AThesis

On

GAINFUL UTILIZATION OF SPENT POT LINING - A HAZARDOUS WASTE FROM ALUMINUM INDUSTRY

Submitted By

Sidharth Sankar Parhi

Roll No. 611CH306

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Prof. Pradip Rath

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Dedicated

To

LORD JAGANNATH

&

MY PARENTS

(*Kaminikanta Parhi& Sabita Panigrahi*)

National Institute of Technology, Rourkela
Department of Chemical Engineering

Certificate

Certified that this Project thesis entitled "Gainful Utilization of Spent Pot Lining-A Hazardous waste from Aluminum Industry"

by

Sidharth Sankar Parhi

(611 CH 306)

during the year 2011 - 2014 in partial fulfillment of the requirements for the award of the Degree of Master of Technology (Research) in Chemical Engineering at National Institute of Technology, Rourkela has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

Date: **Supervisor**

Prof. Pradip Rath
Professor & HOD
Department of Chemical Engineering
National Institute of Technology
Rourkela, Odisha, India.

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Date: *(Sidharth Sankar Parhi)*

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TABLE CAPTIONS

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ABBREVIATIONS

ADJ.SS	Adjusted Sum of Squares
ADJ. MS	Adjusted Mean Squares
Al_2O_3	ALUMINA (Corundum)
$Al(OH)_3$	Gibbsite (Aluminum Hydroxide)
ANOVA	Analysis of Variance
ASTM	American Society For Testing And Materials
A.U.	Arbitrary Units
C	CARBON
$Ca F_2$	Fluorite (Calcium Fluoride)
CHNS	Carbon, Hydrogen, Nitrogen, Sulfur
DOE	Design of Experiment
DF	Degrees of Freedom
DLS	Dynamic Light Scattering
DSC	Differential Scanning Calorimetry
EPA	Environmental Protection Agency
EDX	Energy-Dispersive X-ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
GCV	Gross Calorific Value
HSE	Health Safety and Environmental
L/S	Liquid to Solid
M	Molarity
Na_3AlF_6	Cryolite
$NaAl_{11}O_{17}$	Diaoyudaoite (Sodium Aluminum Oxide)
$Na F$	Villiaumite (Sodium Fluoride)
PSA	Particle Size Analysis
RPM	Rates Per Minute
SD	Standard Deviation
SEM	Scanning Electron Microscope
SEQ. SS	Sequential Sum of Squares

SiO$_2$	Quartz
SPL	Spent Pot Lining
S/N RATIO	Signal to Noise Ratio
TGA	Thermo Gravimetric Analysis
WWSPL	Water Washed Spent Pot Lining
XRD	X-Ray Diffraction

ABSTRACT

Spent Pot Lining (SPL) or Spent Cathode is a solid waste produced by the aluminium industry during the manufacture of aluminum metal in electrolytic cells. After 3-7 years of operation, the cathode liner materials deteriorate and affect the cell's performance and need to be replaced. Due to high fluoride (20 wt. %) and cyanide (1 wt. %) content SPL was listed as hazardous waste by the US Environmental Protection Agency in the year 1988.In the present study, various approaches in the treatment of SPL have been conducted to recover the valuable carbon and fluoride values. Initially a comparative study was investigated by the chemical leaching of water washed SPL with H_2SO_4 and $HClO_4$ acids and the process parameters were optimized via utilization of Multiple Level Factorial design. For H_2SO_4 and $HClO_4$ treatment of water washed SPL, L/S ratio was found to be the most significant factor.The carbon content was increased from 42.19% for raw SPL to 70.83% for H_2SO_4 and 71.76% $HClO_4$ treatment. An approach in chemical leaching of water washed SPL was performed initially with caustic leaching followed by Perchloric acid leaching. In this case, the Temperature was found to be the most significant factor among all the parameters, whereas the L/S ratio was the least significant among the four parameters studied.The carbon percentage of SPL was increased from 42.19 to 87.03% as confirmed from the ultimate analysis. From the proximate analysis, the fixed carbon was increased from 38.96% to 82.86 % from the raw to final treated SPL. Another approach in chemical leaching of water washed SPL was conducted initially with causticleaching followed by sulfuric acid leaching. In this case, Alkali concentration and the Temperaturewere found to be the most significant and least significant factor among the four parameters studied.The process parameters used in above approaches were optimized by Taguchi method and Classical Method.The carbon percentage of SPL was increased from 42.19% to 81.27% as confirmed from the ultimate analysis. From the proximate analysis, the fixed carbon was increased from 38.96% to 78.68% for sulfuric acid from the raw to final treated SPL.Gross calorific values (GCV) were determined for the all optimized samples obtained from above studies. The GCV was found to be increased from 2865.04kcal/kg to 6689.69 kcal/kg for raw SPL and optimized sample obtained from caustic followed by sulfuric acid treatment respectively.

KEYWORDS: Spent Pot Lining; Chemical Leaching; Multiple Level Factorial Design; Taguchi Method; Gross Calorific Value.

Chapter 1

INTRODUCTION

1.1. Aluminum Electrolysis and Cell Design

Aluminum is the most abundant metallic element (8.1 mass %) in the earth's crust. Because of high affinity to oxygen, aluminum does not appear in nature in its pure elemental form and is found attached with in the form of silicates and aluminates. Two process steps are adopted for the aluminum production. The first process step involves the refining of the raw material bauxite (ore), which contains 30-60 % alumina (Al_2O_3)[1] to pure alumina (Al_2O_3), this is known as the Bayer process (1887) which was developed by the Austrian chemist Karl Joseph Bayer (1847-1904). In the second step, alumina is electrochemically reduced by influencing electrical current. Aluminum cannot be produced by the electrolysis of an aluminum salt dissolved in water due to the high reactivity of aluminum[1]. In 1886 an American chemist Charles Martin Hall and the Frenchman Paul Heroult independently discovered the process of producing aluminum electrolytically, which was renamed after them as Hall-Heroult process[1,2]. An attempt to replace the process has not been successful yet. The basic principles have remained unchanged for more than a century now, but the efficiency of the process has increased continuously through scientific and technological progress.

In essence, it is unmanageable to electrolyze pure alumina, due to its high melting point of 2060 °C. Hall and Heroult discovered that it is possible to dissolve 2-8 % alumina in the rather exotic salt cryolite (Na_3AlF_6), and to decompose this mixture by means of electrolysis[3]. Cryolite is mostly found on the west coast of Greenland as a naturally occurring material, but now-a-days it is being replaced by synthetic cryolite. The Hall-Heroult process takes place in an electrolytic "cell" or "pot". The single pots are usually arranged in long rows, the so called "pot lines". The pots can be aligned side-by-side or end-by-end. The fundamentals of aluminum electrolysis are well described by several authors[1,3]. The overall reaction of the Hall- Heroult process is given in Eq. (1.1) and an illustration of a modern cell is given in Figure 1.1.

$$2Al_2O_3\ (dissolved) + 3C\ (s) = 4Al\ (l) + 3CO_2 \qquad (1.1)$$
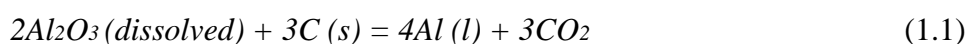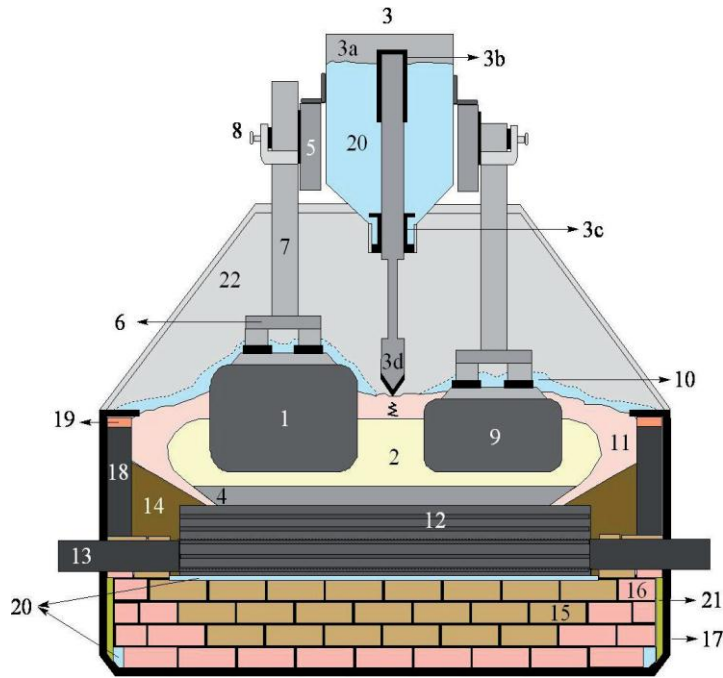
Figure 1.1: Schematic drawing of the main features of an Hall-Heroult aluminum reduction cell: (1) anode (prebaked), (2) electrolyte (bath), (3) Alumina point feeder, (3a) alumina hopper (3b) air cylinder, (3c) metering chamber, (3d) crust breaker, (4) Aluminum pad,(5) anode beam (current supply), (6) anode yoke and stubs (iron), (7) anode rod (aluminum), (8) anode clamp, (9) spent anode (butt), (10) alumina crust/ cover, (11) crust (side ledge), (12) cathode carbon block, (13) current collector bar (steel), (14) ramming paste, (15) refractory, (16) insulation, (17) steel shell, (18) sidewall block, (19) castable, (20) alumina, (21) rockwool and (22) gas collection hood (removable). The details in the lining may vary[2,3].

In the Hall-Heroult process, alumina (Al_2O_3) is dissolved in a carbon lined cell with a bath of molten cryolite (Na_3AlF_6) at a temperature of 960°C[4]. The electrolyte may have certain additives (mainly AlF_3 to lower the cryolite melting point from 1012°C to 960°C)[3].The container of the cell is considered the cathode but from an electrochemical[1] point of view "cathode" is the interface between the aluminum metal and the electrolyte The carbon cathode conducts current to the cell and it has to withstand the corrosive environment, stress attributed to temperature fluctuations and chemical reactions[1].The carbon cathode is often referred to as the most important part of the aluminum electrolysis cell because it is mostly the component that provides the cell its life expectancy[1,2].Joule heating from the flow of electric current is more than adequate to maintain the melt temperature.

The cell comprises of an anode and a cathode. The molten cryolite bath along with alumina is placed in between the electrodes. Besides cryolite and 2-5 wt. % alumina from

the Bayer-Process, the bath contains typically 10-12 wt. % aluminum fluoride (AlF_3) and about 5 wt. % of calcium fluoride (CaF_2). Some plants also add lithium fluoride (LiF) and/or magnesium fluoride (MgF_2) to the bath[5]. The temperature of the bath is about 950 °C, and its composition is a compromise between electrical conductivity, current efficiency, alumina and metal solubility, density and vapor pressure[5].

This molten mixture is named "electrolyte" and it works mainly as a solvent for alumina and enables its electrolytic decomposition to form pure aluminum at the cathode and carbon dioxide gas at the anode. Alumina (Al_2O_3) is fed to the bath through holes punched in the crust. This is done by point feeders in 1 to 2 kg per doses at every 1 to 2 minutes interval[5]. Careful control of the alumina concentration is of essential importance. Too high feeding may lead to "sludge" or "muck" formation of undissolved bath/alumina. The mixture of bath and undissolved alumina will sink down owing to higher density and is then difficult to remove. With too low alumina content, on the contrary, may lead to the so-called anode effect, which interrupts the normal anode process by an abrupt increase in cell voltage and a rapid increase in bath temperature[2]. During an anode effect perfluorocarbon gases are generated which are harmful greenhouse gases[3].

The electrolyte height is used to keep around 20 cm and the temperature during the cell operation is typically between 950°C and 965°C[1]. The anodes are plunged in the bath from the top and gradually eroded due to influence of sodium attack in the lining. At the anode, oxygen from the alumina reacts with carbon to form CO_2. The exhaust gas as carbon dioxide is collected below the hood.

Aluminum oxide is an ionic compound. In the molten or dissolved state the ions are free to move[2]. Pure aluminum is formed at the bath/metal interface. It slides under the bath, due to the higher density and deposits at the cathode surface where it is protected against oxidation. In this way the molten aluminum metal accumulates. It forms a "pad" or pool between the cathode surface and below the bath, which acts as the "real" cathode. The thickness of the molten metal layer is around 20 cm [5]. The aluminum is tapped from this layer on a daily basis into vacuum crucibles, ready to be transported into the cast house. However, the surface of the aluminum pad is not stable during operation, caused by motions and waves due to the magnetic field and convection in the electrolyte. A certain space between anode and cathode or so called inter-polar distance (4-5 cm) is necessary to prevent short-circuits[3,5].

There are two main kinds of anode designs used in modern aluminum cells: The prebaked and the continuous self-baking Soderberg anode[3]. Soderberg is older technology and has been phased out and replaced successfully by the former one. This is due to lower energy consumption and lower degree of emissions. Thus, in this thesis it is focused on the prebaked technology, which uses multiple anodes in each cell. These anodes are made of petroleum coke and coal tar pitch, molded into blocks, baked in separate furnaces and then placed in the cell[3]. Anodes are working as current suppliers. Thus, they need to be connected to the bus bar system. In each case, an iron stub and aluminum rod is casted or rammed into the top of the anode block. A typical feature of the Hall-Heroult process is that the anodes are consumed. The height needs to be adjusted regularly while the anode is consumed to ensure a constant inter polar distance[3]. Therefore the rod ends are flexible fixed to the bus bar system by clamps.

Anode removal and replacement by overhead crane needs to be done, when one third to one fourth of the original anode is left (called "spent anode" or "butt"). The anode change induces disturbances in the temperature and current distribution. When the anodes get in contact with air, they immediately burn away due to combustion. For a protective measure a "layer of alumina" covers the anode surface on top of the "crust". In operation, the bath freezes on top and at the sidewalls of the cell forming a "side ledge" which protects this part of a severe attack by the molten aluminum and the molten electrolyte[3].

Although the molten metal is the actual acting cathode, the name "cathode" is usually used for the entire lower cell construction or "lining". This includes the bath/electrolyte, molten aluminum pad, carbon blocks, collector bars, baked ramming paste, refractories and insulations which are surrounded and supported by an outer steel shell. Collector bars are embedded steel rails into the bases of the carbon block, sealed with cast iron and run horizontally through the entire bottom lining. They serve as electrical current collectors and both ends stick out of openings in the steel shell. Those parts are connected with the electrical bus to interlink the single cells[3,5]. The lining can be further classified into "bottom and side lining" as well as "carbon and non-carbon lining". The non-carbon group contains dense refractories (such as high alumina and chamotte) and thermal insulation bricks (such as diatomaceous, vermiculite, calcium silica or others). They are placed between the steel shell and the carbon blocks to form the foundation of the cell superstructure. The carbon part of the lining consists mainly of

silicon carbide sidewall blocks and prebaked carbon bottom blocks. They are coupled together by using a ramming paste or carbonaceous "seam mix"[3].

1.2. The Cathode Lining

The cathode lining is one of the most important parts in Hall-Heroult cell. It is required to ensure an appropriate service life time. The industry has been able to prolong the average lifetime of the cell lining from 1000 days in 1948 to an average of 2500 days today, mainly due to the improvements in material quality and operational procedures, innovations in cell design as well as process automations[3]. During the last decades, the substitution of anthracitic with graphitized carbon materials has been a significant achievement due to the reduction of the electrical resistivity and a lower total expansion[3]. At the same time the thermal conductivity of the cathode has increased, shifting the isotherms downwards in the lining. Refractory layers are installed below the carbon blocks to maintain the desired heat balance and to protect the insulation bricks underneath against higher temperatures and chemical attack[2]. They have not been improved to the same extent as the carbon materials. The most common refractory materials are found in the Al_2O_3-SiO_2 system. These materials are called alumino-silicates and are distinguished by their alumina content[6]. Alumino-silicates have been and still are the preferred refractory materials due to good performance, light weight, availability and moderate costs[1,3,5]. Despite these properties the refractory material cannot completely withstand the permanent chemical attack caused by the uptake of sodium and electrolyte/bath components. During operation sodium followed by bath components will percolate through the carbon cathode block which causes swelling, heaving[3] and cracking. Cracks are in general one of the main reasons for early cathode failure[2,5].

Underneath the carbon block sodium and bath components start to deteriorate the refractory lining[6–10]. This leads to significant mineralogical transformations in the material. Hence the material performance changes over time, resulting in increased heat loss through the cathode lining, rise in mechanical stresses (due to swelling)and in the worst case it causes a complete pot failure[2,11,12]. An increase in the energy consumption due to thermal instabilities and a shorter lifetime of the cell results in earlier needs for delining and relining are among others unwanted consequences. Since these material and operating expenses have a significant effect on the production cost, the aluminum producers are aiming to decrease in the number of unscheduled shutdowns and increase the average service life span to about 3000-4000 days[13,14]. To date, a significant

magnitude of research has been conducted in order to gain a qualitative understanding of the degradation of the cathode bottom lining materials by means of autopsies of shut down cells and/or laboratory investigation[2]. It was found that sodium plays an important role not only in the degradation of the carbon cathode but also in the sidelining in contact with alumino-silicate materials. The cathode, after continuous operations around variable period of time (1100-3000 days), is discarded and replaced with new one. The dismantled cathode or Spent Pot Lining (SPL) is a hazardous waste comprising of 20 wt.% fluoride and 1 wt.% cyanide which is a major environmental concern[15].

1.3. Motivation of the Thesis

The main motivation of this thesis comes from the importance of the treatment of Spent Pot Lining (SPL). SPL is a hazardous material because it is toxic in nature as it contains leachable fluoride and cyanide. SPL is corrosive in nature due to the presence of alkali metals and oxides which react with water to produce inflammable, toxic and explosive gases. Basically three different methods as stated below are available for treatment of SPL in a commercial process [15, 16, 22]. They are

- Hydrometallurgical process
- Pyrometallurgical process
- Density separation method

However none of these above methods were widely accepted due to the following reasons.

- Did not have minimum number of steps to minimize cost.
- Very low grinding index of SPL (i.e. 22) which implies a high cost for milling and grinding.
- Recovery of valuable materials like graphite and fluoride in form of smelter grade raw materials were practically impossible.
- Removal and elimination of cyanide was impractical.
- Concurrent generation of environmental problem arising out of disposal of treated SPL.

This thesis is of specific interest to get an effective way of treating SPL and recovery of valuable compounds. This thesis gives an idea about the adaptation of optimization techniques to monitor the process parameters and also provide various

approaches in the treatment as well as comparison of treatment processes. The possible use of treated SPL as a fuel is also another scope of this study.

1.4. Organization of the Thesis

The thesis is organized in five chapters. The layout of the chapters are as follows:

- *Chapter-1* is an introductory chapter in the field of aluminum electrolysis and cathode lining.

- *Chapter-2* contains pertinent literature review on Spent Pot Lining (SPL). It highlights various grading as well as production of SPL. It also describes about various treatment methods that has been developed till date to recover and recycle the valuable compounds from SPL.

- *Chapter-3* describes about the materials and instrumentation details as well as the brief introduction of adopted optimization techniques for the treatment of SPL.

- *Chapter-4* represents the results and discussion part which constitutes a total of 4 sections and each section having a different approach to treatment of SPL.

o   Section-1 represents the comparative treatment of water washed SPL with that of Perchloric acid and Sulfuric acid by multiple level factorial design.

o   Section-2 is about an approach to treatment of SPL with Perchloric acid leaching by "Taguchi" and "One factor at a time" method.

o   Section-3 reflects the treatment of SPL with Sulfuric acid by the approach highlighted in section-2.

o   Sections-4 presents the fuel value analysis of all the optimized samples obtained from various treatment techniques.

- *Chapter-5* concludes the findings and future aspects of this study.

Apparently, this thesis highlights the use of different materials for the treatment of SPL as well as its enrichment and utilization. However, as mentioned before, these materials were selected on the basis of their applications. The process parameters were optimized using standard techniques and correlated accordingly.

Chapter 2

LITERATURE REVIEW

With rapid progress in industrialization, many hazardous wastes come into play, which have a detrimental effect on the environment causing a major distress among the industry as well as society. Spent Pot Lining (SPL) is associated with one of the most growing industry mainly in aluminum industry. In this chapter the genesis of SPL and various treatment approaches along with the objectives of the project is discussed in this chapter.

2.1. Spent Pot Lining (SPL)/Spent Cathode Lining

The linings of electrolytic cells are fabricated in a steel shell. The lining comprises of carbon, silicon carbide (SiC) or carbon used in the sidewalls. The refractory bricks (insulating bricks and fire bricks) are lined below the carbon lining to provide mechanical support. During the electrolysis process the lining is subjected to highly reducing conditions and generally fails after 5-8 years of operation depending on the cell construction, design approach and operation[16,22].

Diversified opinions are available in the literature regarding the amount of production of SPL by a cell per tonne of aluminum produced. Generally in Soderbergs produce 35kg/tonne, end to end (EE) prebakes 20-28 kg SPL/tonne and figures may vary depending of lining life achieved. Usually in prebake technology the lining lasts for about 2700-3000 days with amorphous carbon blocks, 2400 days with semigraphite blocks, and 1700-2200 days with graphitized or graphitic blocks. Soderbergs have a typical life of 2500-2700 days with amorphous blocks and 3000 days with graphitized blocks. These data are attributed by amount of aluminum produced per unit area (a reckoner of the volume of cell material). The amount of aluminum is not constant throughout the life period due to rise in amperage in cell systems. That is why a careful observation required in determining the production of SPL per tonne of aluminum produced[9, 13, 22].

After the failure of cell lining it is either dismantled or repaired in the cell rooms or removed from the cell rooms. The final waste product, thus generated is termed as "Spent Pot Lining". It comprises of both first cut and second cut materials (Figure 2.1). First cut is generally carbonaceous in nature with varying proportions of graphite (30-

100%) which is obtained above the collector bars. And below the collector bar, the second cut is obtained which mainly comprises of refractory materials. The composition of Spent Pot Lining (SPL) depends on several factors such as composition of new cell lining which is different for each technology. The dismantling procedure greatly affects the amount of bath and frozen aluminum in the lining components[16].
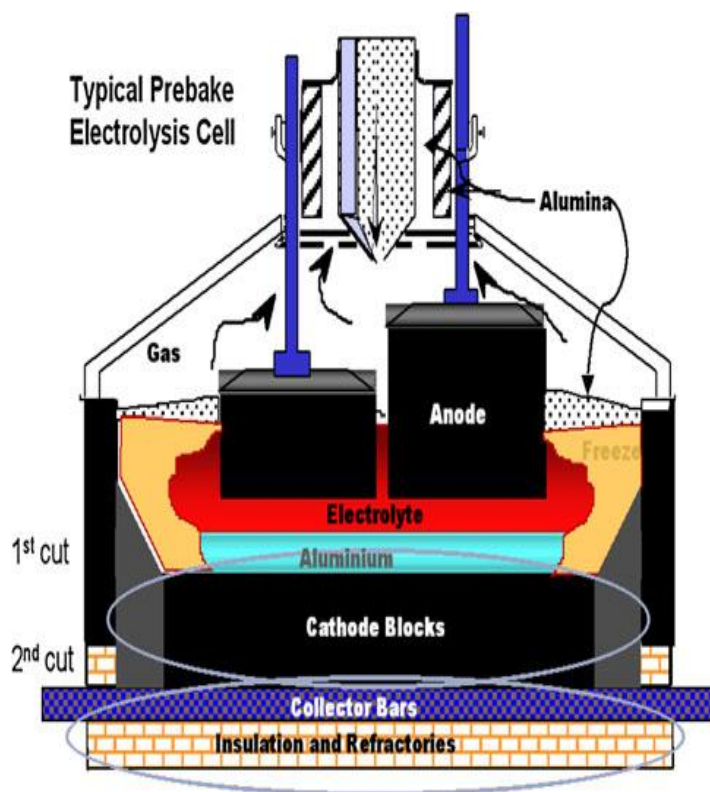
Figure 2.1: Schematic diagram of Hall-Heroult cell[16]

The operating period of the cell is a vital factor which generates different composition of SPL. Intercalations of Sodium and Sodium Fluoride inside the lining materials increase with longer cell operation. Composition of the SPL for three different technologies is given in Table 2.1 (type A and type B are different SS modern prebakes). The composition was obtained from a composite sample of both first and second cut of SPL reduced to 300 mesh. The yield of fluoride and cyanide concentration varies with adopted process. A robust treatment process is needed to obtain non-hazardous byproduct from SPL. Ultimately the first and second cut SPL would be separated during dismantling of pot. It was found that concentration of fluoride and cyanides is prominent in first cut SPL.

2.1.1 Spent Pot Lining (SPL) reactivity and toxicity

Generation of water reactive chemicals happens due to the subjection of SPL at high temperature during the electrolysis process. Varieties of fluoride, sodium and aluminum compounds, cyanide (due to ingress of air through the collector bars), metal (Al, Li and Na), reactive metal oxides (Na_2O), nitrides and carbides are found in SPL. These compounds react with moisture and air to produce NaOH, H_2, C_2H_4 and NH_3.

<div align="center">

Table 2.1: Composition of SPL for different technologies[16]

</div>

Elements	A type	B type	Soderberg	Major phases
Fluorides (wt. %)	10.9	15.5	18	Na_3AlF_6, NaF, CaF_2
Cyanides (ppm)	680	4480	1040	NaCN, $NaFe(CN)_6$, Na_3FeCN_6
Ratio (HCN/Total)	2.7	1.9	3.4	
Aluminum total (wt. %)	13.6	11	12.5	Al_2O_3, $NaAl_{11}O_{17}$
Carbon (wt. %)	50.2	45.5	38.4	Graphite
Sodium (wt. %)	12.5	16.3	14.3	Na_3AlF_6, NaF
Al metal (wt. %)	1	1	1.9	Metal
Calcium (wt. %)	1.3	2.4	2.4	CaF_2
Iron (wt. %)	2.9	3.1	4.3	Fe_2O_3
Lithium (wt. %)	0.03	0.03	0.6	Li_3AlF_6, LiF
Titanium (wt. %)	0.23	0.24	0.15	TiB_2
Magnesium (wt. %)	0.23	0.09	0.2	MgF_2

The wet delining procedure was used earlier to break lining materials, which leads to formation of flammable gases as mentioned above. However, due to health safety and environmental (HSE)[15] concerns, this practice is now abandoned and today the lining is removed under dry condition. The active nature of the material makes it:

- Toxic: Fluoride and cyanide compounds those are leachable in water
- Corrosive: High pH due to alkali metals and oxides
- Reactive with water: Producing inflammable, toxic and explosive gases

The toxic, corrosive and reactive nature of the material means that care must be taken in its handling, transportation (transportation containers must be ventilated) and storage (due to its leach ability). Inter-country hazardous waste transfer is governed by convention.

2.1.2 Handling possibilities for Spent Pot Lining (SPL)

The aluminum industries are trying to develop an economic process to recycle the heterogeneous SPL materials. Considering complete, partial and no recycling of SPL the treatment approaches differ. For complete or partial recycling of SPL pyrometallurgy or hydrometallurgy approaches can be considered. Many researchers have proposed various processes and some of the most promising processes are given in Table 2.2 and 2.3. Due to heterogeneous composition of SPL the total recycling of SPL is a tremendous challenge. In cement industry, a limited quantity of SPL is added in a cement kiln to improve the quality of cement.

The other industries that use SPL are the mineral wool and the iron and steel industries. All hydrometallurgical approaches aim at total recycling of SPL necessitates a separation of the main components such as carbon, brick and fluorides. Partial recycling and disposal is less stringent and depending on the economics, some specific components can be targeted for recycling. For example, during the time that the industry operated smelters with wet effluent treatment centers, cryolite recovery could be achieved. Safe disposal of SPL necessitates some kind of treatment to stabilize the leachable fluoride and to decompose all water-reactive compounds and the cyanides. In reality, each plant must choose between the alternatives allowed by its legislation.

2.1.3 Environmental legislation concerns

Earlier SPL was classified as an industrial or mining waste and was disposed of in lined as well as unlined landfill sites. Many of these sites now require remediation. However, now it being treated as a hazardous waste KO88 since 1988 in the United States[17]and a special waste in Canada. These new classifications meant that SPL had to be stored in special buildings or hazardous waste sites. For industries processing hazardous wastes, environmental regulations have become stricter and it became more difficult for the cement and steel industries to accept unprocessed SPL. This meant partial or total detoxification had to be done before reusing the SPL.

2.1.4 Recent storage of SPL

Storage and processing of SPL depends upon the prescribed norms of various agencies and legislations. It is estimated that a significant amount of SPL (>50%) is still being stored in buildings lined and unlined sites, waiting for treatment.

It could be considered as a passive treatment, which was done in Norway and Iceland, where SPL has been stored on the seashore allowing sea leaching of soluble components. The leachable fluorides present in SPL react with the calcium ions in seawater to form a stable calcium fluoride. An extensive investigation by the University of Iceland[18]did not indicate that the dumping pits had detrimental effects on shore communities.

2.1.5 Industrial practices of Spent Pot Lining (SPL)

The use of SPL in various industries has been investigated over the years and some the possible uses are highlighted in Table 2.2.

Table 2.2: Use of SPL in various industries

Industry	Approach and reason	Disadvantage or problems associated	Location
Cement[19–24]	To use first cut SPL in the kiln as it has reasonable calorific value and fluoride reduce the kiln temperature Second cut used in cement kiln	(i)Necessity for Transportation in a closed container (ii)Maximum allowable limit for sodium ($< 0.6\%$) and fluoride limits the additions up to a few percent of the feed stock	Brazil
Steel[25–27]	Additive to steelmaking because fluoride improves slag formation and small quantities of SPL can substitute for CaF_2	(i)Necessity for Transportation in a closed container. (ii)Limitation of use due to hazardous waste	Italy
Rockwool	First cut SPL used as an additive or substitute for coke	Limited requirement of SPL	Germany
Alumina Plant	Co-processing SPL with salt slags by BEFESA process		Germany

2.2. Treatment and Recovery Processes

Over the years many processes have been developed, out of which hydrometallurgical or pyrometallurgical processes found to be suitable.

2.2.1 Industrial scale improvements

Varieties of furnaces have been tried, including rotary kilns, coffee roasters and specialized (Ausmelt and VORTEC) and arc furnaces at various temperatures. Some of the industrial scale treatment process is shown in Table 2.3.

Table 2.3: Industrial scale treatment process for SPL

Treatment approach	Process condition and purpose	Advantages	Disadvantages
PYROMETALLURGY APPROACH			
ALCOA (Reynold) Gum Spring process[28]	Destruction of cyanides in a rotary kiln and creation of industrial waste for road aggregates. Use of Limestone to fix fluorides	Generation of inert materials	High temperature treatment approach. High cost for the treatment
RT (Comalco) COMTOR[16,19,29]	Destruction of cyanides in a pretreatment reactor. Residue is leached with lime to produce a Bayer-type liquor and kiln-grade Spar for the cement industry	Generation of product used in other industry	High temperature treatment process leading to high energy demand
AUSMELT process[16,19,22,30]	Formation of AlF_3 and reusable industrial waste	Moderate quality of Product	High energy demand
VORTEC process[15,16,19]	Generation of reusable Industrial inert waste by combustion and pyrohydrolysis process	Moderate quality of product	High energy demand
NOVA Pb[16]	Treatment in rotary kiln at 1000°C	Formation of useful product i.e. Calcifrit (High Fluoride and aluminosilicates) and Calcicoke (High Carbon)\ Potentially recyclable products	High treatment cost
Regain Process[16,31]	Partial detoxification of SPL	Low temperature process for the destruction of simple cyanides to deactivate SPL	Still hazardous material
ELKEM process[6,16,22,32]	Use of SPL as a feedstock for pig iron making	As feedstock material	Transportation problems and less requirement of feed
SPLIT process[16,19,30]	Treatment of SPL with $CaSO_4$ at 1000°C	Production of inert materials	High treatment cost
Plasma vitrification[16,30]	Inertization of SPL at high temperature	Generation of inert materials	High temperature treatment
HYDROMETALLURY APPROACH			
BEFESA[16,33]	Co-processing of SPL with salt slags	Formation of suitable components to be used in cement or mineral wool industry. Low temperature treatment process	Not Available
RIO TINTO ALCAN[16,22,31,34,35]	Low caustic leaching and Liming	Formation of Bayer liquor, CaF_2 and industrial waste can be used in other industry. Low temperature treatment approach	High installation cost

2.2.2 Lab scale improvements

Various researchers have examined to mitigate the harmful effect of SPL by employing different approaches and some of the improvements are shown in the Table 2.4 and 2.5.

Table 2.4: Lab scale pyrometallurgical approach for SPL

Sl. No	PYROMETALLURGY APPROACH		
	Year	Authors	Approach and Findings
1	1997	V. A. Utkov et al.[36,37]	Water soluble NaCN was neutralized by treating carbon rich part with an $FeSO_4^-$
2	2000	Wang Y.[38]	Crushed first cut SPL can be used as collar paste for protecting anode stems.
3	2000	Oliveira et al[22,39]	Heating of second cut SPL up to more than 750°C to remove molten and volatile impurities
4	2000	Balasubramanian et al.[22,40]	Vitrification of SPL by adding small additions of glass former along with traces of nucleation agents to aid crystallization and then melting at around 1300°C.
5	2001	Courbariauxet al.[22,29,41]	Treatment of crushed SPL in a circulating fluid bed
6	2004	Karpel S.[22,30] Li and Chen [16,22,42]	Heating of crushed SPL mix to about 1000°C and adding lime to oxidize cyanides and bind the fluoride
7	2007	Lazarinos[22]	Destruction of cyanide compounds in a gasification combustions.
8	2007	Chen and Li [16,22,42]	(i)Presence of graphite and sodium in SPL make it sticky, slippery and difficult to crush (ii)Chemical stability of the fluorides in the SPL
9	2009	Blinov et al.[22,39]	Pyrohydrolysis process to recover fluorine as HF and use of carbon rich part in pig Iron manufacture

Table 2.5: Lab scale hydrometallurgical approach for SPL

Sl. No.	Year	Authors	Findings
			HYDROMETALLURY APPROACH
1	1999	Baranovskii[22]	Mixing of crushed first cut SPL with that of limestone and then adding this mixture to an aqueous slurry for recovery of Soda and Potash
2	2001	Lu et al.[22]	Separation of aluminum electrolysis carbon froth and spent pot lining by froth flotation technique
3	2001	Zhao [43]	(i) Treatment of SPL with water and H_2SO_4 to recover HF (ii) The liquids are filtered for the manufacture of graphite powder, aluminum hydrate and alumina. (iii) Fluoride and sulfates are manufactured from filtrates
4	2001, 2002	Silveira et al.[24,44]	(i) The leaching behavior of SPL was studied (ii) pH of SPL was around 10-11.8 (iii) Total fluoride content was 5.13-11.41% (iv) Total dissolved fluoride at pH 12 and at pH 5 was 6.45-9.39% and 0.26-3.46% respectively
5	2002	Mirsaidov et al.[22]	Use of pine oil and kerosene as a flotation agent to separate cryolite alumina concentrate followed by burning of remaining carbon at 800°C in rotary Furnace.
6	2007	Lisbona and Steel[45]	Determination of Leachability of NaF, CaF_2 and cryolite from SPL Precipitated fluorides in a form that can be recycled back into the pot have been studied by manipulating solution equilibria.
7	2008	Lisbona and Steel[30]	(i)Fluoride extraction of 76-86 mol. % by using 0.34 Al^{3+} solution at 25°C for 24 h (ii)Removal of NaF and Na_2CO_3 from SPL by water washing of SPL (iii)In pH 4.5-5.5 selective precipitation of fluoride as an aluminum hydroxyfluoride hydrate product achieved by neutralization (iv)Higher pH leads to co-precipitation of hydrolyzed sodium fluoroaluminates
8	2012	Lisbona et al.[46,47]	(i)Leaching with Al^{3+} salts to precipitate aluminum hydroxyl fluoride hydrate (ii)Development of low-carbon environmentally sustainable approach
9	2012	Zhong-ning et al.[42]	(i)Two step alkaline-acidic leaching was conducted to achieve 65% leaching rate after NaOH treatment having 72.7% purity of carbon Leaching rate was increased up to 96.2% and purity of carbon up to 96.4%. (ii)Cryolite precipitation rate was 95.6% and purity of Na_3AlF_6 obtained is 96.4%.
10	2013	Lisbona et. al[48]	(i)Leaching behavior of SPL with aluminum nitrate and nitric acid (ii)Following an initial water wash, a single leaching step using 0.5M HNO_3 and 0.36M $Al(NO_3)_3$ at 60°C extracted a total of 96.3% of the remaining fluoride, extraction of Mg and Ca in form of MgF_2 and CaF_2.

2.3. Concluding Statement

Due to the intervention of local communities and lawmakers, the dumping of SPL in lined site has been practiced by aluminum industry ever since it has been regarded as hazardous waste. However, there is no widely accepted technology available for the treatment of SPL due to unknown behavior of its specific chemistry. Recent years hydrometallurgical studies for the treatment of SPL have gained pace as it promises the better recovery of useful compounds and less energy intensive. The presence of the free sodium makes the surface of the SPL slippery and difficult to crush which is another major challenge to find an alternative to the problem of crushing of SPL. Choice of proper chemical reagents for the chemical leaching is yet to be optimized for the treatment and recovery useful fluoride and graphitic carbon from SPL.

The review of literatures in this chapter confirms that most of the treatment processes are optimized by conventional way opening the doors for the treatment by using any of the specific optimization techniques. The new approach of treatment with various other acids need to be studied as well as a comparison between them is the one of the main objectives of this project. The treatment of SPL is considered to be one of the biggest challenges due to presence of highly leachable fluoride and cyanide content. Some of the specific objectives are as follows:

- Characterization of SPL material
- Treatment of SPL with $HClO_4$ and H_2SO_4 for leaching of NaF, CaF_2, $Al(OH)_3$.
- Treatment of SPL with $NaOH$, for leaching of Na_3AlF_6, Al_2O_3, NaF, CaF_2.
- Enrichment of the carbon percentage of SPL samples using leaching process.
- Optimization of process parameters using multiple level factorial design, Taguchi design and conventional or classical approach.
- Fuel value analysis of the optimized sample obtained from leaching process.

The prime aim of this project is to find a way to utilize SPL gainfully without causing any environmental hazards.

Chapter3

MATERIALS AND METHODS

In this chapter the details process condition as well as purpose of this study has been discussed. All the leaching experiments were conducted in batch mode.

3.1. Materials

3.1.1 Chemicals

All the chemicals used in this investigation were analytical reagent grade of highest purity and was procured from Merck (Germany). De-ionized water was used for preparation of stock solutions of alkali and acid.

3.1.2 Glassware and instruments

All glassware (conical flasks, measuring cylinders, beakers, petri-dish and pipette etc.) were purchased from Borosil. The instruments and apparatus used throughout the experiment are listed in the Table 3.1.

3.2. Methodology

3.2.1 Sample preparation

The first cut Spent Pot Lining (SPL) sample was collected from Vedanta aluminum Ltd., Jharsuguda, Odisha, India for the proposed study. The SPL obtained from the aluminum reduction cell was dried at 110 ±1°C for 2 h and then crushed in a ball mill and then dried and sieved to recover desired size fractions that can pass through the 52 BSS sieve (300 micron). The experimental process and setup is shown in Figure 3.1 and 3.2.
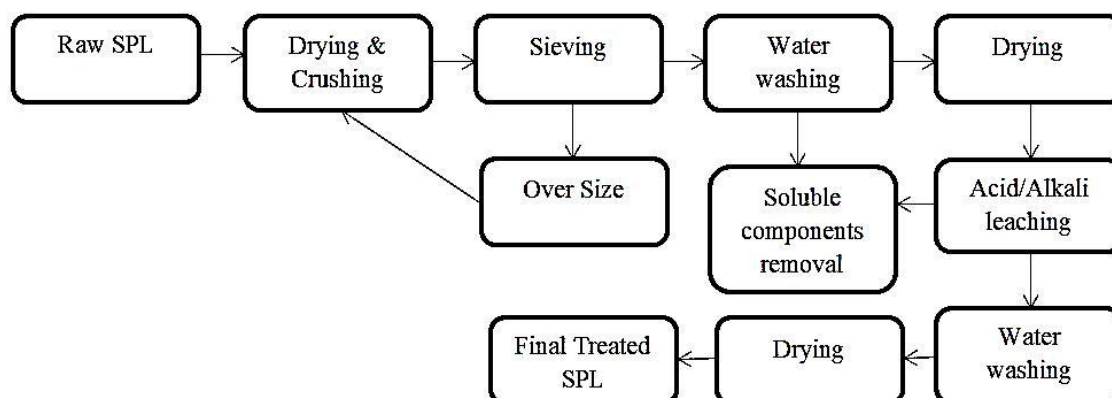
Figure 3.1: Schematic diagram of experimental process
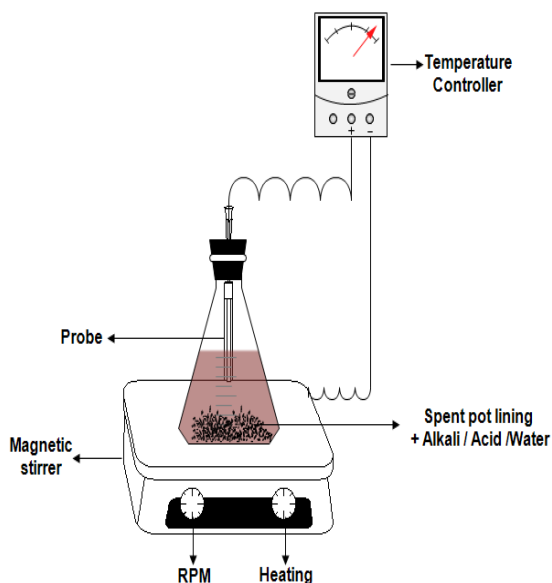
Figure 3.2: Schematic and actual diagram of the experimental setup

3.2.2 Water washing of Spent Pot Lining (SPL)

Initially 50g of raw SPL was treated with 250ml of deionized water at 50 ±1°C for a period of 4h in an orbital shaker at 120rpm. The reason for taking 5:1 L/S ratio (250ml of water /50g SPL) was to leach out leachable fluorides at which the optimum leaching was achieved. Then complete water washing of SPL was done to bring down the pH of residues to neutral range (6.8-7)[44]. The water soluble components were filtered out by using a Macheray-Nagel MN 640 filter paper and the residual SPL was dried in an oven for the period of 4h at 110 ±1°C. Leaching percentage was calculated by the following formula:

$$\% \, Leached \; = [L_0 - L_e]/(L_0) \times 100 \qquad (3.1)$$

L_0, L_e was the initial and final weight of SPL before and after a leaching process in grams.

3.2.3 Leaching experiments

The SPL leaching was done by various steps according to the techniques adopted for the experimentation. Each experimental step was conducted with 4 g of sample weight. Then the treatments were done at 120 rpm and 4 h time either in orbital shaker or magnetic stirrer depending upon the requirement. After each experiment, the leachates were filtered out by filter paper and the residue was dried in an oven for a period of 4 h at 110 ±1°C along with the filter paper. The weight of the filter paper was subtracted to obtain the exact weight of the dried residue. After each treatment, the pH of the residue[44]

was brought down to normal range as per standard practice and then subsequent treatment or characterization was done.

3.2.4 Design of experiment (DOE) and statistical analysis

3.2.4.1 DOE by multiple level factorial design

A general multilevel factorial design was adopted for the optimization of leaching percentage. The factors taken for the optimization were acid concentration having three levels, Liquid to Solid (L/S) ratio having four levels and finally temperature having two levels. Factorial design was being introduced to minimize the total no. of experiments in order to achieve the best overall optimization of the process[49,50]. The design determines the effect of each factor on response as well as how the effect of each factor varies with the change in the level of the other factors[51]. Factorial design comprises the greater precision in calculating the overall main factor effects and interactions of different factors. Factorial designs are strong candidates in examining treatment variations. Instead of conducting a series of independent studies, it is possible to combine these studies into one. The range of experiments is given in the Table 3.1.

Table 3.1: Range of experimental parameters for Multilevel Factorial design

Independent variables	Levels			
Acid concentration (M)	5	7.5	10	-
L/S ratio (cm^3/g)	1.5	2.5	3.5	4.5
Temperature (°C)	50	100	-	-

A two factor interaction model with liner model equation of the actual factors was used for the prediction and the equation was given below.

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 \qquad (3.2)$$

Where b_0= global mean, b_i= represents the other regression coefficients x_1= acid concentration, x_2 = L/S ratio, x_3 = temperature and y = % leaching

3.2.4.2 DOE by Taguchi design

The Taguchi design approach helps in finding the effect of the factors on characteristic properties and the optimal condition of the factors. This is one of the better and simple ways to optimize design for performance, cost and quality[49,50]. In the present Taguchi approach analysis of variance (ANOVA) was used as the tool of analysis which can approximate the effect of a factor on the characteristic properties and the experiment

can be done with orthogonal arrays. The advantage of the Taguchi optimization design over the conventional optimization is the experimental conditions are determined with least variability, whereas in conventional optimization it is determined on the basis of measured values of the characteristic properties. The signal/noise ratio was used to measure the quality characteristics deviating from the desired value in Taguchi method. The experimental conditions having the maximum signal to noise (S/N) ratio were considered as the optimal conditions, and the varying characteristics were inversely proportional to the S/N ratio. The range of experiments is given in the Table 3.2.

Table 3.2: Ranges of experimental parameters for Taguchi design

Independent variables	Levels			
Acid concentration (M)	2.5	5	7.5	10
Alkali concentration (M)	0.5	1.5	2.5	3.5
L/S ratio (cm^3/g)	1.5	2.5	3.5	4.5
Temperature (°C)	25	50	75	100

3.2.5 Classical approach of optimization

For the conventional or "one factor at a time" approach of optimization, the effect studies were done at various process conditions. In the classical approach of optimization, the alkali concentration was optimized initially at various alkali concentration ranges from 0.5 M to 3.5 M. Then on the optimized alkali concentration, the effect of acid concentration (2.5 M-10 M) was done followed by the effect of the L/S ratio (1.5-4.5) and temperature (25-100 °C).

3.3. Characterization of Spent Pot Lining (SPL) samples

Characterizations of the SPL sample were done by several techniques to get the broader idea of all the components present in the SPL. The elemental analysis was done 3 times and the average values are listed in the results and discussion section. The purpose and operating conditions of the experiments are highlighted in the Table 3.3. For XRD analysis the phases of all the materials were identified by the standard software provided with the XRD instrument i.e. "X'Pert Highscore" version 1.0b. The PDF2 database was used for the identification of particular component in the sample. The peak and pattern list is given in appendix I.

3.4. Cryolite precipitation

Filtrates from leaching experiments on SPL acidic and alkaline treatment were combined at 75 ±1°C and pH at 4.5 and 9.5. The solution pH was maintained using water washed filtrate solution which was obtained from the initial water treatment of SPL and having a solution pH around 11.6. The acidic pH was maintained by 1M $HClO_4$or 1M H_2SO_4solution. The precipitates obtained was recovered by centrifugation at 3000 rpm, dried at 110 ± 1°C and ultimately calcined at 500 ± 2°C for a period of 4 h each. Then the obtained samples were analyzed by XRD studies.

3.5. Fuel value analysis

Currently, the energy demands of the whole world are mostly recompensed from fossil based fuels such as fuel-oil, natural gas and coal. Due to the growing demand of the energy, it becomes a necessity for everybody to search for the alternate energy sources. Various renewable and nonrenewable sources have been explored over the years to fulfill the current demand. Energy from the industrial waste is one of the most convenient ways to explore energy. Spent Pot Lining has promised to have a good calorific value so that it can be used in a thermal plant. In the current thesis, the energy values of the various treated SPL are determined by using adiabatic Bomb-calorimeter and presented in table 4.13. Details of all the instruments used along with their purpose during the experimentation are listed in Table 3.3.

Table 3.3: Instruments used and purpose

Instrument	Make	Operation conditions Or specification	Purpose
Analytical balance	Sartorius (BS223S)	1mg - 100g	Weight measurement
pH meter	Systronics (361)	pH 4.5 to 9.5	Measurement of pH, EPA Method 9.045C[44]for solid sample pH
Incubator shaker	Environmental orbital Shaker	• Speed: 120 rpm. • Temperature:25 and 50 ±1 °C.	Shaking of conical flasks used in leaching study
Scanning Electron Microscope-Energy-dispersive X-ray spectroscopy	JEOL (JSM-6480 LV) and Nova Nanosem 450 by BRUKER by FEI	• Magnification: up to 10000X • Resolution : 1μm • Detector: Everhardt Thornley secondary electron detector and Solid state backscattered detector. • X-Ray Analysis: Oxford Instruments ISIS 310 system with "windowless" detector. • Light element analysis: silicon detector with ATW.	To study the clear morphology about the structure and extent of leaching capacity of SPL samples. And the elemental analysis of samples.
Calorimeter	Parr 6100 calorimeter	• Operating pressure 30 atm	Fuel value analysis
Micro Centrifuge	Remi (RM12C)	• 8000 rpm for 10 min	Separation of precipitates from the leachate broth
CHNS analyzer	ElementarVario El Cube CHNSO.	• Measurement of carbon, hydrogen, nitrogen and Sulfur of the SPL sample • Initial wt.- under 10mg	Ultimate analysis- ASTM-D-3176 for Elemental Analysis
X-ray diffraction analysis	Philips X'Pert X-ray diffractometer	• Cu Kα radiation generated at 35 KV and 30 MA • Scattering angle 2θ was ranged from 5° to 80° • scanning rate of 3 degrees/minute	Mineralogical and phase analysis of SPL samples.
TGA-DSC	TASDTQ600	• up to 800 °C (heating rate 10°C/min) under N_2 flow (100 ml/min) • up to 800 °C (heating rate 10°C/min) under O_2 flow (100 ml/min)	Behavior of material under temperature increase
PSA-DLS	Malvern Mastersizer Hydro (2000mu)	• Measuring the random changes in the intensity of light scattered from a suspension or solution.	For particle size analysis by dynamic light scattering
Hot Air Oven	WEIBER	• Done at 110 ±1°C for 4 h maximum	For drying of samples
Magnetic Stirrer	Spinot-Tarson, Spectro	• Speed: 120 rpm • Temperature:75 and100±1°C.	For Stirring at high temperatures
Oven and furnace	Weiber, Adco-electric furnace	• As per standards	For proximate analysis[30] ASTM-D-3172,3173,3174,3175

Chapter 4

RESULTS AND DISCUSSION

The experimental study of this thesis is divided into several sections. The initial approach was to treat the water washed SPL (WWSPL) with two different types of acid i.e. Perchloric and sulfuric acid and compare the leaching behavior of both the acids. The process parameters of the above comparison were optimized by utilization of multiple level factorial designs. In the second section, an approach in chemical leaching of WWSPL was done initially with caustic, followed by Perchloric acid leaching. The third section reflected the chemical leaching of WWSPL by using caustic followed by Sulfuric acid. The process parameters used in section 2 and 3 were optimized by Taguchi method. The last section discussed about the fuel value analysis of all the optimized samples of SPL along with the raw SPL sample for the sake of comparison.

4.1. Utilization of multiple level factorial design for optimizing the process parameters for the chemical leaching of WWSPL

4.1.1. Model fitting and statistical analysis

A total of 24 experiments were performed according to multiple level factorial design approach with 24 base runs and one replicate at the center point. The design matrix for the multiple level factorial design is given in Table 4.1.The actual and predicted results with fitted and residuals values are shown in Table 4.1. The experiments were carried out in randomized run order to determine the effect of the factors on single characteristic response (i.e. leaching percentage). The experimental data on leaching percentage was plotted with deviation in the experiments in the residual plot. The maximum leaching % was found to be 48.13% for H_2SO_4 and 50.62% for $HClO_4$ treatment of water washed SPL.

4.1.2 Effect of acid concentration

4.1.2.1 For H_2SO_4 treatment

To study the effect of acid concentration on leaching percentage, the acid concentration of H_2SO_4 was varied from 5 M to 10 M. From the Table 4.2 it was observed that the acid concentration had no significant effect on the leaching percentage as compared to L/S ratio and temperature. This conclusion was based on the fact that it is

having F value 4.60 among all the parameters and contributed only 4.8% in leaching. During the leaching of SPL with H_2SO_4, the partly leachable CaF_2 got converted to $CaSO_4$ and HF. The optimum amount of acid needed to dissolve the soluble compounds was achieved at 5M concentration.

Table 4.1: The experimental values for leaching percentage under different conditions

Sl. No.	Acid Conc. (M)	L/S Ratio (cm³/g)	Temp (°C)	Leaching % with H_2SO_4			Leaching % with $HClO_4$		
				Experimental	Predicted	Difference	Experimental	Predicted	Difference
1	5.0	1.5	50	37.267	36.4551	0.81192	30.170	30.3324	-0.162375
2	7.5	1.5	50	36.980	36.6528	0.32717	34.175	33.9290	0.246000
3	10.0	1.5	50	35.150	36.2891	-1.13908	38.000	38.0836	-0.083625
4	5.0	1.5	100	41.050	41.8619	-0.81192	33.180	33.0176	0.162375
5	7.5	1.5	100	41.450	41.7772	-0.32717	37.160	37.4060	-0.246000
6	10.0	1.5	100	40.960	39.8209	1.13908	40.560	40.4764	0.083625
7	5.0	2.5	50	36.483	36.9391	-0.45608	42.400	42.2357	0.164292
8	7.5	2.5	50	37.630	37.8838	-0.25383	42.710	42.8648	-0.154833
9	10.0	2.5	50	41.780	41.0701	0.70992	46.875	46.8845	-0.009458
10	5.0	2.5	100	42.050	41.5939	0.45608	43.150	43.3143	-0.164292
11	7.5	2.5	100	42.510	42.2562	0.25383	44.890	44.7352	0.154833
12	10.0	2.5	100	43.140	43.8499	-0.70992	47.680	47.6705	0.009458
13	5.0	3.5	50	38.300	39.0737	-0.77375	42.275	42.5420	-0.267042
14	7.5	3.5	50	40.210	40.3750	-0.16500	42.400	42.4147	-0.014667
15	10.0	3.5	50	45.100	44.1613	0.93875	44.775	44.4933	0.281708
16	5.0	3.5	100	43.850	43.0763	0.77375	44.150	43.8830	0.267042
17	7.5	3.5	100	44.260	44.0950	0.16500	44.562	44.5473	0.014667
18	10.0	3.5	100	45.350	46.2888	-0.93875	45.260	45.5417	-0.281708
19	5.0	4.5	50	45.600	45.1821	0.41792	48.150	47.8849	0.265125
20	7.5	4.5	50	45.900	45.8083	0.09167	47.775	47.8515	-0.076500
21	10.0	4.5	50	46.900	47.4096	-0.50958	49.025	49.2136	-0.188625
22	5.0	4.5	100	46.850	47.2679	-0.41792	49.130	49.3951	-0.265125
23	7.5	4.5	100	47.520	47.6117	-0.09167	50.230	50.1535	0.076500
24	10.0	4.5	100	48.130	47.6204	0.50958	50.620	50.4314	0.188625

With increase in acid concentration, the concentration of soluble component such as NaF, Na_3AlF_6 and Al_2O_3 decreases in leaching solution[54]. Therefore the leaching percentage has no significant change with increase in acid concentration.

The following reaction mechanisms were involved during leaching process[54]

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \tag{4.1}$$

$$2NaF + H_2SO_4 \rightarrow 2HF\ (g) + Na_2SO_4 \tag{4.2}$$

$$NaF.AlF_3 + H_2SO_4 \rightarrow 4HF\ (g) + Na\ Al\ (SO_4)_2 \tag{4.3}$$

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF\ (g) \tag{4.4}$$

$$2Al\ (OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3(aq.) + 6H_2O(l) \tag{4.5}$$
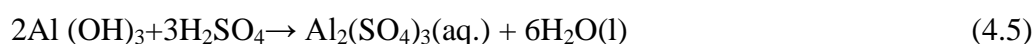
4.1.2.2 For HClO₄ treatment

To examine the effect of change in acid concentration on leaching percentage, the acid concentration was varied from 5 M to 10 M. From the Table 4.3 it was observed that the acid concentration was second most significant factor in the leaching percentage. Acid concentration was found to be one of the significant factors having F value 214.09 among all the parameters and contributed 11.7% in leaching. The following reaction mechanisms were involved during leaching process[54].

$$Al_2O_3 + 3HClO_4 \rightarrow 2Al(ClO_4)_3 + 3H_2O \tag{4.6}$$

$$NaF + HClO_4 \rightarrow HF\ (g) + NaClO_4 \tag{4.7}$$

$$CaF_2 + 2HClO_4 \rightarrow Ca\ (ClO_4)_2 + 2HF\ (g) \tag{4.8}$$

$$Al\ (OH)_3 + 3HClO_4 \rightarrow Al_2(ClO_4)_3(aq.) + 3H_2O(l) \tag{4.9}$$
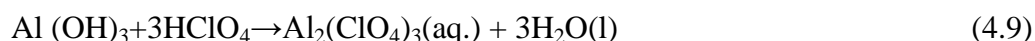
4.1.3. Effect of Liquid to Solid (L/S) Ratio

4.1.3.1 For H₂SO₄ treatment

To study the effect of the L/S ratio on leaching percentage, the L/S ratio was varied from 1.5 to 4.5 cm^3/g. The effect of the L/S ratio on leaching percentage was found to be most significant factor having F value 44.81 and contributed 46.7% in leaching. There was an appreciable increase in leaching percentage observed with increase in the L/S ratio.

4.1.3.2 For HClO₄ treatment

The effect of the L/S ratio of leaching percentage was found to be most significant having F value 1421.99 and contributed 77.9% in leaching. The leaching percentage was increased substantially with increase in L/S ratio.

4.1.4. Effect of temperature

4.1.4.1 For H_2SO_4 treatment

The effect of temperature on leaching percentage was studied at two different values (i.e. 50 ±1°C and 100 ±1 °C). From Table 4.2, it was observed that the temperature was the second most significant factor having F value 41.38 and was contributed 43.2% in leaching.

4.1.4.2 For $HClO_4$ treatment

From the Table 4.3, it was observed that the effect of temperature was the third most significant factor having F value 146.33 and contributed only 8.0% in leaching. There was a marginal increase in leaching percentage with increase in temperature from 50 °C to 100 °C (Table 4.1). This was due to the fact that the solubility of leachable compounds such as NaF, Na_3AlF_6 and CaF_2 increased with increase in temperature.

4.1.5. Analysis of Variance (ANOVA)

The ANOVA was carried out to investigate the significance of design parameters. "Fisher (F) test"[49]was conducted to test the significant effect on the output parameters. The most and least significant factors were decided on the basis of higher and lower "F" value. The percentage contribution of each factor is decided in terms of their "F" value From the ANOVA, for leaching percentage of H_2SO_4 treatment (Table 4.2) the L/S ratio and acid concentration were found to be most and least significant factor, respectively. The (acid concentration * temperature) and (L/S ratio * temperature) were found to be the least and most significant terms among interaction terms, respectively. From the ANOVA, for leaching percentage of $HClO_4$ treatment, the L/S ratio and temperature were found to be most and least significant factor among all the linear terms (Table 4.3). But within the interaction terms, (acid concentration * temperature) and (acid concentration * L/S ratio) were observed to be least significant and most significant, respectively. For the linear terms with two factor interaction model expressed by (Eq. 3.2), whereby the variables take their coded values, represent 'y' as a function of acid concentration(x_1), L/S ratio (x_2) and temperature(x_3).The model was evaluated by design of experiment (DOE) surface response analyzer, which indicated that the regression model was statistically significant at 95% confidence level for both types of acid treatment. The interaction terms were not significant as its corresponding P values were higher than prescribed 0.05 (Table 4.2). The value of adjusted correlation coefficient (R^2) reflects the

percentage of variation in response variable which is explained by its relationship with one or more predicted variables. The adjustment is important because the adjusted R^2 for any model will always increase when a new parameter is added[50]. The adjusted R^2 is a useful tool for comparing the explanatory power of models with different numbers of predictors. Statistically, the values of adjusted R^2 for H_2SO_4 treatment and $HClO_4$ treatment were determined to be 89.08% and 99.55%, respectively, indicating the significant regression of the model by using three parameters.

Table 4.2: Analysis of variance for leaching percentage, using adjusted sum of squares (Adj. SS) tests for H_2SO_4 treatment

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P	% Contribution
Acidic Concentration	2	14.704	14.704	7.352	4.60	0.061	4.798
L/S Ratio	3	214.62	214.62	71.541	44.81	0.000	46.745
Temperature	1	66.068	66.068	66.068	41.38	0.001	43.167
Acid Concentration*L/S Ratio	6	18.081	18.081	3.014	1.89	0.230	1.971
Acid Concentration * Temperature	2	4.088	4.088	2.044	1.28	0.344	1.335
L/S Ratio * Temperature	3	9.100	9.100	3.033	1.90	0.231	1.982
Residual Error	6	9.580	9.580	1.597			
Total	23	336.24					100

S = 1.26360   R-Sq. = 97.15%   R-Sq. (Adj.) = 89.08%

Table 4.3: Analysis of Variance for leaching percentage, using adjusted sum of squares (Adj. SS) tests for $HClO_4$ treatment

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P	% Contribution
Acidic Concentration	2	58.167	58.167	29.083	214.09	0.00	11.724
L/S Ratio	3	579.515	579.515	193.172	1421.9	0.00	77.872
Temperature	1	19.878	19.878	19.878	146.33	0.000	8.013
Acid Concentration*L/S Ratio	6	27.257	27.257	4.543	33.44	0.000	1.831
Acid Concentration * Temperature	2	1.259	1.259	0.629	4.63	0.061	0.253
L/S Ratio * Temperature	3	2.270	2.270	0.757	5.57	0.036	0.305
Residual Error	6	0.815	0.815	0.136			
Total	23	689.160					100

S = 0.368573   R-Sq. = 99.88%   R-Sq. (Adj.) = 99.55%

4.1.6. Residual plots

All the four residual plots are presented in a single graph for the sake of comparing the plots to assess whether the proposed model fits the assumptions of the analysis or not. The residual plots in the graph include:

(i) Histogram indicating whether the data are skewed or outliers exist in the data

(ii) Normal probability plot indicating whether the data are normally distributed, other variables are influencing the response, or outliers exist in the data.

(iii) Residuals versus fitted values indicating whether the variance is constant, a nonlinear relationship exists, or outliers exist in the data.

(iv) Residuals versus order of the data indicating whether there are systematic effects in the data due to time or data collection order.
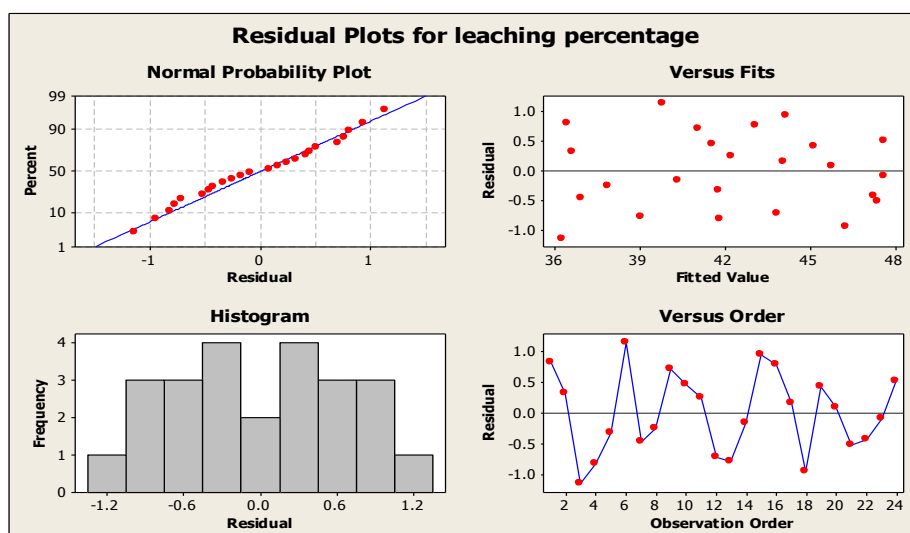

Figure 4.1: Four in one residual plot for leaching percentage of H_2SO_4 treatment.
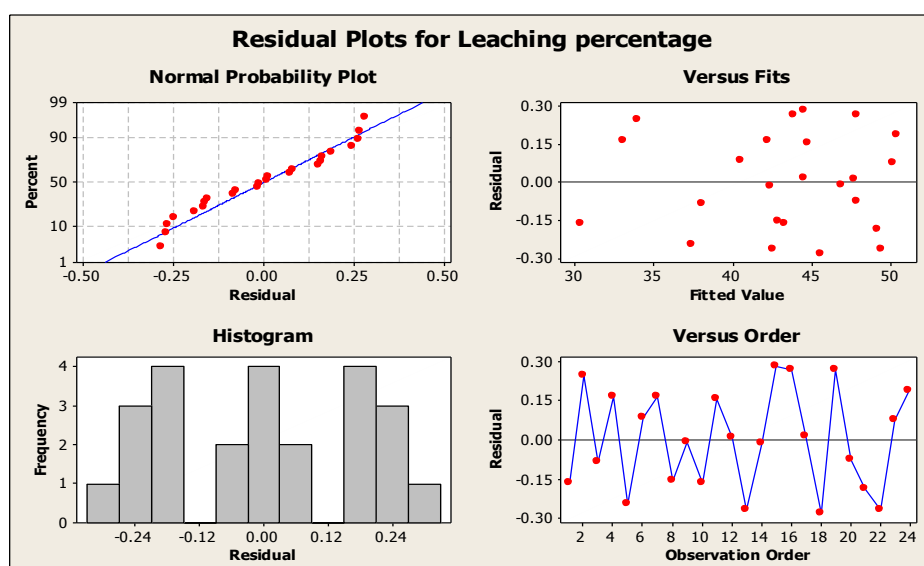

Figure 4.2: Four in one residual plot for leaching percentage of $HClO_4$ treatment.

From the residual plots for leaching percentage it was observed that the maximum deviation of predicted results with that of the actual values lies within 1.13% in case of H_2SO_4 treatment and 0.28% in case of $HClO_4$ treatment of water washed SPL. From the Figure 4.1 and 4.2, it was found that, the residuals were almost falling on a straight line. This indicates that the residuals were normally distributed and the normality assumption is valid. The adequacy of ANOVA model was also tested through the correlation between calculated and experimental values, which is shown in scattered plot i.e. residual and fitted value. Furthermore, the standardized residuals also exhibited a random, irregular pattern, as observed in the residual versus observation order plot. This validates that the experimental data has been obtained purely on random basis with no specific trend in the residual data. This also validates the independence of the data. The model assumptions for both the types of acid treatment with leaching percentage as response were found to be valid.

4.1.7. Characterization

From the water treatment of SPL leachable components such as NaF and Na_2CO_3 components were removed[30,46–48] as confirmed form the XRD analysis (Figure 4.3.1).

4.1.7.1 Elemental composition

The elemental compositions of the different treated SPL samples were found out by CHNS analyzer primarily for two reasons. The first reason was to establish the presence of the heteroatom content in each fraction that was removed or increased after treatment of SPL with various acids. The second reason was that the determination of hydrogen to carbon ratio of each fraction, which is an indicator of the aromaticity and the anticipated H_2 reduction during SPL leaching. From the Table 4.4 it was concluded that the aromaticity has no significant effect with increase in concentration of acid and water. Whereas the heteroatom compositions were increased by the treatment of acid due to increase in sulfur content, but there was no such trend in increment observed. The carbon content was found to increase from raw SPL (42.19%) to H_2SO_4 (70.83%) and $HClO_4$ (71.76%) treatment. The other parameters were kept constant for both the acids (i.e. 10 M acid concentrations, 4.5 L/S ratio and temperature 100 ºC). From the elemental analysis it was observed that nearly same degree of carbon enrichment was obtained for both the treatment approach. The increased concentration of H_2SO_4 for the treatment of SPL showed that there was very small rise in carbon percentage, whereas a reasonable increase in carbon percentage was observed in case of $HClO_4$.

Table 4.4: Elemental composition of Spent Pot Lining (SPL) by ultimate analysis

Component	Weight percentage (%)						
	C	H	N	S	H/C	N/C	S/C
Raw SPL	42.19	0.616	0.59	1.24	0.0146	0.013984	0.029391
Water Washed SPL	48.08	0.21	0.40	1.72	0.00437	0.008319	0.035774
5 M H_2SO_4 treated SPL	68.81	0.15	0.54	3.50	0.00218	0.007848	0.050865
5 M $HClO_4$ treated SPL	64.17	0.26	0.57	2.58	0.00405	0.008883	0.040206
10 M H_2SO_4 treated SPL	70.83	0.17	0.60	5.57	0.0024	0.008471	0.078639
10 M $HClO_4$ treated SPL	71.76	0.21	0.53	3.42	0.00293	0.007386	0.047659

4.1.7.2 X-Ray Diffraction (XRD) analysis

From the X-ray diffraction data, the peaks at 38.801º, 56.066º and 70.299º of 2Θ value were attributed to Villaumite (NaF) (Figure 4.3.1) which vanished upon treatment with acids (Figure 4.3.2). The peaks at 26.426º, 44.462º and 54.512º corresponded to carbon fractions which get more prominent with the treatment of SPL by that of various acids. The peak of sodium iron cyanide at 32.533º was found only on the raw SPL which was completely removed by acid leaching. Fluorite (CaF_2) having the peaks at 28.282º, 47.020º and 55.770º are found in almost all the SPL as it was sparingly leachable during the acid treatment process. The peaks of cryolite (Na_3AlF_6) are found at 19.537º, 20.027º, 22.884º, 32.570º, 38.766º and 46.764º in the raw SPL. The leachable components such as NaF, Na_3AlF_6 and part of $NaAl_{11}O_{17}$ were removed by the acid leaching process.
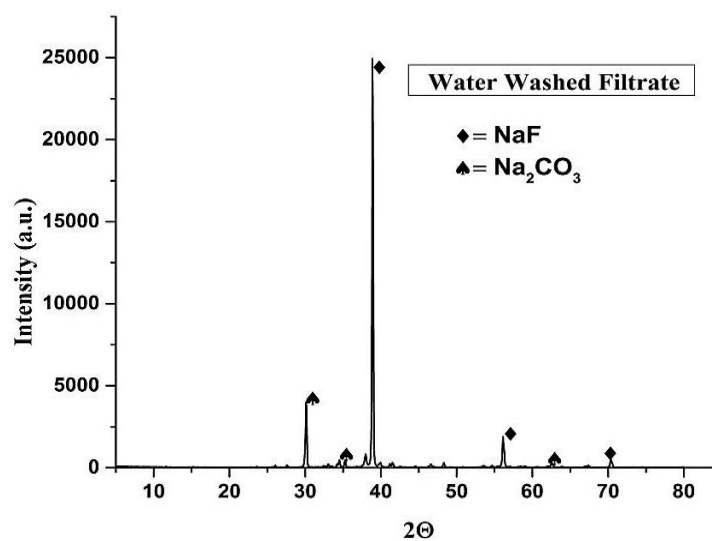
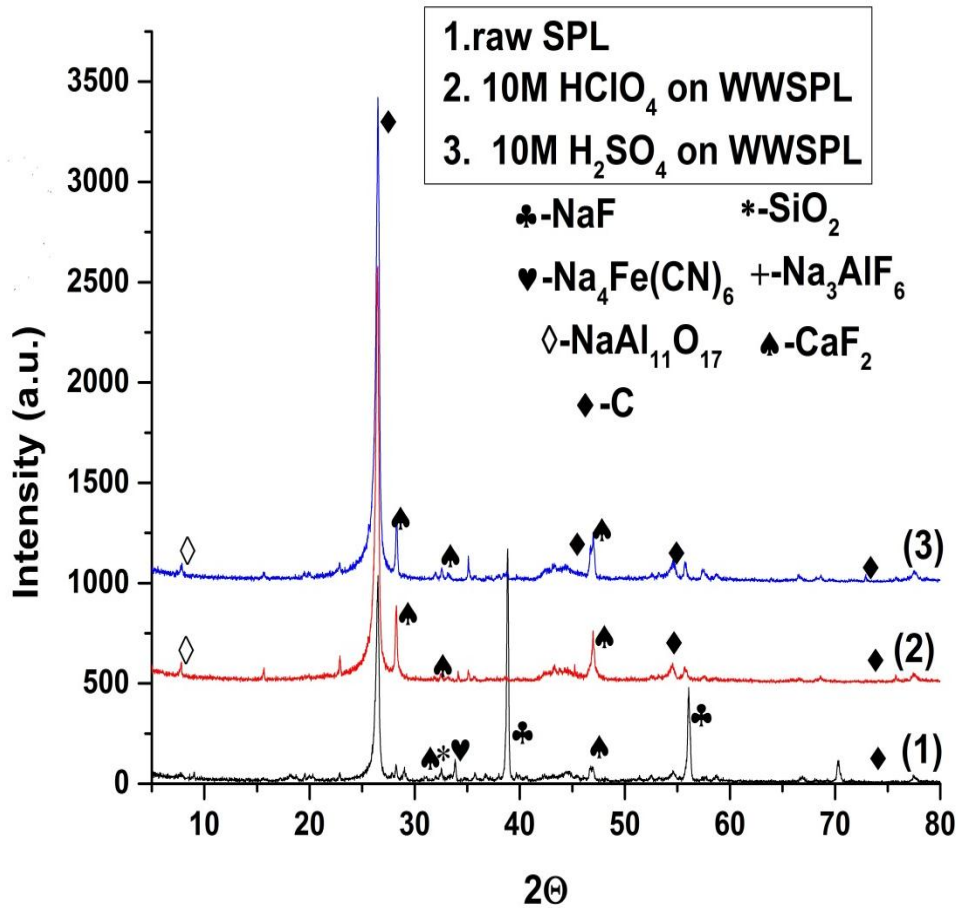**Figure 4.3.1:** XRD analysis of water washed filtrate

Figure 4.3.2: XRD analyses of Spent Pot Lining (SPL) samples

4.1.8. Outcome

- The predominating factor can be characterized by higher "F" value. The F-test and Analysis of variance (ANOVA) analysis was used to find the significant factors which played a vital role in the determination of leaching percentage. For H_2SO_4 and $HClO_4$ treatment of water washed SPL, L/S ratio was found to be the most significant factor.

- Statistically, the values of adjusted R^2 for H_2SO_4 treatment and $HClO_4$ treatment were determined to be 89.08% and 99.55%, respectively, indicating the significant regression of the model by using three parameters.

- The maximum leaching percentage was found to be 48.13% for H_2SO_4 and 50.62% for $HClO_4$ for 10M concentration. From the residual plots for leaching percentage, it was found that the maximum deviation of predicted results with that of the actual values lies within that of 1.13%.

- The carbon content was found to increase from 42.19% for raw SPL to 70.83% for H_2SO_4 and 71.76% $HClO_4$ treatment.

4.2. Chemical Leaching Treatment of Spent Pot Lining (SPL) by Taguchi Method using Caustic leaching followed by Perchloric acid leaching

4.2.1. Taguchi approach for optimization

The main objective of the optimization was to know the effect of acid concentration, alkali concentration, temperature, L/S on the leaching percentage in terms of percentage contribution. The experimental outcome for the leaching percentage of water washed SPL with that of $HClO_4$ at different setting parameters with corresponding signal to noise (S/N) ratio is demonstrated in Table 4.5. The predicted value of the leaching percentage was found by fitting the linear regression model with that of the results obtained. There was good agreement of the predicted value with that of the actual value of leaching percentage observed and is presented in Appendix II.

Table 4.5: Taguchi design matrix with experimental and predicted values

Sl. no	Alkali Conc. (M)	Acid Conc. (M)	L/S ratio (cm^3/g)	Tempe rature (°C)	Actual Leaching percentage (%)	Actual S/N ratio	Predicted leaching percentage (%)	Predicted S/N ratio
1	0.5	2.5	1.5	25	29.15	29.2928	29.2931	29.4162
2	0.5	5.0	2.5	50	39.67	31.9692	39.1331	31.8352
3	0.5	7.5	3.5	75	40.30	32.1061	40.7056	32.1417
4	0.5	10.0	4.5	100	50.45	34.0572	50.4381	34.0323
5	1.5	2.5	2.5	75	39.55	31.9429	39.5381	31.9180
6	1.5	5.0	1.5	100	45.12	33.0874	45.5256	33.1230
7	1.5	7.5	4.5	25	35.85	31.0898	35.3131	30.9557
8	1.5	10.0	3.5	50	42.79	32.6268	42.9331	32.7502
9	2.5	2.5	3.5	100	47.71	33.5722	47.1731	33.4381
10	2.5	5.0	4.5	75	44.12	32.8927	44.2631	33.0161
11	2.5	7.5	1.5	50	41.13	32.2832	41.1181	32.2582
12	2.5	10.0	2.5	25	36.10	31.1501	36.5056	31.1858
13	3.5	2.5	4.5	50	44.73	33.0120	45.1356	33.0476
14	3.5	5.0	3.5	25	36.79	31.3146	36.7781	31.2896
15	3.5	7.5	2.5	100	51.24	34.1922	51.3831	34.3156
16	3.5	10.0	1.5	75	46.79	33.4031	46.2531	33.2690

4.2.1.1 Analysis of the signal to noise (S/N) ratio

The word "signal" represents the desirable value (mean) for the output characteristics and the word "noise" signifies the undesirable value (SD) for the output characteristics in Taguchi method. Thus the S/N ratio is the ratio of the mean to the SD. The Taguchi method uses the S/N ratio to measure the quality characteristic deviating from the desired value. The "larger is better" was selected for the optimum leaching

percentage calculation. The Signal to Noise (S/N) ratio Y was determined by means of following equation,

$$Y = -10\log \sum\nolimits_{k}^{n} \binom{n}{k} x_k^{-2}$$

(4.10)

Where n is the number of test and x_k are the comparison variables in the kth experiment.

From the main effect plot for S/N ratio and from the equation, it was observed that greater the value of S/N ratio smaller was the variance of leaching percentage around the desired value. From the Figure 4.4 it can be attributed that more the effect of the parameter was significant, the deviation from the horizontal line was more. However, the relative importance among the process parameters for leaching percentage calculation still need to be known so that optimal combination of the process parameter levels can be determined more accurately. It was explained through the analysis of variance of S/N ratio.
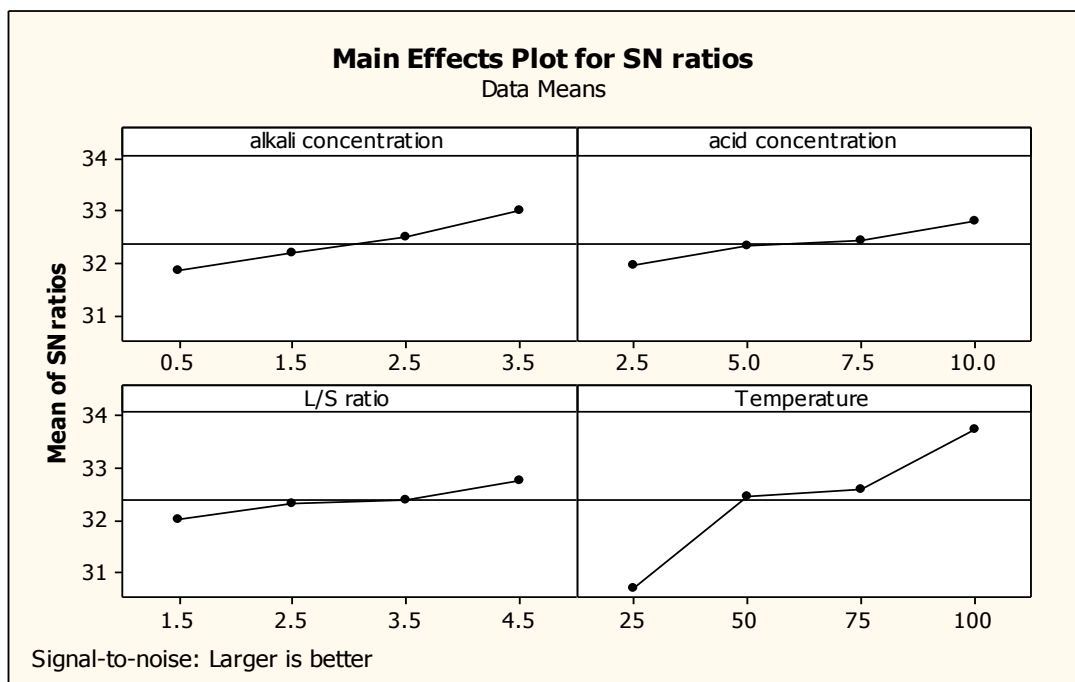

Figure 4.4: Main effect plot for the Taguchi optimization

4.2.1.2 Analysis of variance (ANOVA)

ANOVA is a collection of statistical models used to analyze the differences between group means and their associated procedures. The reason for performing ANOVA was to investigate which design parameters significantly affect the quality characteristics. "Fisher (F)" test was conducted to recognize the significant effect on the quality characteristic. The "F" value is the ratio of the mean of the squared deviations to

the mean of squared errors. Generally, when F>4 indicates that the design parameter has a significant effect on the quality characteristics. The results of analysis of variance (ANOVA) for leaching percentage at various process and response conditions are presented in Table 4.6. After the selection of optimal level of the design parameters, the final step was to predict and verify the improvement of the quality characteristics using the optimal level of the design parameter. The estimated S/N ratio using the optimal parameters for leaching percentage can be obtained and the related other parameters can be calculated by the Eq. (4.10). It is perceived that there was a good correspondence between the predicted and actual leaching percentage from Table 4.5. From Table 4.6 it was found that, the temperature was the most significant and L/S ratio as the least significant parameter among all the independent parameters according to percentage contribution.

Table 4.6: Analysis of variance of Signal to Noise (S/N) ratio

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P	Percentage Contribution
Alkali concentration	3	2.7238	2.7238	0.90792	19.41	0.018	11.4
Acid concentration	3	1.4815	1.4815	0.49383	10.56	0.042	6.2
L/S ratio	3	1.1344	1.1344	0.37813	8.08	0.060	4.7
Temperature	3	18.5956	18.5956	6.19852	132.50	0.001	77.7
Residual error	3	0.1403	0.1403	0.04678			
Total	15	24.0756					100

S = 0.2163   R-Sq. = 99.4%   R-Sq. (Adj.) = 97.1%

4.2.2. Classical approach of optimization

4.2.2.1 Effect of alkali concentration

In this step the optimal values of NaOH concentration was predicted in the range of 0.5-3.5M. Water washed SPL was treated with varying NaOH concentration at 5 L/S ratio, at a temperature of 50 °C for 4 h. From the Figure 4.5 it can be seen that leaching percentage increased with increasing the alkali concentration in the range of 0.5 M to 1.5 M. But after 1.5 M the leaching percentage was nearly constant. This was because at 1.5 M NaOH concentration, it furnished the required amount of OH$^-$ sites for the dissolving of unleached cryolite (Na_3AlF_6), alumina (Al_2O_3) fractions in the SPL sample[42].
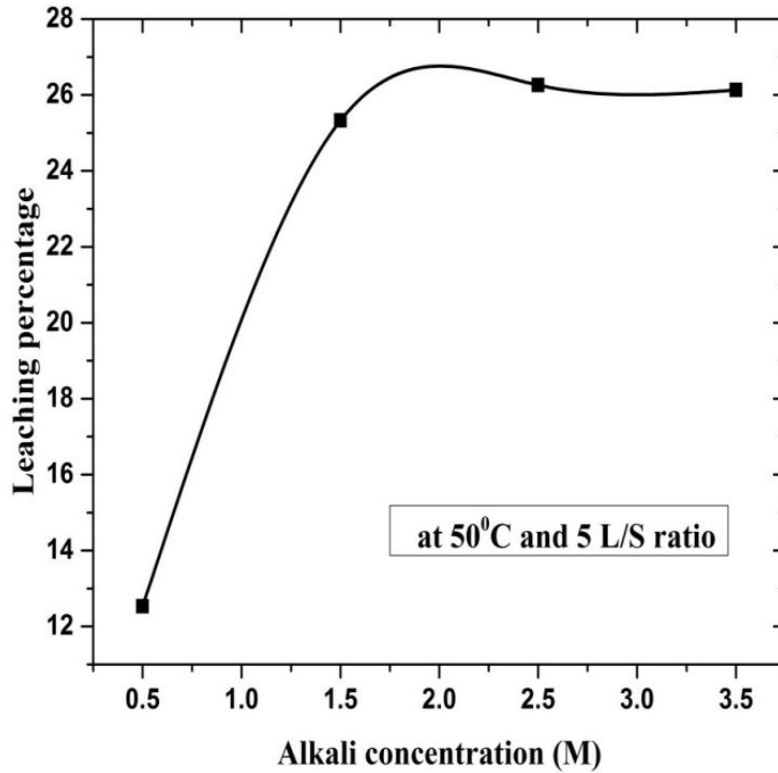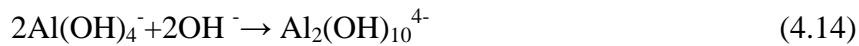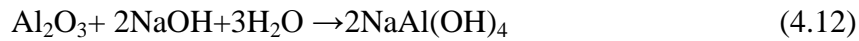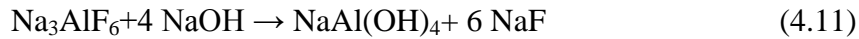
Figure 4.5: Influence of alkali concentration on leaching percentage

For the leaching process following reaction mechanisms[42]wasinvolved.

$$Na_3AlF_6 + 4\ NaOH \rightarrow NaAl(OH)_4 + 6\ NaF \qquad\qquad (4.11)$$

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4 \qquad\qquad (4.12)$$

$$Al(OH)_4^- + 2OH^- \rightarrow Al(OH)_6^{3-} \qquad\qquad (4.13)$$

$$2Al(OH)_4^- + 2OH^- \rightarrow Al_2(OH)_{10}^{4-} \qquad\qquad (4.14)$$

4.2.2.2 Effect of acid concentration

In the solution of 1.5M NaOH with an L/S ratio of 5 at 50°C, the water washed Spent Pot Lining (WWSPL) was leached for 4h at different $HClO_4$ concentration in the range of 2.5-10M.From the Figure 4.6 it was observed that the leaching percentage hardly increased as the acid concentration rose from 2.5 M to 10 M. The concentration of leachable components decreased with increasing acid concentration leading to lesser rise in leaching percentage. Hence 2.5 M of $HClO_4$ was taken as the optimized value for the acid treatment.
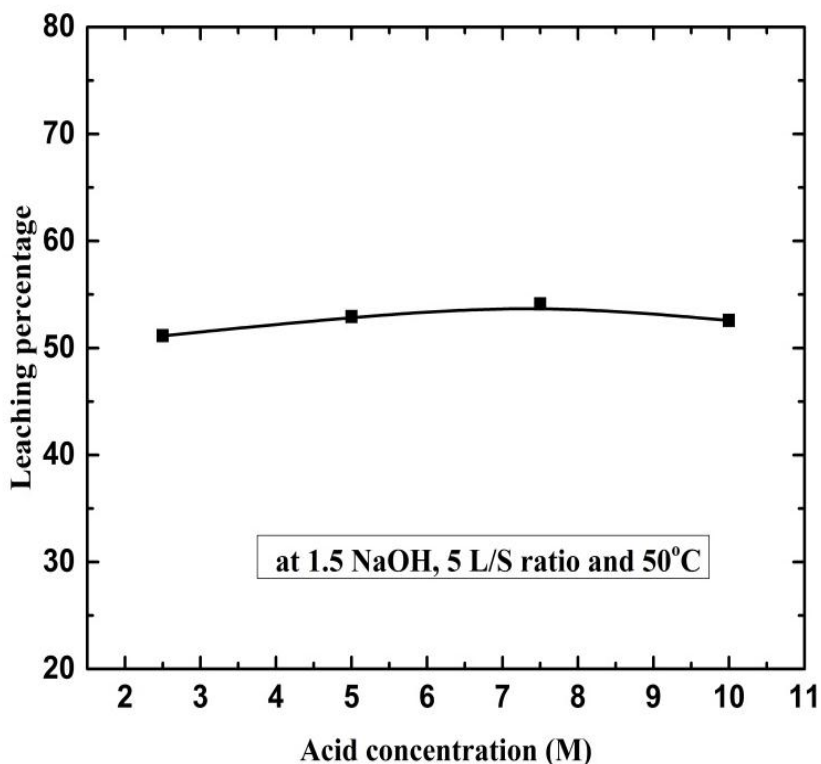
35

Figure 4.6: Influence of acid concentration on leaching percentage

4.2.2.3 Effect of liquid to solid (L/S) ratio

The water washed Spent Pot Lining (WWSPL) samples were taken for the alkali leaching. The samples were leached in 1.5M NaOH followed by 2.5M $HClO_4$ solution for 4 h at 50 °C, and the L/S ratio was varied in the range of 1.5-4.5 cm^3/g. The Figure 4.7 shows the total leaching percentage obtained after both alkali and acid leaching. It was observed that the leaching percentage marginally increased with an increase in the L/S ratio in the range of 1.5-2.5. This was due to increase in mass of mass of OH^- ions with the increase in L/S ratio which reacts with the soluble Na_3AlF_6 and Al_2O_3. The concentration of soluble Na_3AlF_6 and Al_2O_3 in the leaching solution decreased with the increase of L/S ratio, which made the leaching percentage gradually constant with further increase in the L/S ratio in case of alkali leaching[42]. Similarly, in the case of acid leaching the rise in leaching percentage was due to the mass of ClO_4^- ions which react with the $Al(OH)_3$ and sparingly soluble CaF_2 in the range 1.5-2.5.
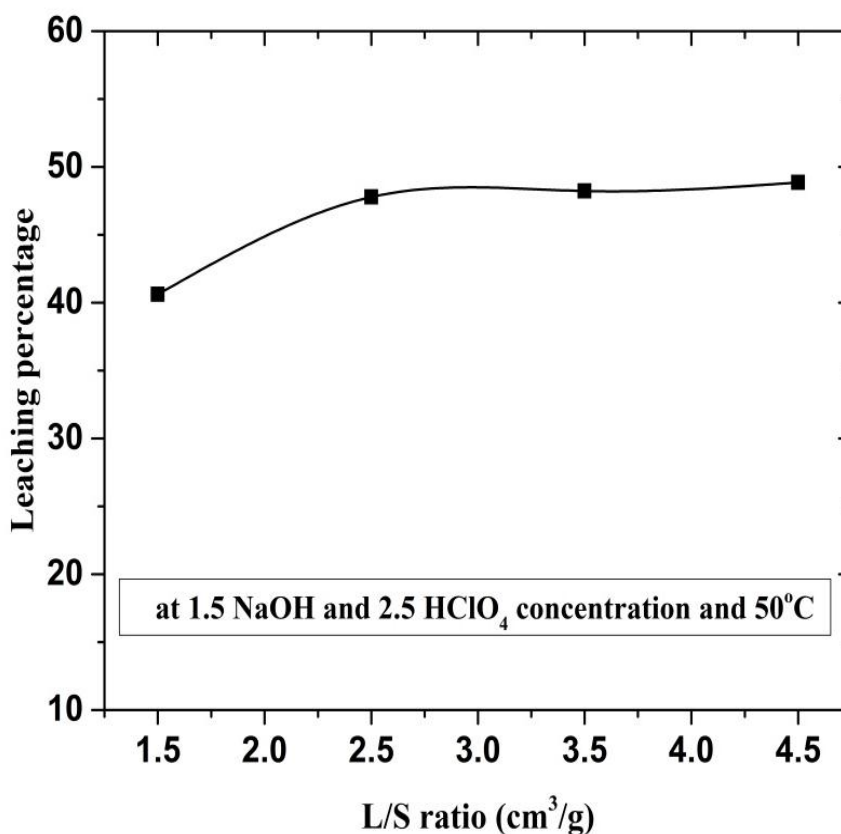
36

Figure 4.7: Influence of liquid to solid (L/S)ratio on leaching percentage

4.2.2.4 Effect of temperature

Spent Pot Lining (SPL) samples were leached in 1.5 M NaOH followed by 2.5 M HClO$_4$ solution for 4 h using 2.5 L/S ratio in the temperature values of 25, 50, 75 and 100 ±1°C. It is perceived from Figure 4.8 that the temperature has an appreciable effect on the leaching percentage. The leaching percentage increased from 35.62% to 54.04% when the temperature increased from 25 ±1°C to 100 ±1°C. This was because the solubility of leachable compound Al(OH)$_3$ increased with the temperature. But after 50 ±1 °C there was a gradual increase in the leaching percentage due to the CaF$_2$ was not fully leachable as confirmed from the XRD studies. Finally, from both Taguchi method and one factor at a time approach, it was concluded that 1.5 M NaOH, 2.5 M HClO$_4$, 2.5 L/S ratio and 50 ±1°C were the best combination for the optimum leaching percentage and considered as "final treated SPL". For "alkali treated SPL" the condition required were1.5M NaOH, 2.5 L/S ratio and 50 ±1 °C.
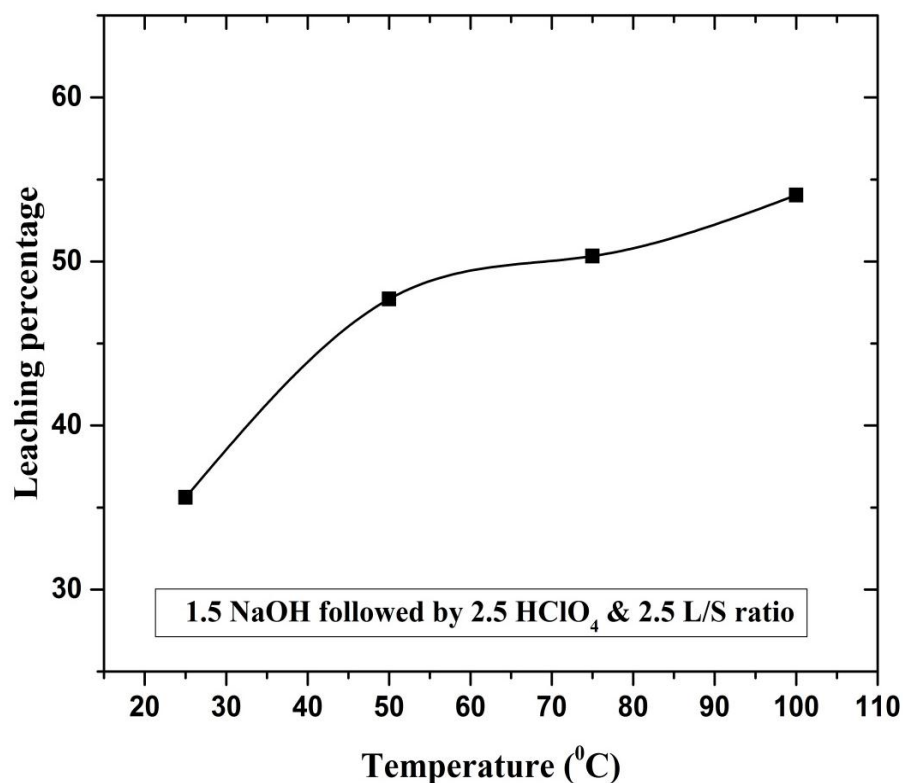
Figure 4.8: Influence of temperature on leaching percentage

4.2.3. Characterization of Spent Pot Lining (SPL) samples

4.2.3.1 Thermo gravimetric analysis-differential scanning calorimetry (TGA-DSC)

From the Figure 4.9.1, it can be noticed that the removal of moisture started at from 99 °C and continued up to 104 °C with a mass reduction of 0.74%. Then there was a 4.3% rise in mass % in between 104-434 °C. The gain in weight in the TGA graph may be attributed to the following two reasons:

(i) Chemical reaction (reactions with gaseous substances in the purge gas such as O_2, CO_2 with the formation of non-volatile or partially volatile compounds).

(ii) Physical transitions (adsorptions of gaseous substances on samples such as active carbon).

After that decomposition occurred with total mass reduction of 36.23 % from 434 °C to 749 °C. The sample was tested in O_2 flow just to confirm the reason for the gain in mass which was happening with N_2 flow. From the Figure 4.9.2, there is no such gain in mass is observed in O_2 flow. From the DSC curve exothermic process occurring during the combustion is confirmed. The reason for rise in mass was due to the formation of NaCN compound at high temperature[52].
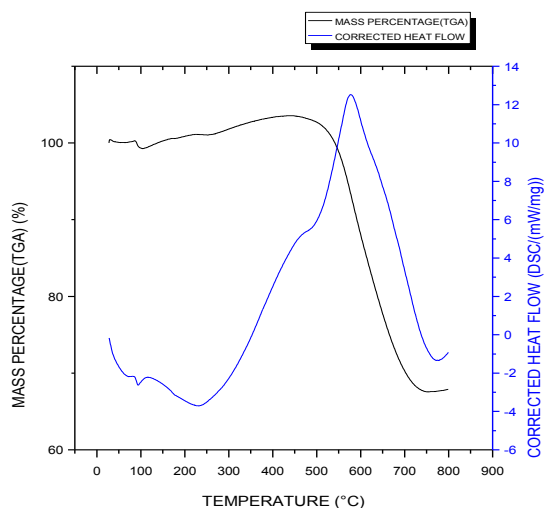
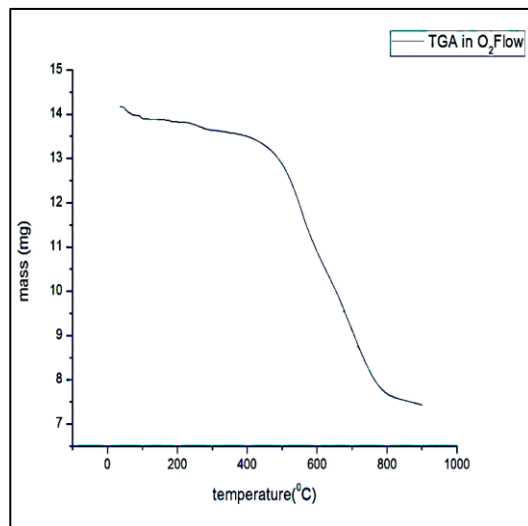**Figure 4.9.1:** TGA-DSC under N_2 flow   **Figure 4.9.2:** TGA under O_2 flow

4.2.3.2 Proximate analysis

The proximate analysis was done on the raw Spent Pot Lining (SPL) samples along with the optimized samples obtained from the leaching experiments. From Table 4.7, it was observed that the fixed carbon percentage increased after treatment. Similarly the residue content was decreased as the removal of leachable component occurred during treatment of SPL.

Table 4.7: Proximate analysis of SPL samples treated with HClO$_4$

Sample	Moisture content (%)	Residue content[30] (%)	Volatile matter (%)	Fixed carbon (%)
Raw SPL	3.46	51.39	6.18	38.96
Water Washed SPL	2.40	51.32	5.91	40.37
Alkali treated SPL	2.20	25.25	4.78	67.77
Final treated SPL	2.10	14.84	0.20	82.86

4.2.3.3 Particle size analysis (PSA) of sieved and treated SPL samples by dynamic light scattering (DLS)

The particle size distribution of SPL was done in de-ionized water and the profile is shown in Figure 4.10 and 4.11. A reduction in average particle size was observed from raw SPL to final treated SPL. The raw SPL was having average particle size of 102.138μm with maximum and minimum diameter of particle 296.079 and 13.964 μm, respectively. The final treated SPL was having average particle size of 15.5628 μm with maximum and minimum diameter of particle 107.93 and 2.851 μm, respectively. From

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the Figure 4.10 and 4.11, it may be anticipated that the leachable particles that mainly comprised of inorganic fractions were being removed during leaching process. In order to assess how the leaching of inorganic fractions occurred during treatment, Scanning Electron Microscope-Energy Dispersive X-ray diffraction (SEM-EDX) analysis was performed.
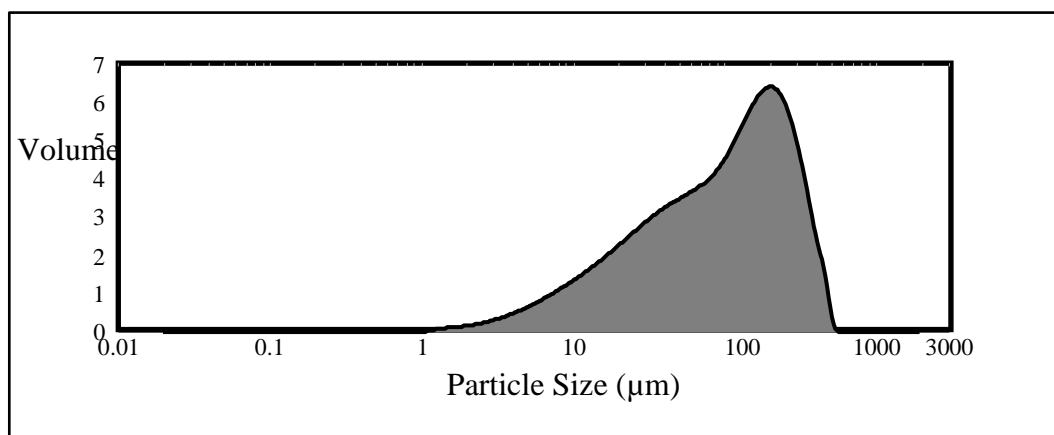

Figure 4.10: Particle size analysis of raw SPL
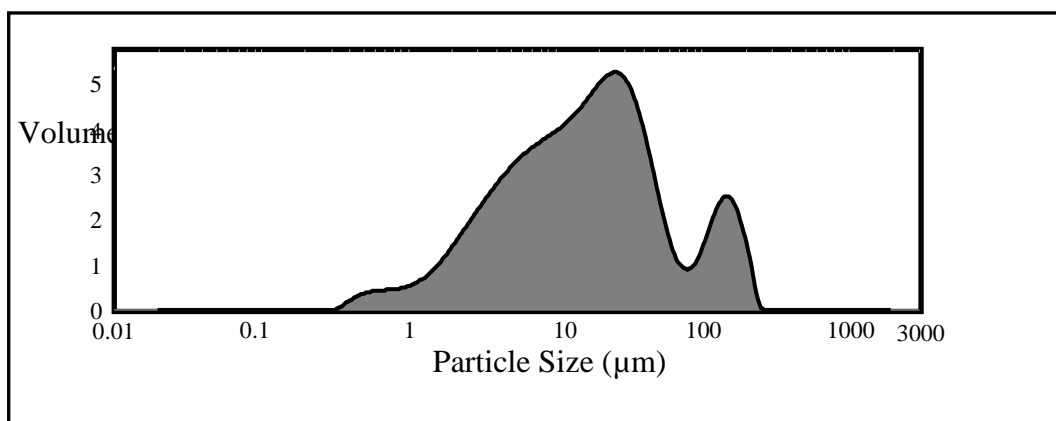
Figure 4.11: Particle size analysis of treated SPL

4.2.3.4 SEM-EDX and ultimate analysis

The 300μm size fraction SPL particles are mainly comprised of carbonaceous and finely divided inorganic materials attached to the exposed surfaces. This occurred due to breakage along the inside layers of bath material between the layers of graphene[2,30,46–48]. In Figure 4.12 and 4.16, it was observed that the partial mineral liberation or exposure of the inorganic materials from the carbon fraction was possible to a large extent leading to better leachability. From Figure 4.12 (iv and v), some elongated graphite particles (dark color) appeared completely exposed at this size fraction. After magnification it was found that, finely divided inorganic (brighter colored) particles attached loosely to graphite

particles or appeared as independent units. Figure 4.12(iv, v and vi) proposed a closer look of partially liberated graphite particles. It reflected that most of the inorganic fractions, which remained attached to graphite particles, were in the form of a relatively thin layer (~1 μm).These inorganic fractions were fully accessible to any leaching solution. To know more about the structure about inorganic fractions, the SEM analysis of residual SPL samples (Figure 4.13) were performed and it was found that the needle like structure comprised of inorganic fractions. The appearance of inorganic fractions was becoming less prominent due to removal of leachable components leading to less bright particles present in the materials (Figure 4.14, 4.15, 4.17 and 4.18). The average values of all the components obtained after 3 times repetition of sampling is shown in Table 4.8. The ultimate analysis was done for the SPL samples and results are included in the Table 4.8.
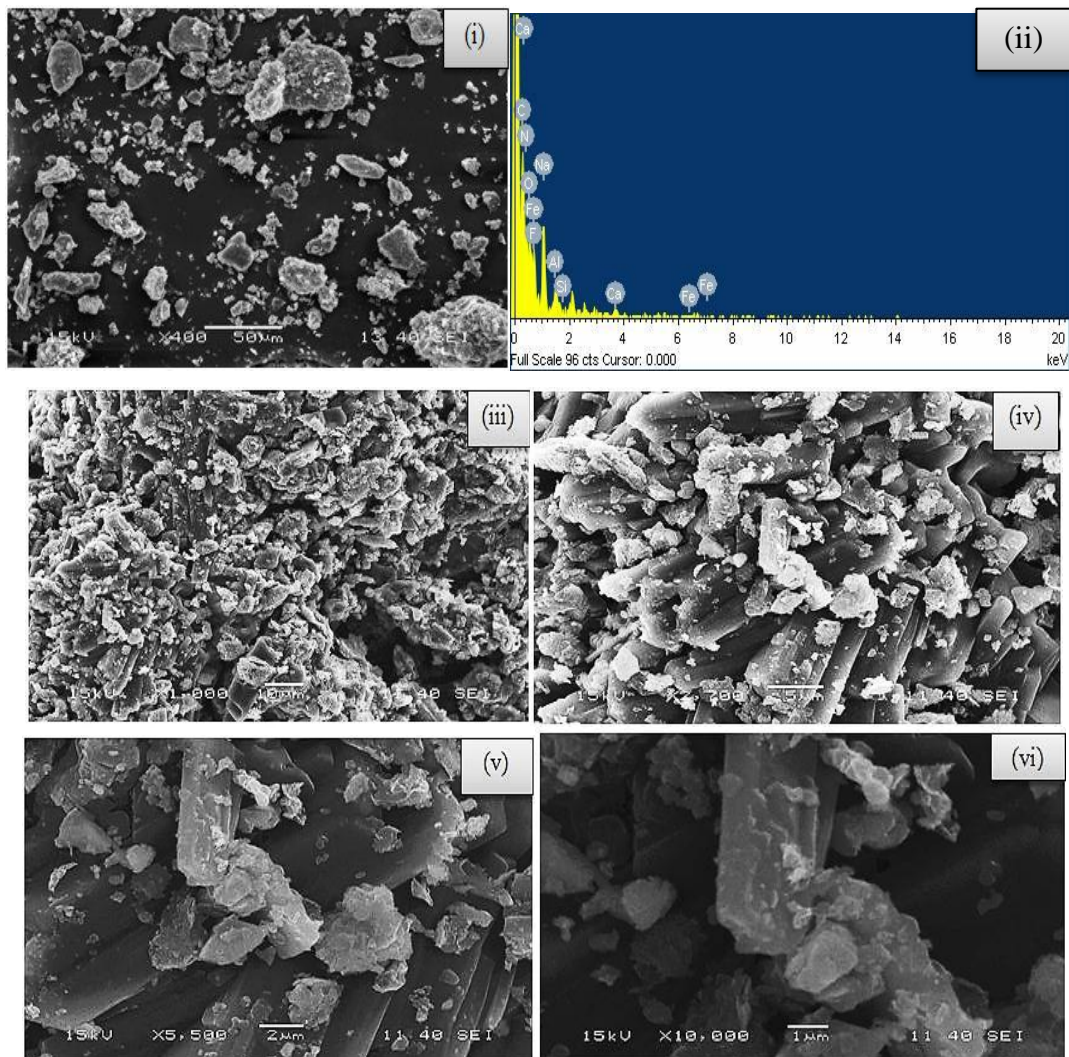
Figure 4.12: SEM-EDX images of Raw SPL, having particle size of D minimum - 13.964 μm, D mean -102.136 μm, D Max - 296.079 μm
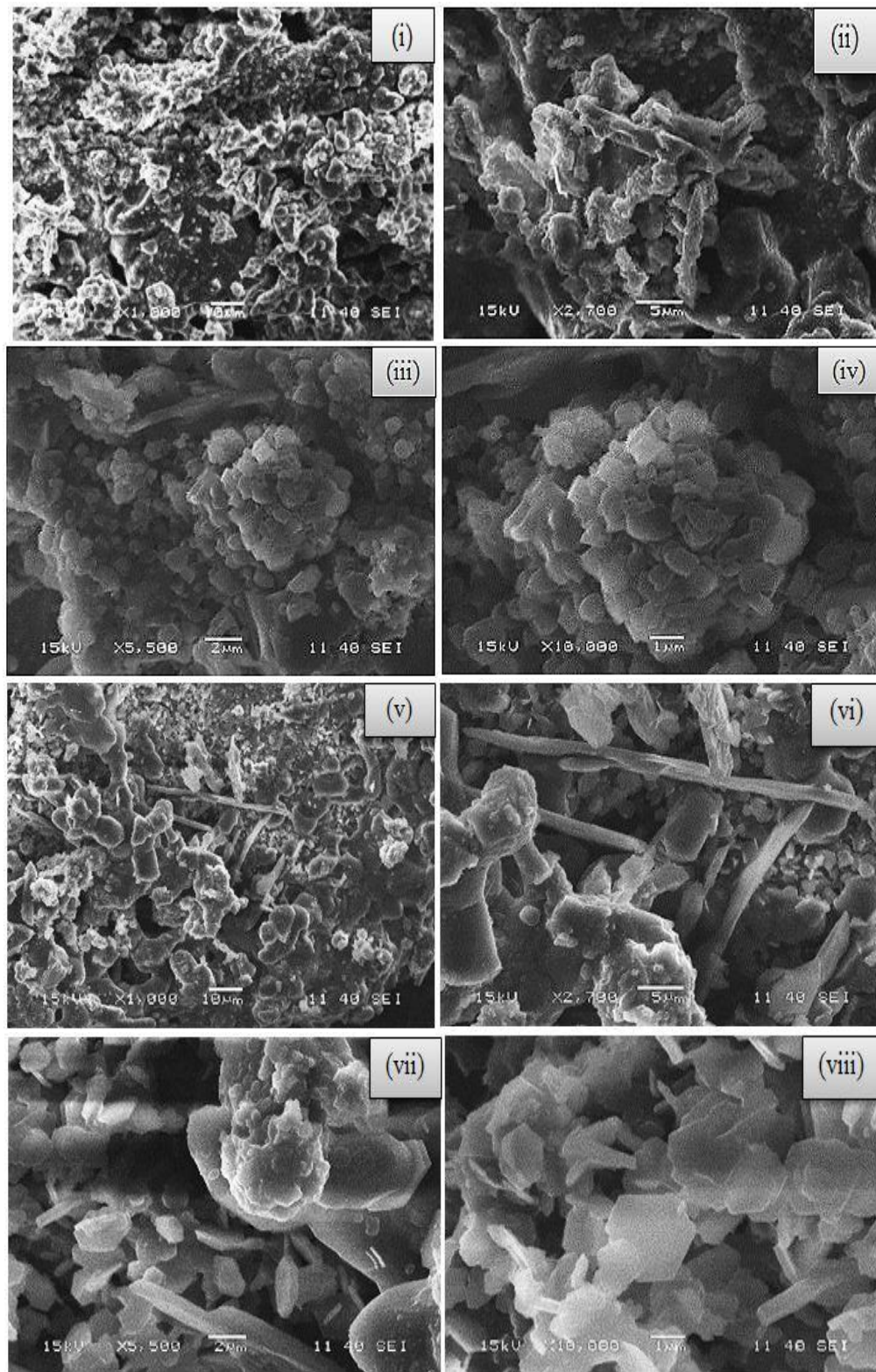
Figure 4.13: SEM images Raw SPL sample burned at 800°C for 1.5h (i, ii, iii, iv) and 800°C for 5h(v, vi, vii, viii)
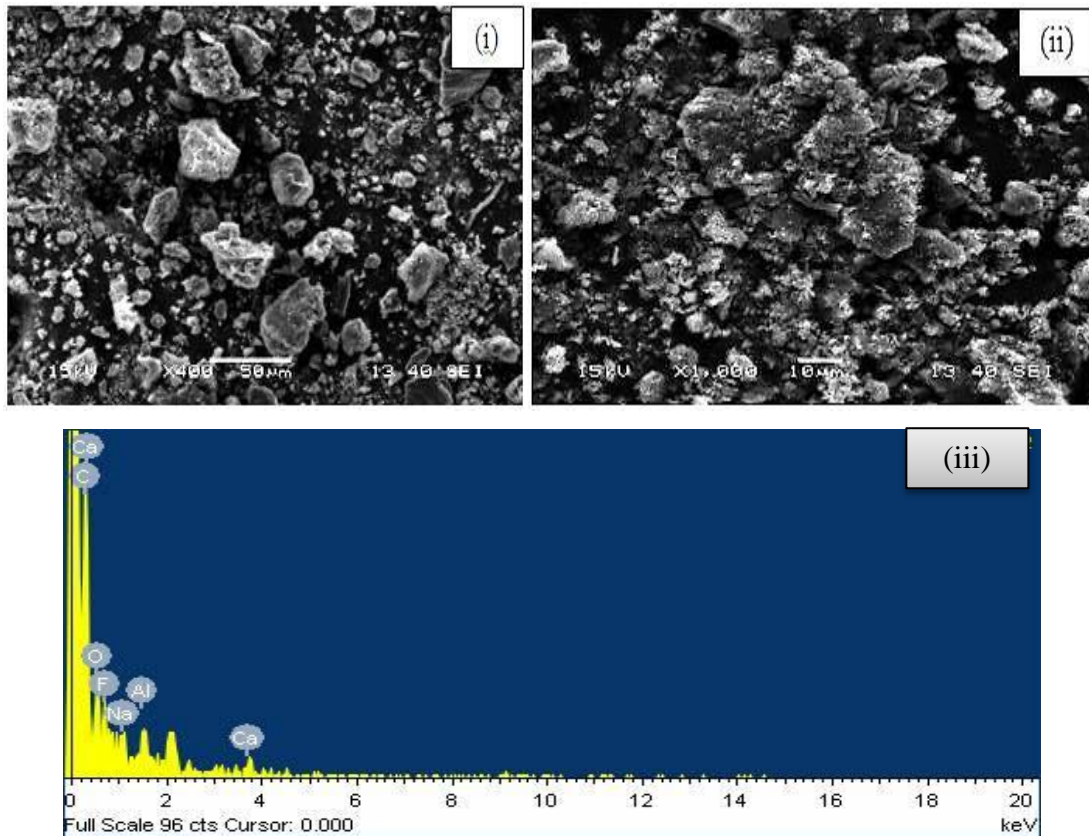
Figure 4.14: SEM-EDX images of alkali treatment of SPL at 1.5M NaOH concentration (i, ii, iii)
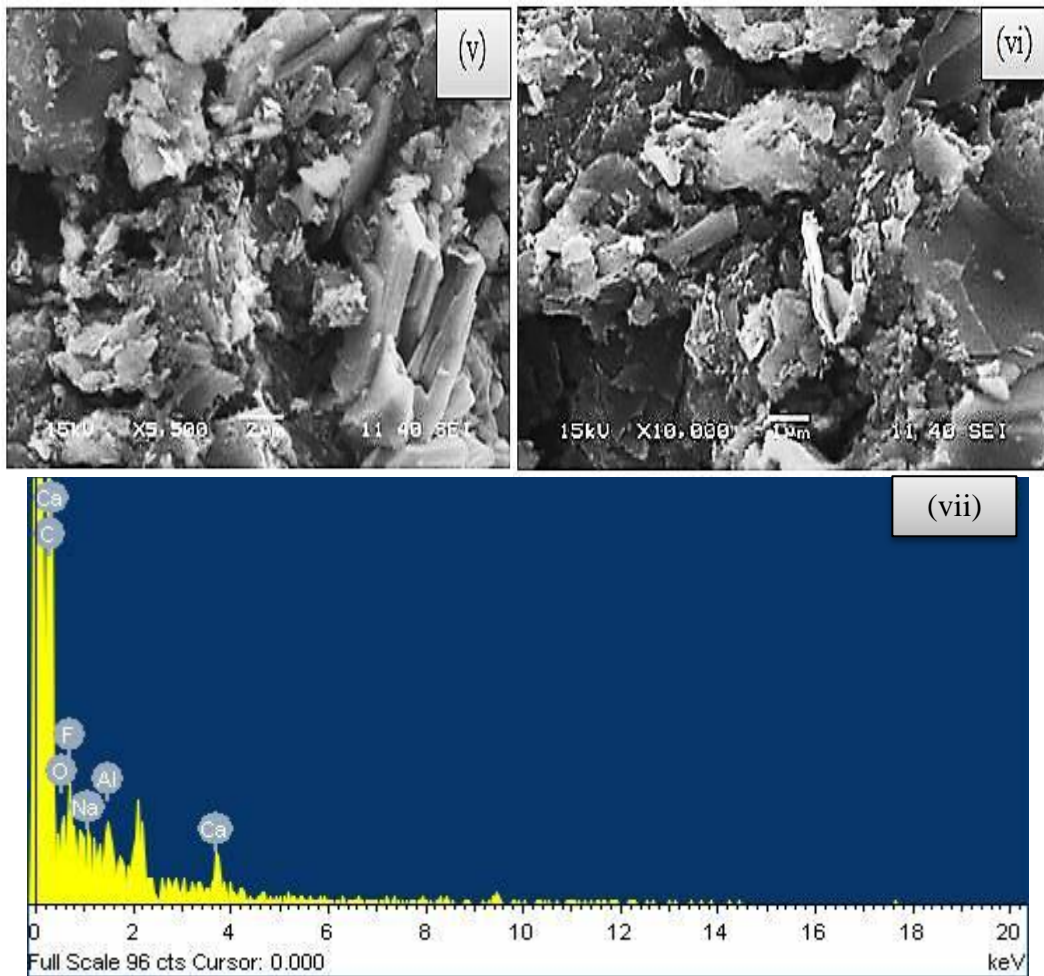
Figure 4.15: SEM-EDX images of the final treated SPL (i, ii, iii, iv, v, vi, vii) having D min = 2.851 μm, D mean = 15.5628 μm, D max = 107.93 μm
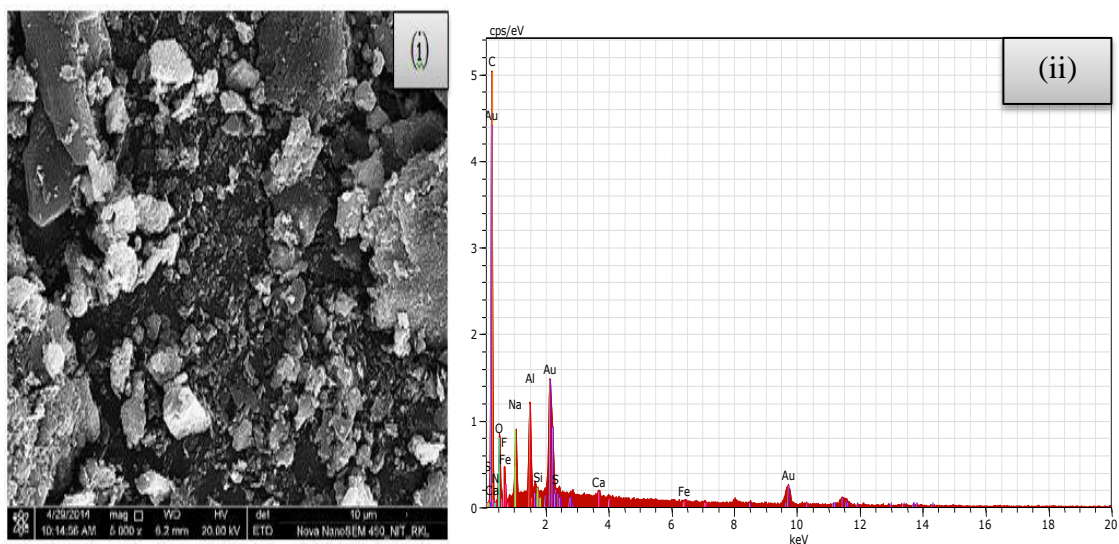
Figure 4.16: FESEM-EDX images of raw SPL (i, ii)
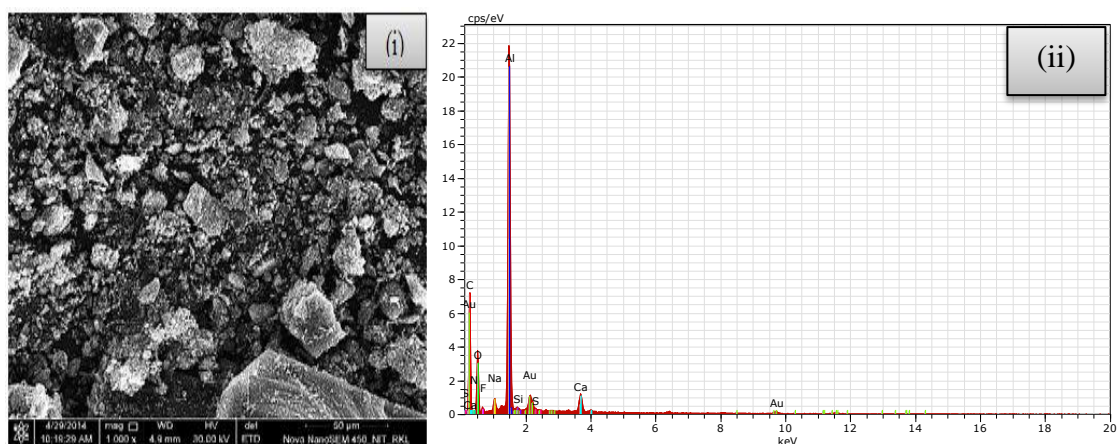
Figure 4.17: FESEM-EDX images of 1.5M NaOH treated SPL
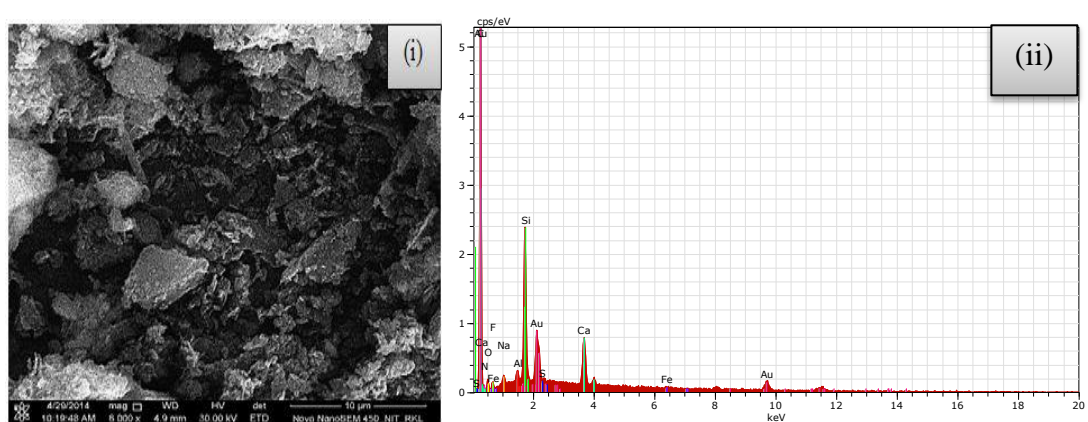
Figure 4.18: FESEM-EDX images of Final Treated SPL

Table 4.8: Ultimate and elemental (SEM-EDX) analysis of SPL samples

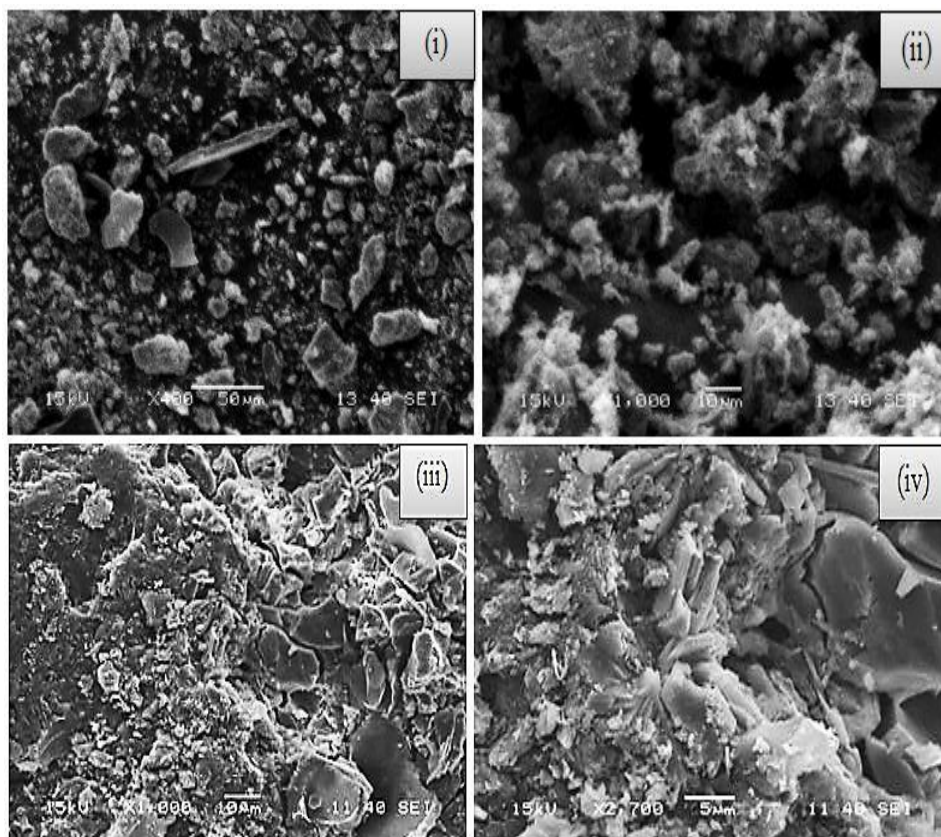| Component	Weight percentage (%)										
	Na	F	Al	C	Ca	N	S	H	Fe	Si	O
Raw SPL	14.23	14.66	4.78	42.19	1.32	0.59	1.24	0.616	0.001	0.0007	20.372
Water Washed SPL	8.26	10.25	3.97	48.08	1.32	0.40	1.72	0.211	0.001	0.0007	25.787
Alkali treated SPL	2.12	6.35	1.10	72.01	1.54	0.55	2.46	0.154	0.011	0.009	13.696
Final treated SPL	1.51	3.42	0.10	87.03	2.03	0.62	2.69	0.21	0.09	0.01	2.30

4.2.3.5 X-ray diffraction (XRD) analysis

The XRD analysis of optimum sample along with that of raw SPL was performed. The peaks of graphitic carbon (C), cryolite (Na_3AlF_6), villaumite (NaF), fluorite (CaF_2), sodium iron cyanide ($Na_4Fe(CN)_6$) and gibbsite ($Al(OH)_3$) phases were found. After washing and filtering of alkali treated SPL, the solid residue contained insoluble compounds of CaF_2, $Al(OH)_3$ and $NaAl_{11}O_{17}$ is shown in Figure 4.19.

45
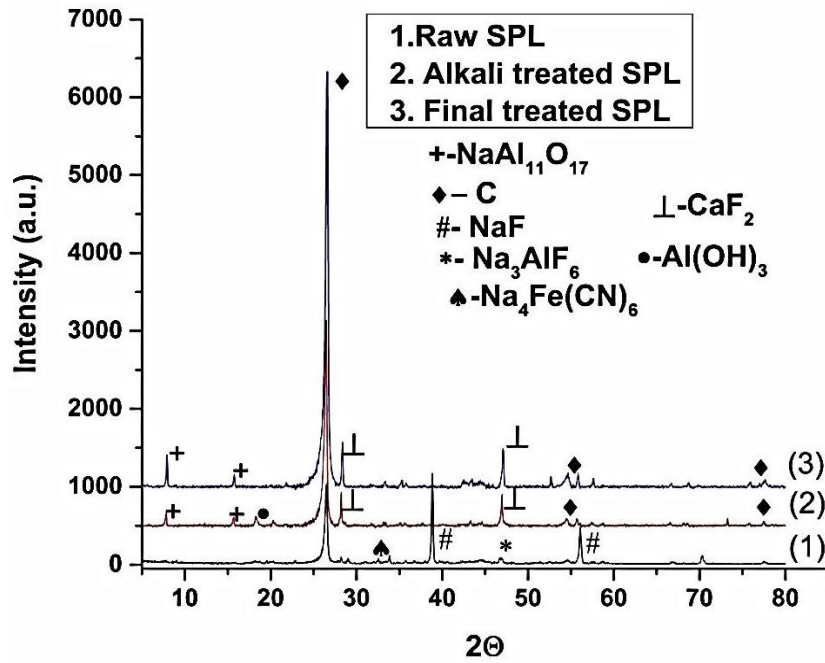
Figure 4.19: XRD analysis of SPL samples

4.2.4. Cryolite precipitation

In order to check the feasibility of the cryolite precipitation the leachates were analyzed at 2 different pH values. At pH 4.5 (Figure 4.20) the aluminum ions have existed in the form of $Al(OH)_4^-$ or $[Al_8(OH)_{26}]^{2-}$ leading to precipitation of cryolite[42]. While at pH 9.5 (Figure 4.21) Cl⁻ prevails over the precipitation of cryolite leading to the formation of NaCl as confirmed from XRD analysis. The acid leaching solution containing H^+ ion was added with alkali leaching solution having Na^+, F^- and its complex anion (AlF_x^{3-x}) to form cryolite (Na_3AlF_6) at suitable pH value (Eq. 4.15).

$$Al(OH)_4^-+4H^++3Na^++6F^-\rightarrow Na_3AlF_6+4H_2O \qquad (4.15)$$
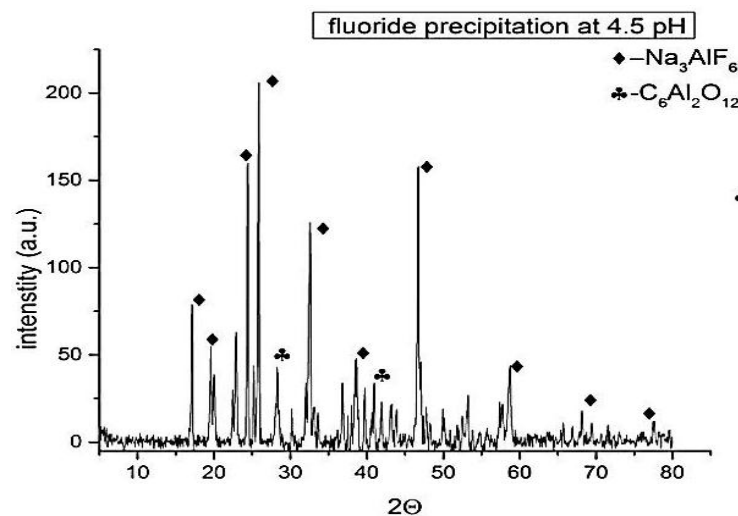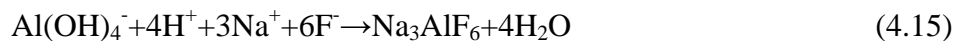
Figure 4.20: XRD analysis of fluoride precipitation at pH value of 4.5
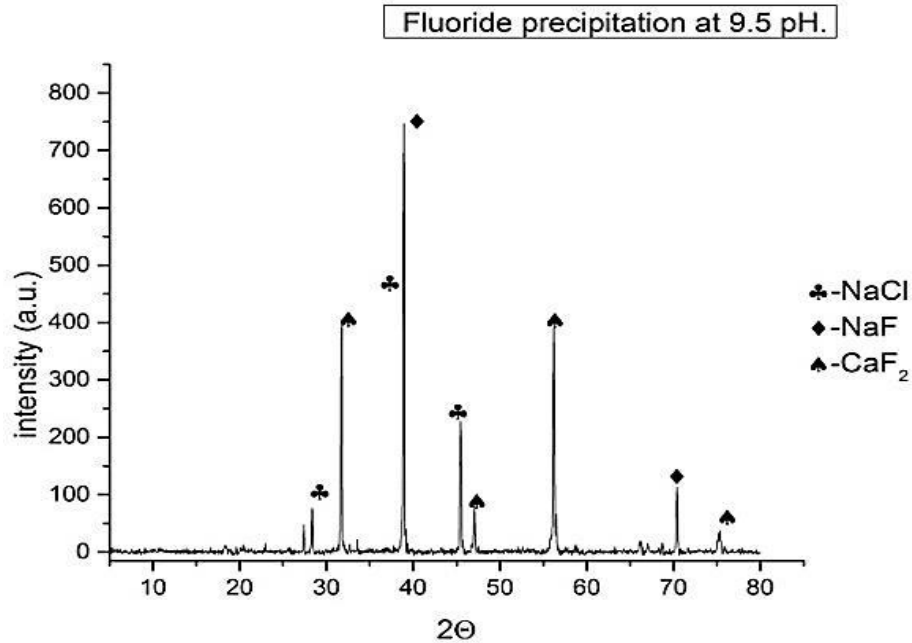
Figure 4.21: XRD analysis of fluoride precipitation at pH value of 9.5

4.2.5. Outcome of the study

- Temperature was found to be the most significant factor among all the parameters, whereas the L/S ratio was the least significant among the four parameters studied.

- Temperature contributed 77.7% in the leaching process, whereas L/S ratio contributed only 4.7 %. The maximum leaching percentage was found to be 54.04% for the classical approach of optimization, whereas in Taguchi optimization method the maximum leaching percentage was 51.24%.

- From the S/N ratio analysis, the optimum condition was achieved at 3.5 M NaOH concentration, 7.5 M $HClO_4$, 2.5 L/S ratio and at 100 ±1°C. From both Taguchi method and one factor at a time approach, it was concluded that 1.5 M NaOH, 2.5 M $HClO_4$, 2.5 L/S ratio and temperature 50°C was the best combination for the optimum leaching percentage for "final treated SPL" and 1.5M NaOH, 2.5 L/S ratio and temperature 50 ±1°C for "alkali treated SPL".

- The carbon percentage of SPL was increased from 42.19% to 87.03% as confirmed from the ultimate analysis. From the proximate analysis, the fixed carbon was found to be increased from 38.96% to 82.86% from the raw to final treated SPL.

- From the XRD analysis, it was concluded that a lower pH value of the solution favors higher degree of precipitation of cryolite.

4.3. Chemical leaching treatment of Spent Pot Lining (SPL) by Taguchi method using Caustic leaching followed by Sulfuric acid leaching

4.3.1. Taguchi optimization of NaOH followed by H_2SO_4

The experimental results for the leaching percentage of water washed SPL with that of H_2SO_4 at different setting parameters with corresponding S/N ratio is shown in Table 4.9. There was good agreement of the predicted value with that of the actual value of leaching percentage observed and is presented in Appendix II.

Table 4.9: Taguchi design of NaOH followed by H_2SO_4

Sl. No.	Alkali Conc. (M)	Acid Conc. (M)	L/S ratio (cm^3/g)	Temperature (°C)	Actual Leaching Percentage (%)	Actual S/N ratio	Predicted Leaching Percentage (%)	Predicted S/N ratio
1	0.5	2.5	1.5	25	31.24	29.8942	33.0544	30.3514
2	1.5	7.5	4.5	25	51.37	34.2142	51.3669	34.1840
3	2.5	10.0	2.5	25	48.27	33.6735	48.3844	33.6403
4	3.5	5.0	3.5	25	52.39	34.3850	50.4644	33.9912
5	0.5	5.0	2.5	50	41.77	32.4173	41.7669	32.3871
6	1.5	10.0	3.5	50	51.47	34.2311	53.2844	34.6883
7	2.5	7.5	1.5	50	49.12	33.8252	47.1944	33.4314
8	3.5	2.5	4.5	50	48.49	33.7130	48.6044	33.6798
9	0.5	7.5	3.5	75	45.50	33.1602	45.6144	33.1270
10	1.5	2.5	2.5	75	47.08	33.4567	45.1544	33.0630
11	2.5	5.0	4.5	75	50.96	34.1446	52.7744	34.6018
12	3.5	10.0	1.5	75	47.72	33.5740	47.7169	33.5438
13	0.5	10.0	4.5	100	50.28	34.0279	48.3544	33.6341
14	1.5	5.0	1.5	100	48.45	33.7059	48.5644	33.6726
15	2.5	2.5	3.5	100	50.32	34.0348	50.3169	34.0047
16	3.5	7.5	2.5	100	50.24	34.0210	52.0544	34.4782

4.3.1.1 Analysis of the signal to noise (S/N) ratio

The "larger is better" was selected for the optimum leaching percentage calculation. The S/N ratio "Y" was determined by the formula given in the Eq. (4.10). Graphically the effects of parameters are shown in Figure 4.22.
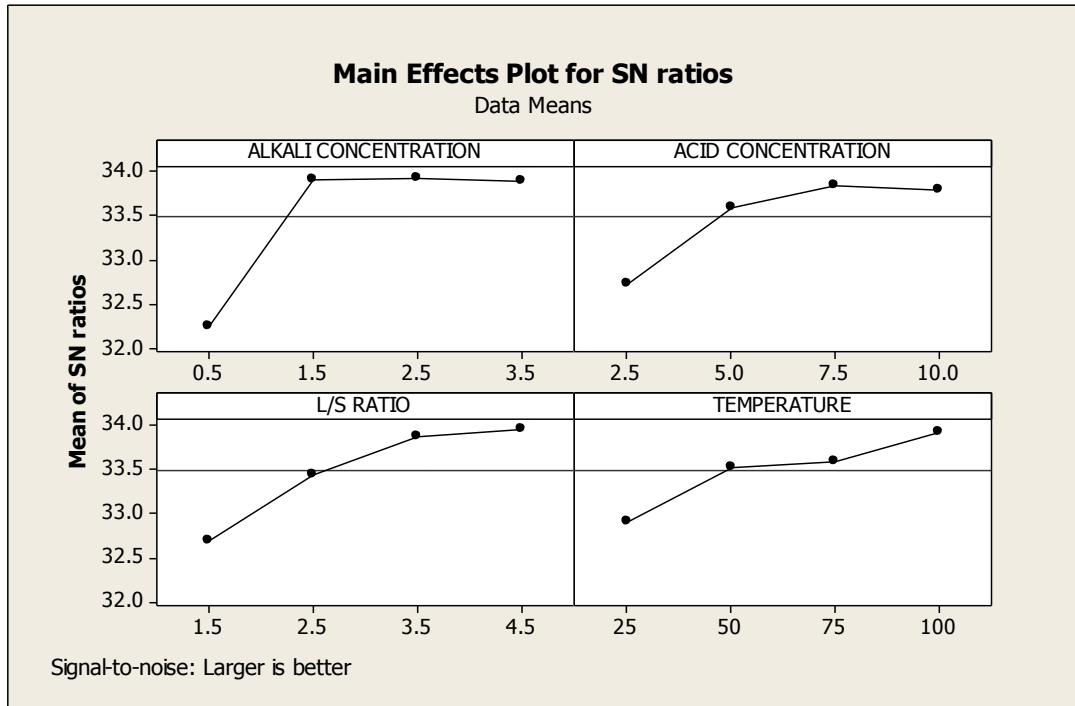
Figure 4.22: Main effect plots for Signal to Noise (S/N) ratio

4.3.1.2 Analysis of variance (ANOVA)

The results of ANOVA for leaching percentage at various process and reaction conditions are shown in Table 4.10. The comparison of the predicted leaching percentage and the actual leaching percentage and the actual Signal to Noise (S/N) ratio with that of Taguchi predicted S/N ratio is shown in the Table 4.9. There was a good agreement between the predicted and actual leaching percentage observed. From the Table 4.10, alkali concentration was found to be the most significant factor and the temperature as a least significant factor on the basis of percentage contribution.

Table 4.10: Analysis of Variance for Signal to Noise (S/N) ratio

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P	% Contribution
Alkali concentration	3	166.95	166.95	55.649	5.95	0.089	45.52
Acid concentration	3	67.91	67.91	22.638	2.42	0.243	18.52
L/S ratio	3	99.97	99.97	33.323	3.56	0.162	27.24
Temperature	3	32.11	32.11	10.705	1.14	0.457	8.72
Residual Error	3	28.05	28.05	9.351			
Total	15	394.99					100

S = 3.058   R-Sq. = 92.9%

4.3.2. Classical approach of optimization of NaOH followed by H$_2$SO$_4$

4.3.2.1 Effect of alkali concentration

The optimum value of NaOH concentration was predicted in the range of 0.5-3.5 M and discussed in the section 4.2.2.1. The results were plotted in the Figure 4.5.

4.3.2.2 Effect of acid concentration

In this step, the optimum value of H$_2$SO$_4$ concentration was proposed in the range of 0.5-10 M. The Spent Pot Lining (SPL) sample obtained from the alkali leaching of 1.5 M NaOH was treated with H$_2$SO$_4$ under setting parameters of 5 L/S ratio, temperature 50 ±1°C, 120 rpm and time 4 h. From the Figure 4.23, it was observed that after 2.5 M concentration the leaching percentage was almost constant showing no more effect of acid concentration.
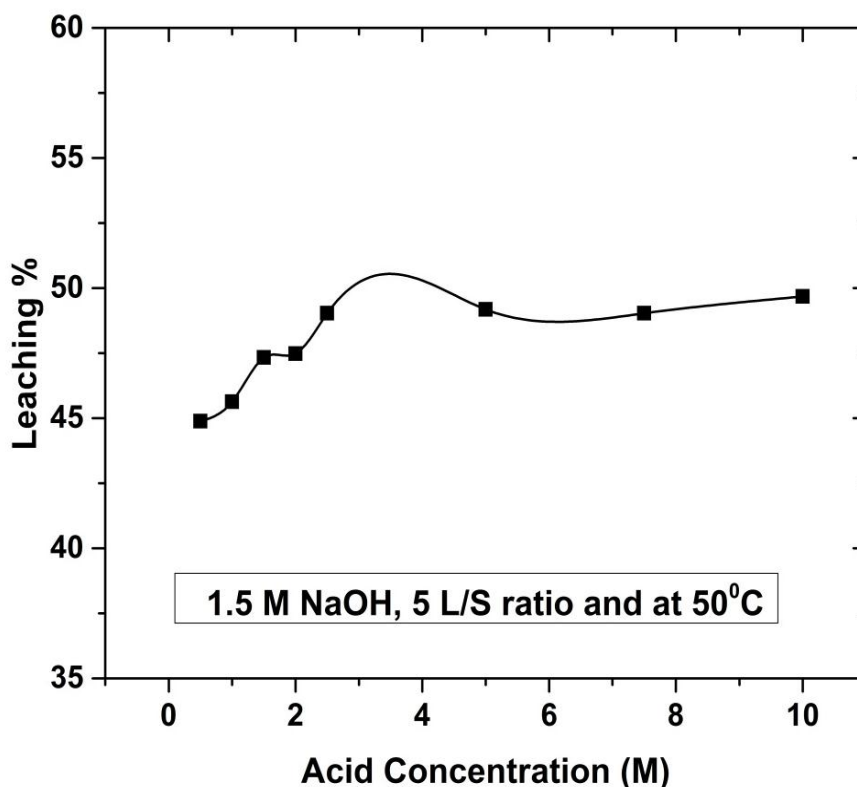
Figure 4.23: Influence of acid concentration on leaching percentage

4.3.2.3 Effect of liquid to solid (L/S) ratio

The water washed SPL samples were leached in 1.5 M NaOH followed by 2.5 M H$_2$SO$_4$ solution for 4 h at 50 ±1°C and the L/S ratio was varied in the range of 1.5-4.5 cm^3/g. It was observed from Figure 4.24 that the leaching percentage substantially increased with increasing the L/S ratio in the range of 1.5-3.5. There was no effect on the

leaching percentage after 3.5 L/S ratio because at this point the required mass of OH⁻was available to react with the soluble $Na_3AlF_6$and Al_2O_3.Similarly in acid leaching, the rise of leaching percentage was due to the mass of SO_4^{2-}which react with the sparingly soluble CaF_2 and $NaAl_{11}O_{17}$ and fully soluble $Al(OH)_3$in the range of 1.5-3.5 L/S ratio.
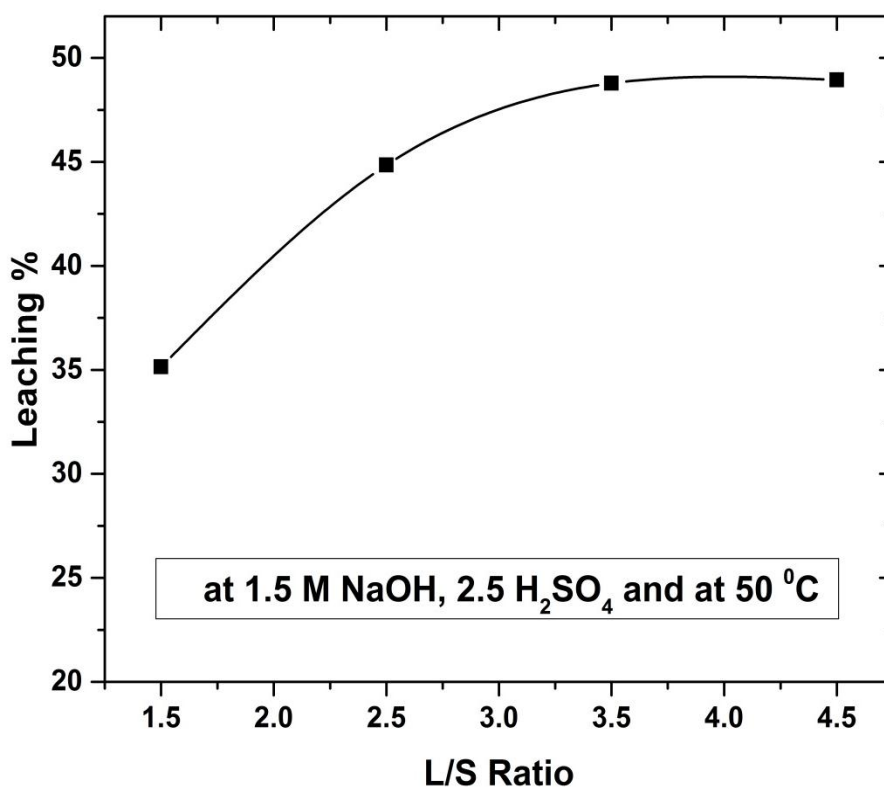
Figure 4.24: Influence of liquid to solid (L/S) on leaching percentage

4.3.2.4 Effect of temperature

The water washed Spent Pot Lining (SPL) samples were leached in 1.5MNaOH followed by 2.5 M H_2SO_4 solution for 4 h and 3.5 L/S ratio at a different temperature ranging from 25-100 ±1°C. From the Figure 4.25, it can be perceived that there was a small rise in the leaching percentage from temperature 25 to 50 °C. But a decrease in leaching percentage was observed from temperature 50 to 100 °C. This was due to the solubility of leachable component such as Na_2SO_4 decreasing with increasing temperature. In this step, 25°C was considered as optimum temperature. Ultimately, from both Taguchi and classical approach it was concluded that 1.5 M NaOH, 2.5 M H_2SO_4, 3.5 L/S ratio and 25 ±1°C were the best combination for the optimum leaching percentage, considered as "final treated SPL" and 1.5M NaOH, 3.5 L/S ratio and 25 ±1°C for "alkali treated SPL".
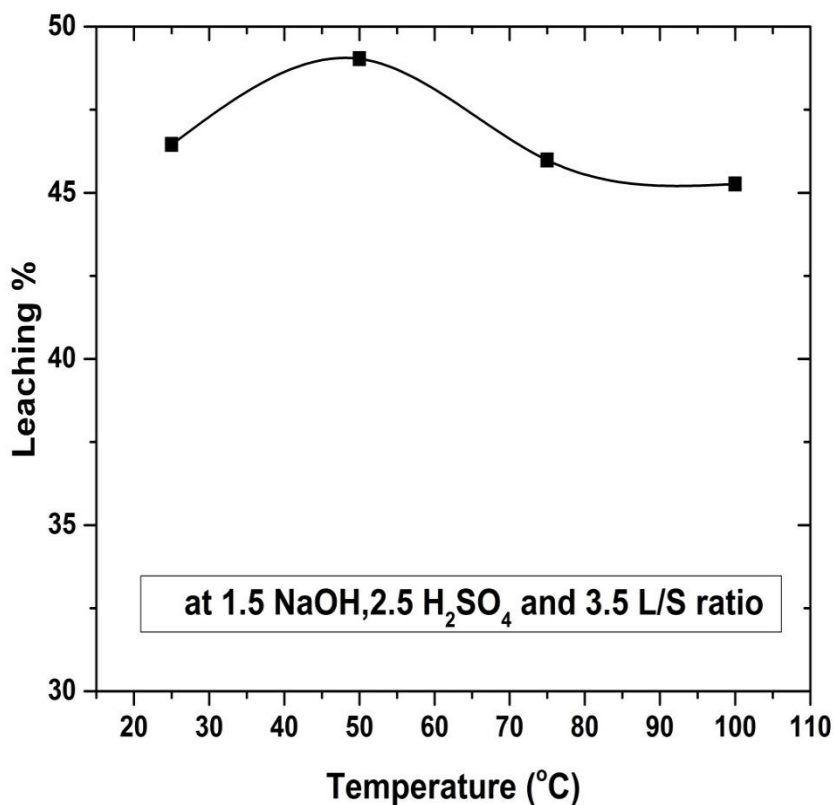
Figure 4.25: Influence of temperature on leaching percentage

4.3.3. Characterization of Spent Pot Lining (SPL) samples

4.3.3.1 Proximate analysis

The proximate analysis was performed on the SPL samples and is shown in Table 4.11. It was found that the fixed carbon percentage increased upon subsequent treatment. The volatile component and residual content were found to be decreased upon treatment by alkali and acid.

Table 4.11: Proximate analysis of SPL samples treated with H_2SO_4

Sample	Moisture content (%)	Residue content[30](%)	Volatile matter (%)	Fixed Carbon (%)
Raw SPL	3.46	51.39	6.18	38.96
Water Washed SPL	2.40	51.32	5.91	40.37
Alkali treated SPL	2.20	25.25	4.78	67.77
Final treated SPL	2.13	16	3.19	78.68

4.3.3.2 SEM-EDX and Ultimate analysis

Morphological studies were conducted to examine the extent of leaching and to get better access about the behavior of material on the micron scale. The morphological studies of raw and alkali treated SPL were discussed in the section 4.2.3.4. In this section an elemental analysis of the final treated sample obtained from the sulfuric acid treatment was performed. The ultimate analysis was conducted to get the compositional details of SPL samples. The elemental composition of SPL samples is shown in the Table 4.12. The carbon content of the treated sample increased up to a certain level, which make these treated SPL samples, can be used for the preparation anode or cathode.
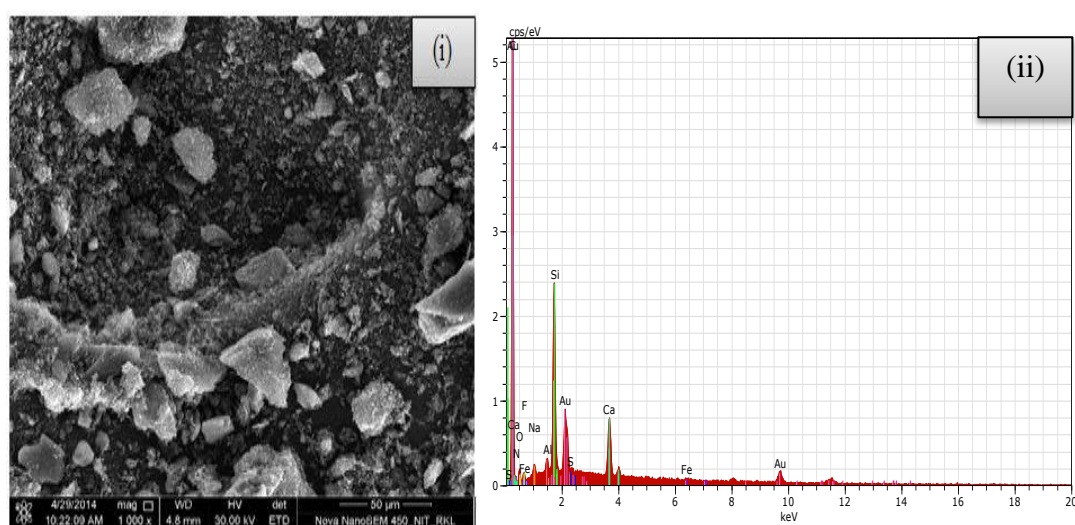
Figure 4.26: FESEM-EDX images of Final Treated SPL

Table 4.12: Ultimate and elemental (SEM-EDX) analysis of SPL samples

Component	Weight percentage (%)										
	Na	F	Al	C	Ca	N	S	H	Fe	Si	O
Raw SPL	14.23	14.66	4.78	42.19	1.32	0.59	1.24	0.62	0.001	0.0007	20.372
Water Washed SPL	8.26	10.25	3.97	48.08	1.32	0.40	1.72	0.21	0.001	0.0007	25.787
Alkali treated SPL	2.12	6.35	1.10	72.01	1.54	0.55	2.46	0.15	0.011	0.009	13.696
Final treated SPL	1.51	3.52	0.10	81.27	2.53	0.64	4.42	0.21	0.09	0.01	5.80

4.3.3.3 XRD analysis

The XRD analysis of treated SPL along with that of raw SPL was done. The peaks of graphitic carbon (C), cryolite (Na_3AlF_6), villaumite (NaF), fluorite (CaF_2), sodium iron cyanide ($Na_4Fe(CN)_6$), gibbsite ($Al(OH)_3$) phases were found. The phases of cryolite (Na_3AlF_6), villaumite (NaF), sodium iron cyanide ($Na_4Fe(CN)_6$) and gibbsite ($Al(OH)_3$were eliminated due to the removal of these leachable compounds by treatment with alkali and acid treatment.
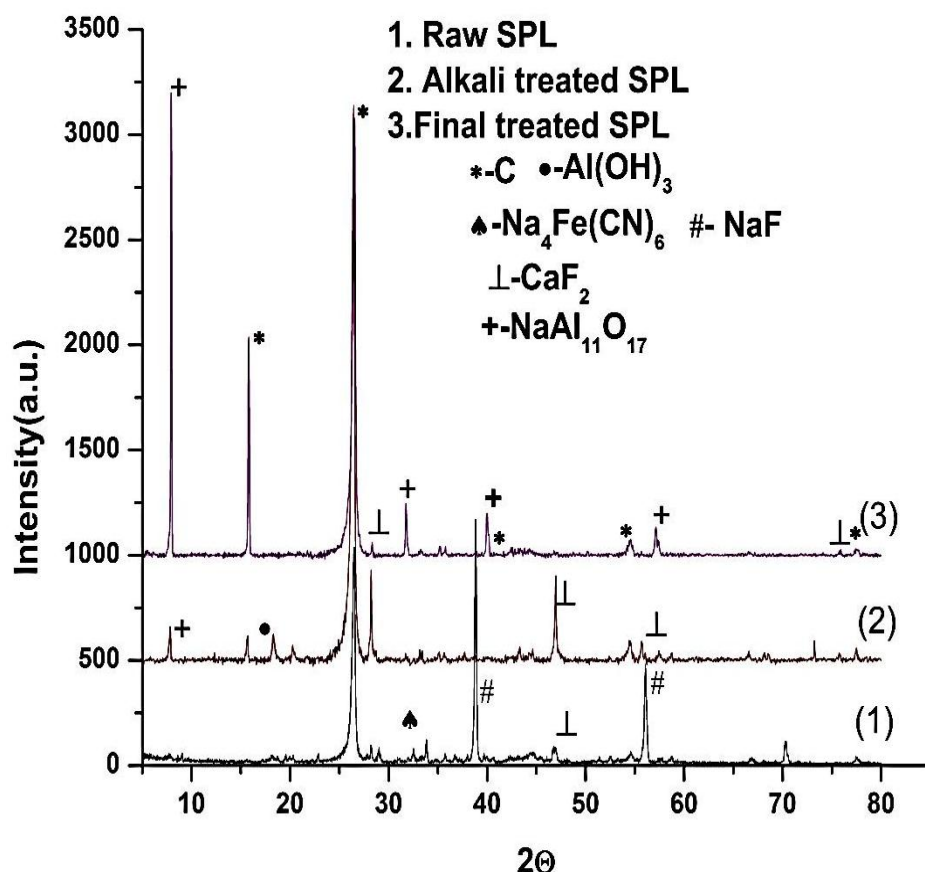
Figure 4.27: XRD analysis of raw SPL, alkali treated SPL and final treated SPL

4.3.4. Cryolite precipitation

In order to check the feasibility of the cryolite precipitation the leachates were analyzed at two different pH values. At pH 4.5 and 9.5 the aluminum ions exist in the form of $Al(OH)_4^-$ or $[Al_8(OH)_{26}]^{2-}$leading to precipitation of cryolite[42]. It was found that both the conditions of pH suitable for the precipitation of cryolite. From the XRD analysis (Figure 4.29), it was found that at higher pH the co-precipitation of ammonium salt occurred. The mechanism for the precipitation of cryolite was described in the Eq. (4.15).
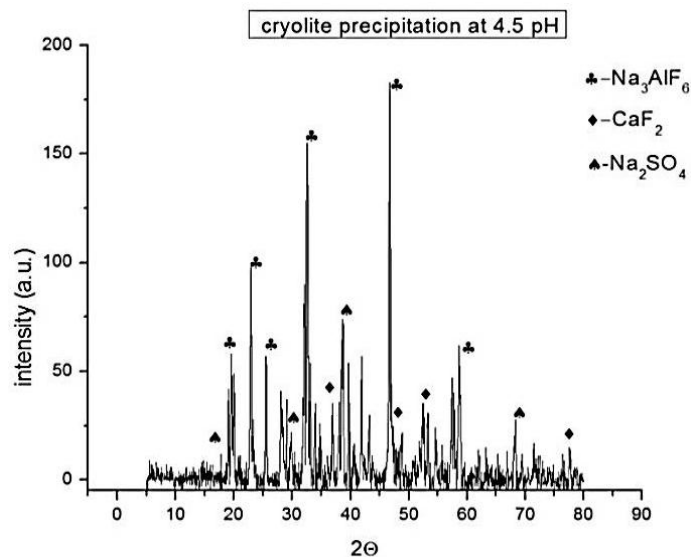
Figure 4.28: XRD analysis of fluoride precipitation at pH value of 4.5
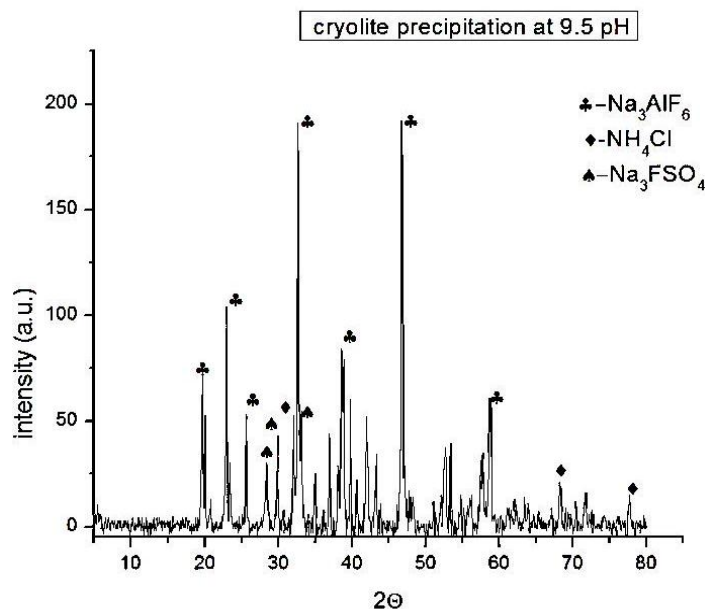
Figure 4.29: XRD analysis of fluoride precipitation at pH value of 9.5

4.3.5. Outcome of the study

- Alkali concentration and the Temperature were found to be the most significant and least significant factor among the four parameters studied. Alkali concentration contributed 45.52% whereas temperature contributed only 8.72%.

- In the classical approach of optimizing the maximum leaching percentage was found to be 49.18% for sulfuric acid whereas in Taguchi optimization method the maximum leaching percentage was 52.39%.

- From the S/N ratio analysis, the optimum condition was achieved at 3.5 M NaOH, 5.0 M H_2SO_4, 3.5 L/S ratio and temperature 25 °C. From both Taguchi and classical

approach it was concluded that 1.5 M NaOH, 2.5 M H_2SO_4, 3.5 L/S ratio and temperature 25 ±1°C were the best combination for the optimum leaching percentage and considered as "final treated Spent Pot Lining (SPL)" and 1.5M NaOH concentration, 3.5 L/S ratio and 25 ±1°C for "alkali treated SPL".

- The carbon percentage of SPL was found to increase from 42.19% to 81.27% as confirmed from the ultimate analysis. From the proximate analysis, the fixed carbon was found to be increased from 38.96% to 78.68% from the raw to final treated SPL, respectively.

- From the XRD analysis, it was concluded that in case of sulfuric acid treatment, both the conditions of pH were satisfied for the cryolite precipitation.

4.4. Fuel value analysis of SPL samples

Gross calorific values (GCV) were determined for all optimized samples obtained from above studies. The GCV was increased from 2865.04 kcal/kg to 6689.69 kcal/kg for raw SPL and final treated SPL obtained from caustic followed by sulfuric acid treatment, respectively.

Table 4.13: Fuel value analysis of SPL samples

SAMPLE NAME	C	H	N	S	MC	RC	VM	FC	ACTUAL GCV(Kcal/Kg)
Raw SPL	42.19	0.616	0.59	1.24	3.46	51.89	6.18	38.46	2865.04
Water washed SPL	48.08	0.21	0.4	1.72	2.4	51.32	5.91	40.37	3924.90
5 M H_2SO_4 on water washed SPL	68.81	0.15	0.54	3.5	2.2	28.14	5.51	64.15	5842.86
5M $HClO_4$ on water washed SPL	64.17	0.26	0.57	2.58	2.01	37.29	0.51	60.19	5540.48
10 M H_2SO_4 on water washed SPL	70.83	0.17	0.6	5.57	2.21	24.39	6.35	67.05	5906.11
10M $HClO_4$ on water washed SPL	71.76	0.21	0.53	3.42	1.98	27.48	0.7	69.84	5837.10
1.5M NaOH on water washed SPL	72.01	0.154	0.55	2.46	2.2	25.25	4.78	67.77	5057.56
1.5M NaOH followed by 2.5 M $HClO_4$ on water washed SPL	87.03	0.21	0.62	2.69	2.1	14.84	0.2	82.86	6533.65
1.5M NaOH followed by 2.5M H_2SO_4 on water washed SPL	81.27	0.21	0.64	4.42	2.13	16	3.19	78.68	6689.69

4.4.1. Outcome of the analysis

The calorific values of enriched SPL samples were found to increase equivalent to "A grade" coal from the raw SPL which was equivalent to "F grade" coal in context to Indian standards[53].

Chapter 5

CONCLUSION AND FUTURE WORK

- Initial treatment of SPL with acid alone was not a better approach for the leaching due to higher requirement of acid. Whereas as compared to initial caustic leaching followed by acid leaching leads to more beneficial approach as the requirement of acid was found to be less.

- Cooling of hot SPL in the presence of air leads to the formation of hazardous compound such as NaCN due to the N_2 content of air. So it required to cool the hot SPL in N_2 free environment.

- It was concluded that in terms of quality of graphite obtained, $HClO_4$ treatment was better compared to H_2SO_4 treatment as confirmed from XRD analysis.

- In terms of volatile matter, which emits hazardous gases like SO_2, H_2S during combustion and $HClO_4$ was found to be the better treatment approach compared to H_2SO_4 treatment, which leads to environment related issues.

- Treated SPL can be a good alternative for energy source due to high calorific value.

5.1. Future Recommendations

- pH and temperature studies for the cryolite precipitation and the mechanism for the precipitation should be investigated in detail.

- Exploration of treatment of SPL with other types of acids such as HCl, HNO_3 and H_3PO_4 can be done.

- Use of final treated SPL as preparation of ramming paste in cathode lining or preparation of green anode in aluminum industry can be investigated.

- Use of water washed filtrate as an additive to maintain the cryolite ratio can be studied.

- A model equation can be proposed for the prediction of calorific value using the multiple linear regression of ultimate and proximate analysis.

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APPENDIX I

XRD analysis of water washed filtrate SPL sample
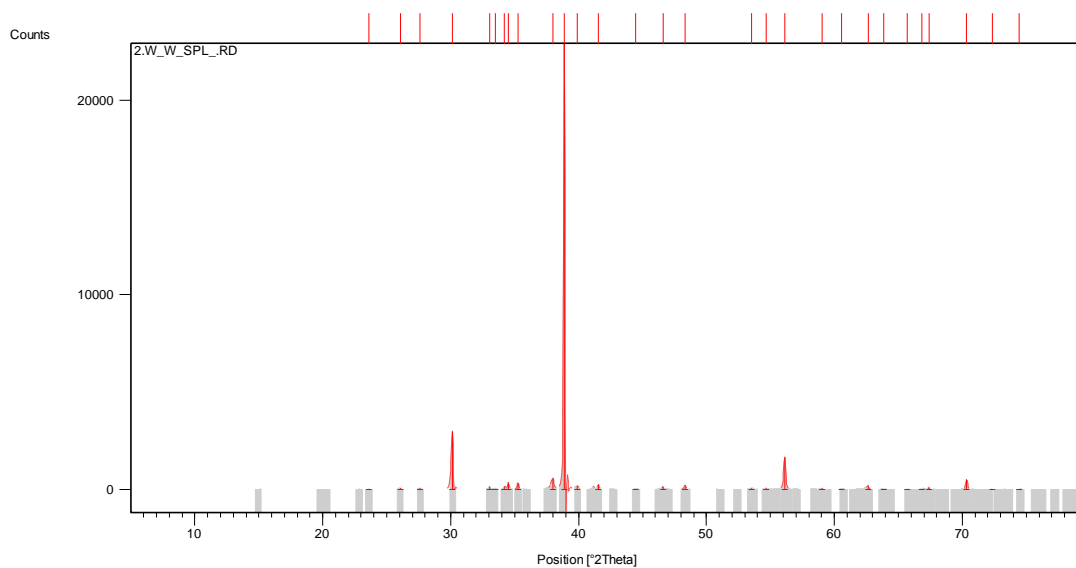
Peak List

Position [°2 Θ]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Relative Intensity [%]	Tip width [°2 Θ]	Matched by
23.5782	29.94	0.1800	3.77024	0.13	0.1500	72-0628
26.0523	73.33	0.2400	3.41754	0.32	0.2000	72-0628
27.6029	87.62	0.2400	3.22898	0.38	0.2000	72-0628
30.1260	3005.06	0.1800	2.96405	13.02	0.1500	72-0628
33.0371	150.01	0.2400	2.70921	0.65	0.2000	72-0628
33.5076	52.14	0.2400	2.67224	0.23	0.2000	04-0793
34.2006	154.43	0.1800	2.61966	0.67	0.1500	72-0628
34.5009	355.57	0.1800	2.59755	1.54	0.1500	72-0628
35.2570	342.38	0.1800	2.54355	1.48	0.1500	72-0628
37.9657	572.00	0.3000	2.36807	2.48	0.2500	72-0628
38.8798	23089.16	0.1200	2.31448	100.00	0.1000	04-0793
39.9230	203.19	0.2400	2.25637	0.88	0.2000	72-0628
41.5320	222.57	0.2400	2.17260	0.96	0.2000	72-0628
44.4816	51.59	0.1800	2.03514	0.22	0.1500	72-0628
46.6006	144.01	0.2400	1.94741	0.62	0.2000	72-0628
48.3051	230.48	0.1800	1.88260	1.00	0.1500	72-0628
53.5089	59.72	0.3600	1.71114	0.26	0.3000	72-0628
54.6406	70.12	0.2400	1.67834	0.30	0.2000	72-0628
56.1131	1668.69	0.2400	1.63774	7.23	0.2000	72-0628
59.0276	76.27	0.3600	1.56364	0.33	0.3000	72-0628
60.5710	19.94	0.7200	1.52743	0.09	0.6000	72-0628
62.6485	171.80	0.4200	1.48168	0.74	0.3500	72-0628
63.8434	26.69	0.4800	1.45680	0.12	0.4000	72-0628
65.7237	17.58	0.1800	1.41960	0.08	0.1500	72-0628

66.8670	30.82	0.3600	1.39808	0.13	0.3000	72-0628
67.3917	107.66	0.1800	1.38847	0.47	0.1500	72-0628
70.3381	527.43	0.1800	1.33735	2.28	0.1500	72-0628
72.3595	17.26	0.2400	1.30488	0.07	0.2000	72-0628
74.4650	15.52	0.3600	1.27311	0.07	0.3000	72-0628

Identified Patterns List

Ref. Code	Score	Compound Name	Scale Factor	Chemical Formula
72-0628	49	Sodium Carbonate	0.044	Na_2CO_3
04-0793	37	Villiaumite, syn	0.142	Na F

XRD analysis of raw SPL sample:
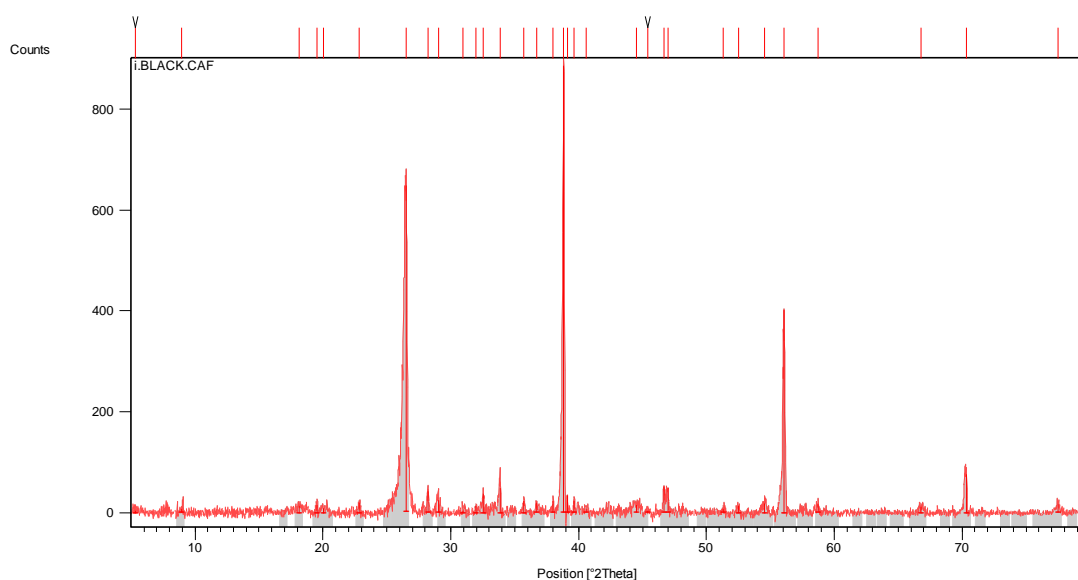
Peak List

Pos. [°2Θ]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2Θ]	Matched by
5.3322	4.63	0.7680	16.56007	0.52	0.6400	
8.9501	6.96	0.2880	9.87242	0.79	0.2400	01-1077
18.1320	13.86	0.7680	4.88856	1.57	0.6400	01-1077
19.5233	15.24	0.1440	4.54320	1.72	0.1200	12-0257
20.0254	9.00	0.7680	4.43040	1.02	0.6400	12-0257
22.8310	20.62	0.1440	3.89192	2.33	0.1200	12-0257
26.4932	646.22	0.2400	3.36166	73.06	0.2000	08-0415
28.2202	42.55	0.1440	3.15973	4.81	0.1200	04-0864

29.0374	24.99	0.3840	3.07265	2.83	0.3200	01-1077
30.9584	4.65	0.5760	2.88622	0.53	0.4800	04-0876
31.9462	14.94	0.1440	2.79919	1.69	0.1200	12-0257
32.5490	38.13	0.1200	2.74871	4.31	0.1000	12-0257
33.8761	49.02	0.1200	2.64401	5.54	0.1000	01-1026
35.7331	24.29	0.1920	2.51075	2.75	0.1600	11-0252
36.7216	19.55	0.2880	2.44540	2.21	0.2400	12-0257
37.9957	22.65	0.0960	2.36627	2.56	0.0800	12-0257
38.8462	884.45	0.2160	2.31640	100.00	0.1800	04-0793
39.1070	34.72	0.0960	2.30155	3.93	0.0800	04-0793
39.6638	23.38	0.1440	2.27051	2.64	0.1200	12-0257
40.5812	8.08	0.2880	2.22128	0.91	0.2400	12-0257
44.5527	14.62	0.5760	2.03205	1.65	0.4800	08-0415
45.4076	3.67	0.2880	1.99576	0.42	0.2400	01-1026
46.6555	51.89	0.1440	1.94525	5.87	0.1200	12-0257
46.9663	49.24	0.1440	1.93310	5.57	0.1200	04-0864
51.3058	6.96	0.2880	1.77932	0.79	0.2400	12-0257
52.5190	14.91	0.1920	1.74104	1.69	0.1600	12-0257
54.5507	19.57	0.3840	1.68090	2.21	0.3200	08-0415
56.0723	402.21	0.1680	1.63884	45.48	0.1400	04-0793
58.7029	17.10	0.1920	1.57151	1.93	0.1600	12-0257
66.8025	12.23	0.5760	1.39928	1.38	0.4800	04-0793
70.3168	76.83	0.2400	1.33770	8.69	0.2000	04-0793
77.4974	16.56	0.2880	1.23070	1.87	0.2400	08-0415

Identified Pattern List

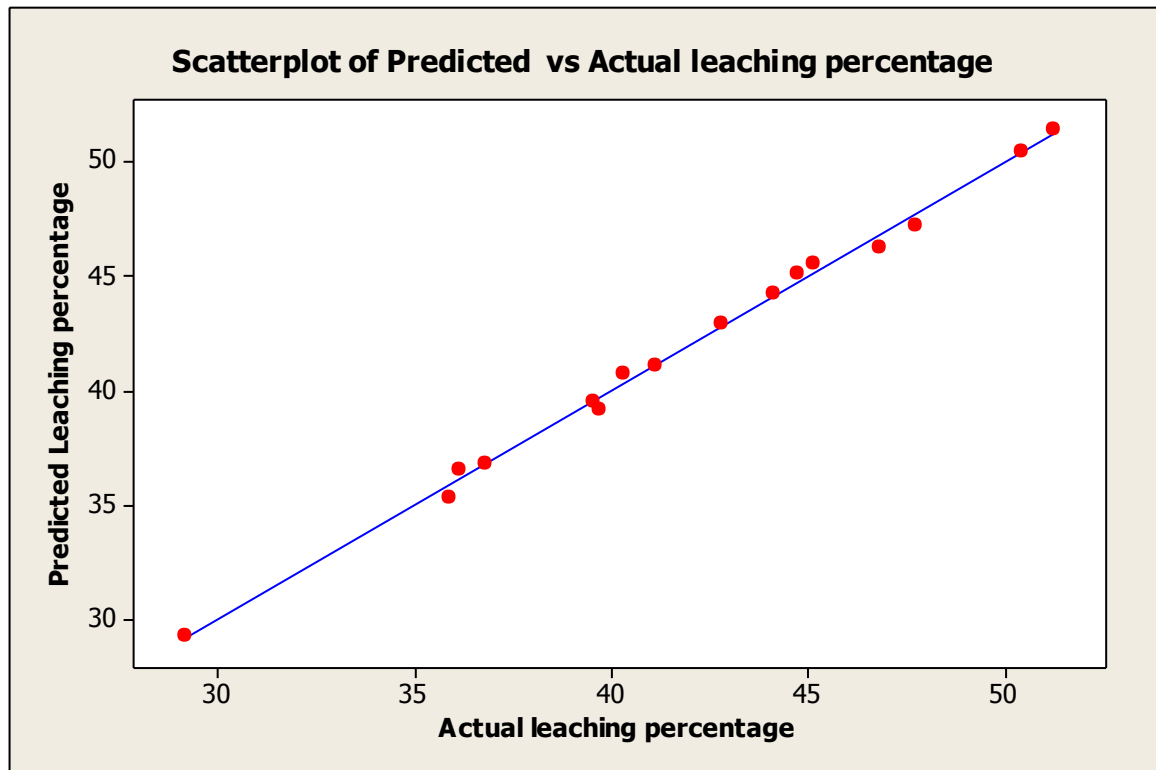| Ref. Code	Score	Compound Name	Scale Factor	Chemical Formula
04-0793	55	Villiaumite, syn	0.794	Na F
08-0415	39	Graphite	0.702	C
04-0864	21	Fluorite, syn	0.040	Ca F2
12-0257	14	Cryolite	0.142	$Na_3Al F_6$
04-0876	Matched Strong	Aluminum Oxide	0.024	Al_2O_3
11-0252	12	high quartz	0.254	SiO_2
01-1077	12	Troma	0.052	$Na_3H(CO_3)_2 . 2 H_2O$
01-1026	7	Sodium Iron Cyanide	0.040	$Na_4Fe(CN)_6$

APPENDIX II

Figure A1: Scatter Plot for predicted and actual leaching percentage for HClO$_4$ treatment.
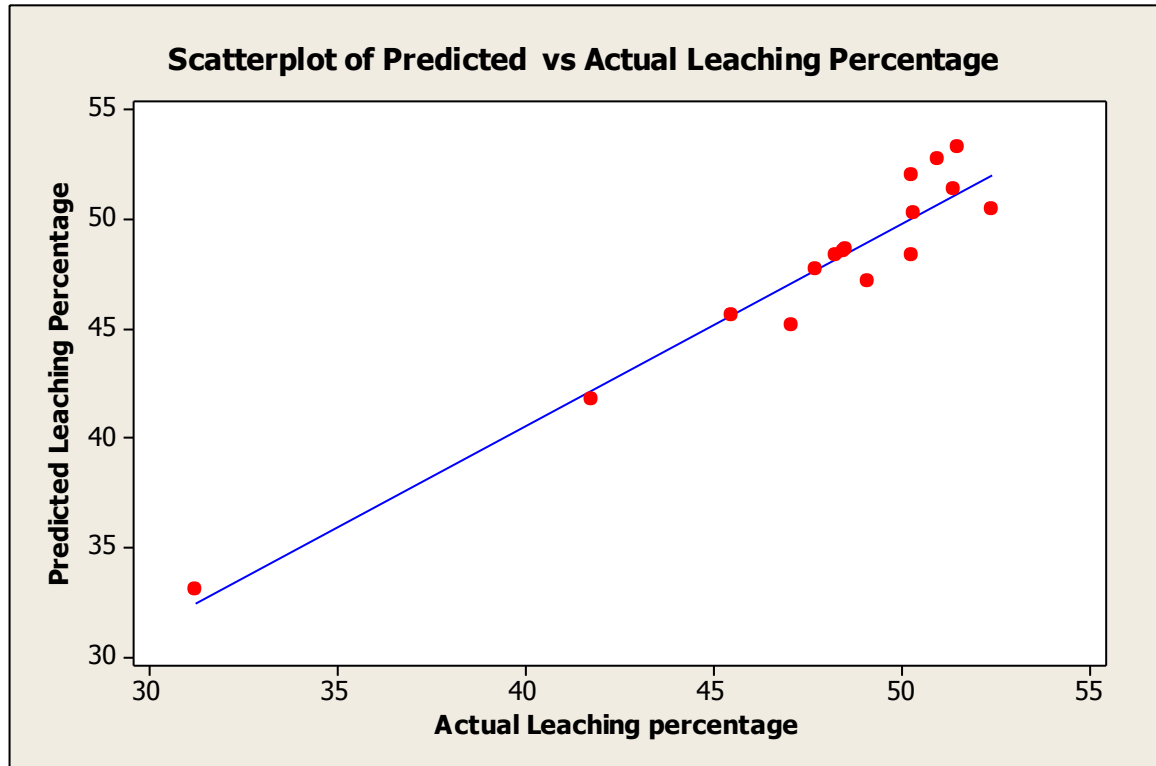

Figure A2: Scatter Plot for predicted and actual leaching percentage for H$_2$SO$_4$ treatment.

Bio Data

Sidharth Sankar Parhi

Date of Birth: 25/05/1990

Email: sidharth.nitj2007@gmail.com

Permanent Address: S/O-Kamini kanta Parhi,
House no.-243/23, Church Lane, Bhaskarganj, Balasore,
Pincode-756001,
Odisha, India.

Education:

2014   M.Tech. Research (Chemical Engineering) Dissertation Submitted

        National Institute of Technology, Rourkela, Odisha, India.

2011   B.Tech. (Chemical Engineering)

        National Institute of Technology, Jalandhar, Punjab, India.

Research Experience:

1. **"Gainful Utilization of Spent Pot Lining- A Hazardous waste from Aluminium industry" [M.Tech.(R)]**
2. **"Effect of Pretreatment on Algal Biomass for Removal of Hexavalent Chromium" [B. Tech.]**

List of Papers:

1. Comparative chemical leaching treatment of Spent Pot Lining - A hazardous waste from aluminium industry by multiple level factorial design (Communicated)
2. A novel approach in chemical leaching treatment of Spent Pot Lining by Taguchi Method using caustic leaching followed by Perchloric acid leaching (Communicated)
3. An approach in chemical leaching treatment of SPL by Taguchi method using caustic leaching followed by sulfuric acid leaching (Under preparation)