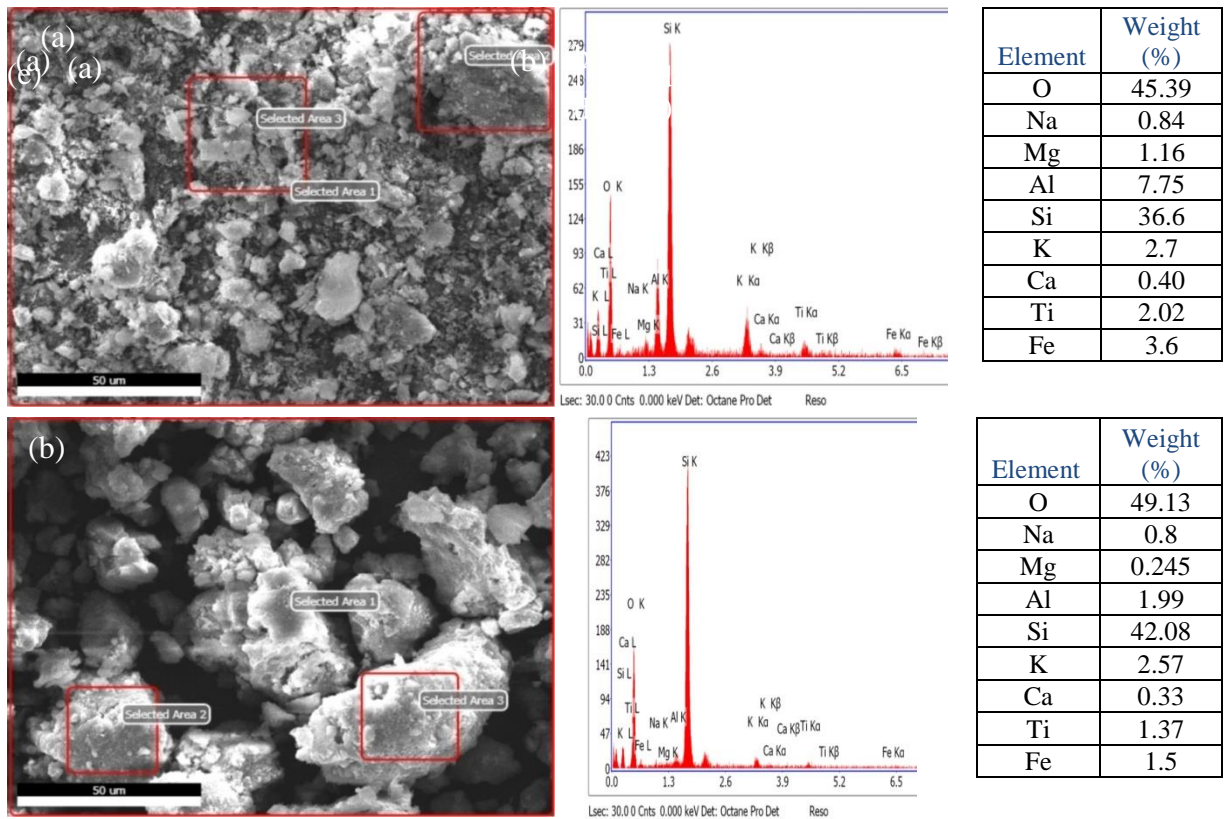


Fig.4.36 EDX analysis of Leach Residue (a) MF treated (b) MA+MF treated.

TGA/DTA analysis of (G + NaOH) system

In DTA curve there are four endothermic peaks at 68°C, 138°C, 236°C and 296°C, first two endothermic peaks are due to volatilization of physically absorbed water in NaOH, corresponding weight loss can also be seen in TG curve, weight loss is also due to the dehydration of mineral. Endothermic peak at 296°C is due to the melting of NaOH, though the melting temperature is 318°C but due to mixing with other compounds it has decreased [37].

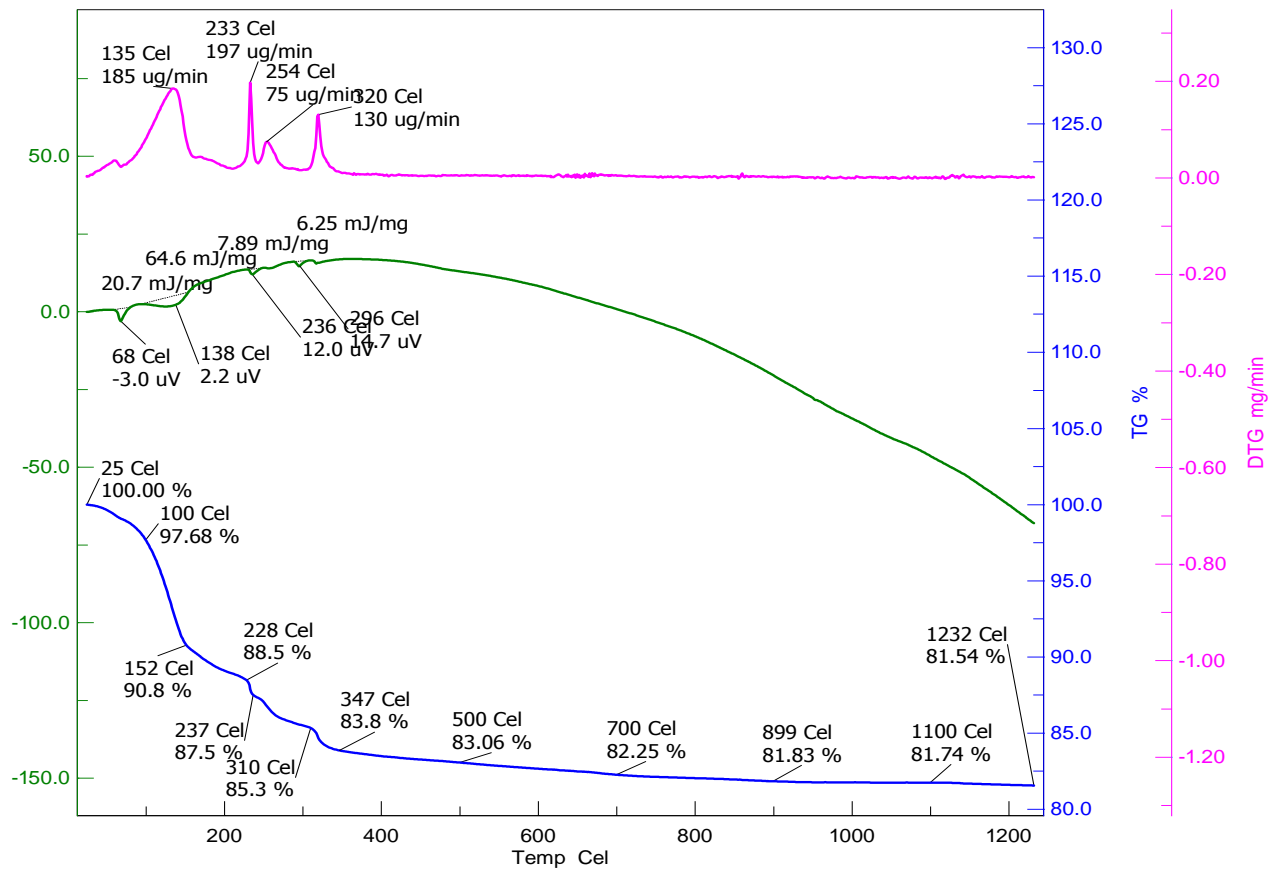


Figure 4.37. TGA/DTA analysis of (G+NaOH) system.

4.4.3 In case of feed treated with CaCO₃

The feed sample was mixed with CaCO₃ mechanically activated, thermally treated in muffle furnace and leached in citric acid 2% solution the behavior of sample at each stages were recorded by XRD, FESEM and TGA/DTA.

X ray diffraction analysis of sample

XRD analysis is shown in Fig.4.38 tells that when XRD analysis of mechanical activated (G+CaCO₃) without thermal treatment was performed then due to mechanical activation all peaks of glauconite and some of muscovite, microcline and quartz disappeared. Some peaks of microcline, muscovite and quartz were still present in the curve but peak height is decreased.

When XRD analysis of thermally treated MA (G+CaCO₃) was recorded then it shows that the formation of new phases of Kaliophilite, Wollastonite, Anorthite and potassium carbonate occurred due to thermal interaction of muscovite and microcline with calcium carbonate. When this heat treated sample was leached in 2% citric acid solution and XRD analysis was done then

it shows that most of the peak of Kaliophilite and all peaks of potassium carbonate disappeared this disappearance of phases was due to solubilization of phases during leaching.

The possible reaction according to XRD analysis can be written as-

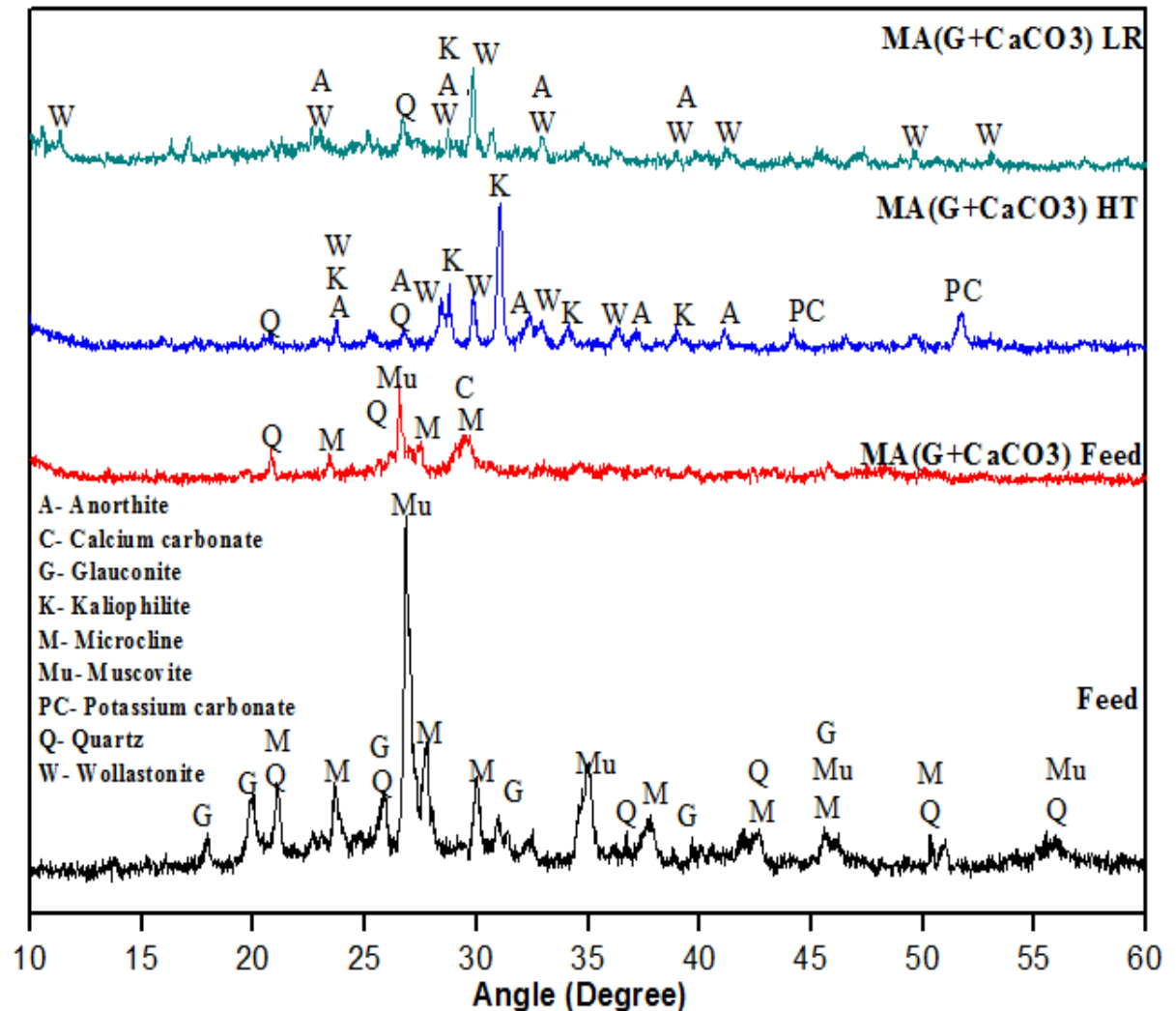


Fig.4.38. XRD analysis of MA (G+CaCO₃) system.

Scanning electron microscopy/Electron dispersive X ray studies- The SEM images are shown in Fig.4.39 and it can be inferred from 1st image that due to mechanical activation the structure of particles was totally disrupted and in 2nd image it is clear that after heat treatment the particles want to form agglomerate. In the third image it is clear that only wollastonite is remains in the structure after leaching. In fourth image which is at higher magnification

wollastonite flakes can be clearly seen. The EDX analysis of leach residue was shown in Fig. 4.44 and it can be seen that the K amount is only 1.88% which was 8.71% in feed material. It shows that almost all K has been released in the leaching.

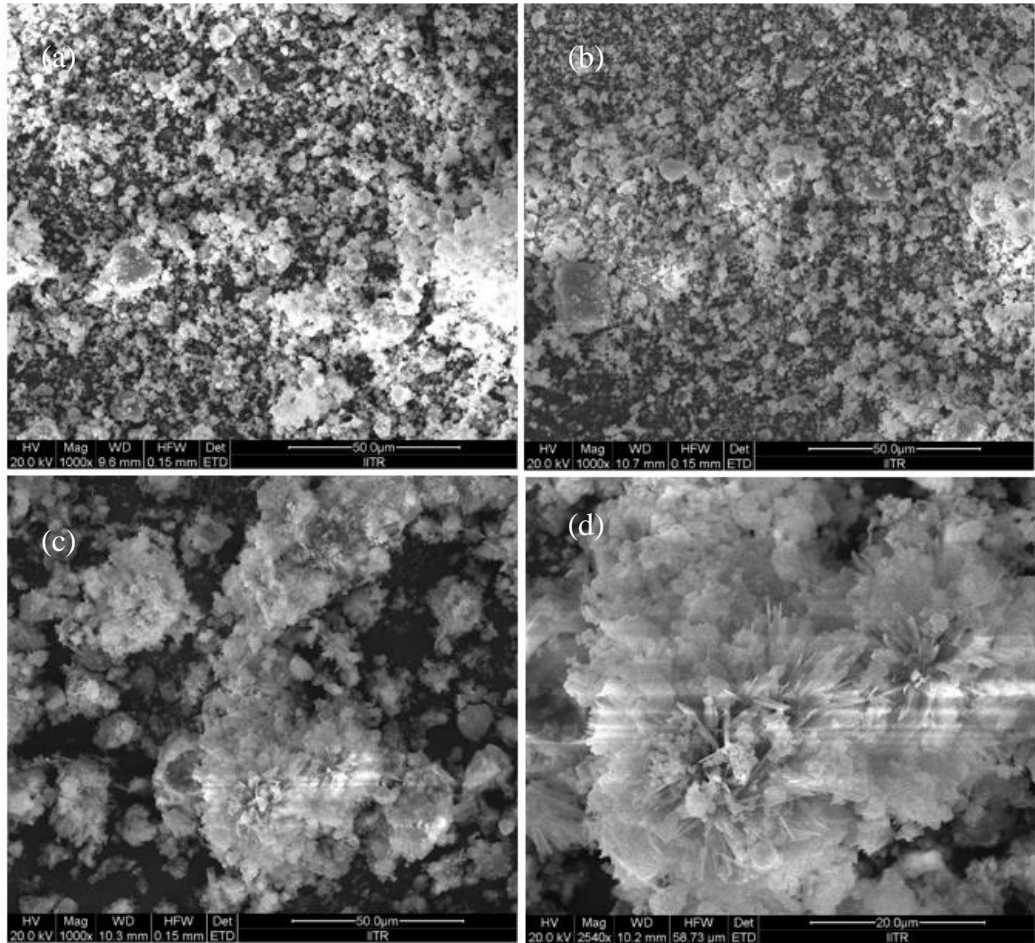


Fig.4.39. MA (G+CaCO₃) (a) Feed (b) HT(c) LR at 1000X (d) LR at 5000X.

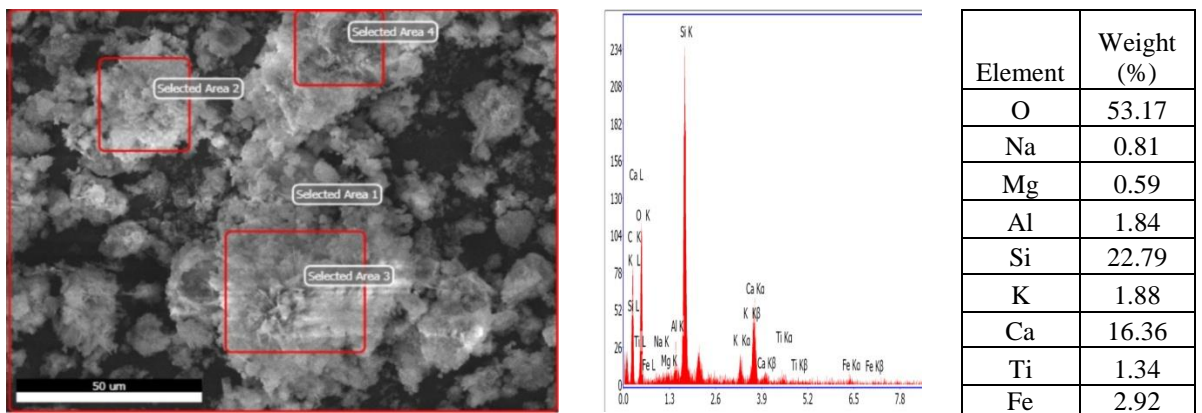


Fig.4.40. EDX analysis of leach residue sample.

TGA/DTA analysis of MA (G+CaCO₃) system

Due to dehydration and dehydroxylation initial 17.46% mass loss can be seen from the TG curve. In DTA at 637°C there is an endothermic peak which is due to the decomposition of CaCO₃, due to mechanical activation effective surface area has increased thus reactivity has also increased so decomposition temperature of CaCO₃ has decreased from 825°C to 637°C, corresponding mass loss can be seen from TG curve up to 699°C. Exothermic peak between just ahead of 900°C in DTA curve is attributed to the formation of new phase kaliophilite which has been assured by XRD analysis [38].

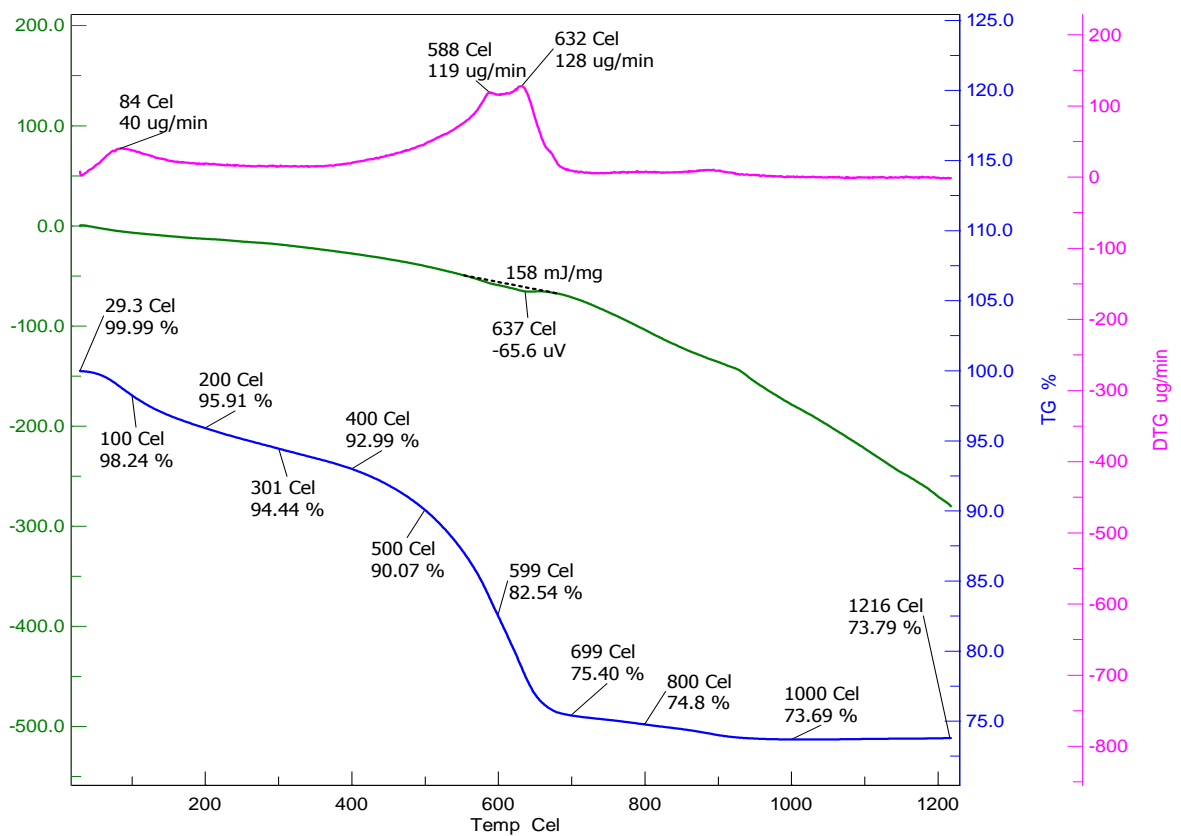


Fig. 4.41. TGA/DTA analysis of MA (G+CaCO₃) system.

CHAPTER 5.

CONCLUSION

In the whole study most of the calcium bearing as well as sodium bearing fluxes were tried in context of the K dissolution. The following conclusions were made from the whole study-

1. Direct leaching of feed in different leachant was proved ineffective in context of K dissolution.
2. Thermal treatment of feed without flux followed by leaching in different media was found to be ineffective in context to K dissolution performance.
3. The treatment with fluxes such as Na_2SO_4 , NH_4Cl , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl , CaCO_3 , CaO , $\text{Ca}(\text{OH})_2$, $\text{Ca}_3(\text{PO}_4)_2$ followed by leaching in water was found to be ineffective in context to K dissolution.
4. In case of calcium chloride flux all three methods such as muffle furnace treatment, microwave treatment and mechanical activation followed by thermal treatment give good results in context of K dissolution. In case of only muffle furnace treatment glauconite gave 88 % of K extraction at 900°C , 60 minutes residence time and with 90% flux. In case of (mechanical activation + muffle furnace treatment) glauconite gave 85% of extraction but at only 700°C it shows that by mechanical activation temperature of treatment was decreased. In case of microwave treatment 70% of extraction was achieved but this K recovery was much faster than in other two methods.
5. In case of Calcium carbonate, pre- treatment of mechanical activation was proved to be a revolutionary method to extract K. In case of mechanical activated (feed+ flux) followed by roasting and leaching with citric acid gave about 78% of extraction which was only about 8 % when experiment was done without pre-treatment.
6. In case of NaOH glauconite gave 70.32% of extraction when experiment was done without pre- treatment of milling. But at the same conditions extraction was 96% when pre-treatment was given to the (G + NaOH) system. So we can say that mechanical activation was also reliable technique for improving K dissolution performance.
7. In case of Na_2CO_3 only furnace treatment was performed to extract K from the rock sample. And muffle furnace treatment followed by roasting gave 70% of extraction.

LIST OF PUBLICATIONS

Journal-

1. **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-

1. 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.
2. 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.

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