# The Physical and Chemical Reclamation and Recycling of Elements from Black Aluminium Furnace Residues

A Thesis submitted for degree of Doctor of Philosophy

by

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June 2003

*For*

*Dr Gilbert Vandenput,*
*thank you.*

*And*
*my father.*

# ACKNOWLEDGEMENTS

I would like to sincerely thank my supervisor, Professor Susan M. Grimes for her guidance, support and encouragement throughout the research and preparation of this thesis. I also extend my thanks to Professor John Donaldson for his supervision and help over the whole period of my research work.

I am extremely grateful to Dr. Abdul Jabbar Chaudhary for his assistance, advice, and patience throughout the research work.

Many thanks to my friends and colleagues of the environmental research group for providing a friendly and stimulating atmosphere. Also, thanks to Maggie, Herman and Douglas for their assistance during my research period.

I would like to acknowledge financial support throughout my research work from the Centre for Environmental Research through a DTI/EPSRC/WMR3 programme in collaboration with Brunel and Birmingham Universities and industry.

My special thanks to my husband Humphrey for his knowledge, patience and support.

Most importantly, I would like to express my thanks to my parents who showed a lot of concern about my studies and extended their best wishes throughout the period of this research work. Finally, thanks to my sister Rukhsana for keeping me cheerful during the period of this work.

# ABSTRACT

Dross is the inevitable waste product generated by the world-wide primary and secondary aluminium industries. Around 3.5 million tonnes of white dross and 0.85 million tonnes of black dross are produced per year. Drosses are classified depending on metal content. White dross contains 40% and black dross contains 10% of aluminium. About half of the white dross is currently landfilled along with almost all of the black dross, and the annual cost to the UK industry of landfilling this waste is about £90 million per year. There is no commercially viable method of recovering the aluminium, which is potentially recyclable from these drosses, and no current conventional process has the custom-built capability to avoid their disposal to landfill. The practice of landfilling aluminium dross has raised problems for both industry and environment, because of potential leaching of heavy metals into groundwater from the landfill.

The black dross has been physically and chemically characterised. The results show that the dross contains mostly metallic aluminium, aluminium nitride, alumina, sodium chloride, potassium chloride and silica with almost 50% of the dross being a mixture of sodium chloride and potassium chloride. A counter current leaching process has been developed to recycle the salts back to the secondary furnace.

The environmental impact of black dross has been investigated using simulated landfill conditions. Leachability studies were carried out using water, and other leach media to model the following conditions: humic acid-containing systems, acid rain (pH 2.5), and acetic acid solutions (pH 5). Up to 60% of the dross was leached out in all media with the production of the saline solution providing the major impact. Only small amounts of aluminium were leached out under all these condition. No leachability behaviour was detected once the black dross was washed. So landfilling washed black dross can minimise both environmental and economical problems.

Black dross residue, after washing with water, is enriched with alumina. Added value chemicals (of >95% purity) including aluminium hydroxide, alumina, aluminium chloride, aluminium nitrate, aluminium sulphate and aluminium carboxylates have been prepared using the washed black dross. Preliminary calculations have shown that the technology developed to recycle black dross to added-value chemicals is economically viable.

A methodology has been developed which enables low grade alumnium waste, black dross, to be treated, commercially viable chemicals to be prepared, reagent use to be minimised through recycle and the diversion of millions of tonnes of furnace residue from landfill.

# The Physical and Chemical Reclamation and Recycling of Elements from Black Aluminium Furnace Residues

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# CHAPTER ONE

# INTRODUCTION

## 1.1 BACKGROUND

"Dross" is the inevitable waste product generated by the world-wide primary and secondary aluminium industries, which generate around 3,500,000 tonnes of white dross and 850,000 tonnes of black dross per year[1]. Drosses are classified by means of their metal content. Dross with a high metal content is called white, or wet dross; it is rich in free metal (40 wt%). Dross with a low metal content (10 wt%), which typically occurs when scrap is remelted with salts in an open furnace, is called black, or dry dross. There is no commercially viable method of recovering the aluminium from these drosses, and no current conventional process has the custom-built capability to eliminate landfilling. Less than half of the white dross is recycled and over half of the white dross dust residues are landfilled by the dross reclamation industry. Almost all of the black dross is disposed to landfill, causing industries loss of valuable aluminium metal and costing an enormous landfill tax. The practice of landfilling of aluminium dross has raised problems for both industries and environment.

### 1.1.1 Environmental issues

There are potentially very serious environmental and health risks associated with disposal of material to landfill. Waste dumped in the past has leached into the groundwater and eventually into drinking water reserves, posing a threat to future generations. There is a link between the ingestion of certain heavy metals (held most prominently within black dross) and serious deleterious effects to health.

The metal industries are well known for causing soil contamination from their operations. In parts of North Wales the toxic effects of spoil from Roman lead and silver mines are still evident[2]. More recently, high levels of cadmium were found in soil in the Shipham area of Somerset, caused by the extraction of zinc[2]. This has affected the home-grown vegetables in that area. Another serious problem with landfilling the waste is the build up of methane gas to potentially explosive levels.

Once a pollutant reaches the soil a number of events may occur. The soil may break down or be neutralised, pollutants may be washed out by rain (causing water pollution) or evaporate (causing air pollution), or may remain in the soil, building up to high concentrations with successive additions.

### 1.1.2 Legislation

The landfill of dross is of great international concern. There is ever-increasing pressure from the EU to update the Environmental Protection Act 1991 to significantly increase landfill taxes or ban the landfill of black and white dross altogether. In October 1996 landfill tax was introduced in UK by the Finance Act 1996 and the Landfill Tax Regulation 1996[2]. The purpose of the tax, as stated in the March 1998 Review Report by the Department of Customs and Excise, is firstly 'to ensure that landfill waste disposal is properly priced so as to reflect its environmental cost' and secondly 'to promote a more sustainable approach to waste management in which less waste is produced and more waste is either reused or has value recovered from it[3]. The tax is based on the mass of the waste to be disposed. Active waste is taxed at £11 per tonne and the lower risk waste is £2 per tonne[2].

### 1.1.3 The size of Waste Problem for the Aluminium Industry

An appreciation of the size waste problem in the industry is indicated below[1]:

Cost of producing 1 tonne of aluminium from Primary Ore is 16.1 Mwh/tonne
Cost of producing 1 tonne of aluminium from Secondary Ore is 0.805 Mwh/tonne
Typical Bauxite Ore is 60% $Al_2O_3$ and therefore contains 30% aluminium metal

Waste generated:
Black Dross: 850,000 tpa @ 10% aluminium metal typically
White Dross: 3,500,000 tpa (of which around half is recycled)
therefore 1,750,000 tpa @ 40% aluminium metal typically

Therefore, total aluminium metal lost per annum:-

| | | |
|---|---|---|
| Black Dross | 10% of 850,000 | = 85,000 tonnes aluminium |
| White Dross | 40% of 1.75 million | = 700,000 tonnes aluminium |
| | Total aluminium lost | = 785,000 tonnes |

Energy lost due to the loss of 785,000 tonnes of aluminium metal by primary route = 12,638,500 MWh

Hence the number of tonnes of Bauxite ore (at 30% aluminium) which would need to be mined to replace this loss would be: 785,000 x 100/30 = **2,616,666 tonnes of bauxite**

The cost of disposing these resources to landfill is around £35.00 per tonne (subject to very high variations depending on country), which equates to:

| Waste generated (tonnes): | | |
|---|---|---|
| Black Dross: | 850,000 | |
| White Dross: 3,500,000(of which around half is recycled) | 1,750,000 | |
| | Total 2,600,000 | @£35.00 |

This equates to **£91 million in landfill cost per year**.

## 1.2. ALUMINIUM

### 1.2.1 The Uses of Aluminium[5,6]

Aluminium is the third most abundant element in the earth's crust after oxygen and silicon. It accounts for about 8% (by weight) of the earth's crust[4]. It is however, a comparatively new industrial metal that has been produced in commercial quantities for over 100 years. Measured either in quantity or value, aluminium's use exceeds that of any other metal except iron, and it is important in virtually all segments of the world economy[5]. Table-1.1 shows the major metal consumption in United Kingdom in 2000.

**Table-1.1. United Kingdom consumption of major metals in 2000[5]**

| Metals | Million tonnes |
|---|---|
| Steel | 37 |
| Aluminium | 0.75 |
| Copper | 0.35 |
| Lead | 0.33 |
| Zinc | 0.24 |

Aluminium is a versatile metal with a range of valuable properties. It is moderately soft and weak when pure, but it is much stronger when alloyed with other metals[6]. Its main advantage is its lightness (low density 2.73g $cm^{-3}$). Some of its alloys are used for special purposes: duralumin, which contains about 4% Cu, and several aluminium bronzes (alloys of Cu and Al with other metals such as Ni, Sn and Zn). There are many uses for aluminium and its alloys:

1. Because of its lightness and also toughness, aluminium is very useful to the aircraft, space vehicle, ship and car industries.

2. The outer layer of aluminium forms a natural coating of aluminium oxide when exposed to air. This protects aluminium from corrosion (rusting) so it is used frequently in out door applications, such as the framework of windows and doors.

3. It is the most commonly used metal in the electronics industry because of its excellent electrical and thermal conductivity (on a weight for weight basis it conducts twice as well as copper).

4. It is very familiar material in the home with products such as thin flexible aluminium foil, containers such as cans for drinks, tubes for toothpaste, cooking utensils etc.

6. Finely divided aluminium powder is called "aluminium bronze", and is used in preparing aluminium paint.

7. Its compounds: $Al(OH)_3$ is widely used as an anti-acid treatment for indigestion and $Al_2(SO_4)_3$ is used to treat drinking water.

### 1.2.2 Extraction of Aluminium[6]

Aluminium is not found as a free element in nature because of its extreme reactivity. It is obtained from the ore called bauxite which may be AlO.OH ($Al_2O_3.H_2O$) or $Al(OH)_3$ ($Al_2O_3.3H_2O$). The largest sources (based on year 2000 statistic) are Australia 39%, Brazil 10%, Guinea 11%, Jamaica 8%, China 6% and the Russia 3%. Bauxite contains aluminium oxides (>45%), iron oxides (<12%), water, silica (<8%) and other impurities, such as clay and titanium.

The first step in the extraction process is to purify the ore. To separate out the aluminium, the ore is washed, ground and placed in a vessel (at 200-240$^0$C, 30atm) of sodium hydroxide (caustic soda) solution. The aluminium oxide in the ore combines with sodium hydroxide to form soluble sodium aluminate, while the clay and other impurities remain undissolved in a sludge called "red mud".

$$AlO(OH)_{(s)} + NaOH_{(aq)} + H_2O_{(l)} \longrightarrow Na[Al(OH)_4]_{(aq)}$$

The insoluble waste materials are removed by filtering. The filtrate clear sodium aluminate solution is cooled with stirring and then seeded with large quantities of aluminium hydroxide, whereupon a large part of the dissolved hydroxide precipitates out as aluminium hydroxide.

$$Na[Al(OH)_4]_{(aq)} + H_2O \longrightarrow Al(OH)_{3(s)} + NaOH_{(aq)} + H_2O_{(l)}$$

The precipitated $Al(OH)_3$ is removed by filtration and calcined (1100-1300$^0$C) in large rotary kilns which converts it to purified $Al_2O_3$. The caustic soda is returned to the start of the process and used again. This initial conversion of bauxite to aluminium oxide is called the Bayer Process. The aluminium oxide can be utilised in technical ceramics (laboratory ware, electronic applications etc.) or can be converted into other chemicals, but most of it (90%) is converted to aluminium. Martin Hall developed a process of reducing the aluminium oxide to aluminium in 1886 and the process is currently known as the Hall-Héroult Process. To convert the filtered aluminium oxide it is dissolved in molten cryolite $Na_3(AlF_6)$. Some cryolite is mined in Greenland, but this is insufficient to meet the world demand for it, and most is therefore made synthetically:

$$Al(OH)_3 + 3NaOH + 6HF \longrightarrow Na_3\,[AlF_6]\;6H_2O$$

Cryolite improves the electrical conductivity of the cell as $Al_2O_3$ is a poor conductor. In addition, the cryolite serves as an added impurity and lowers the melting point of the mixture from 1500$^0$C to about 950$^0$C.

The dissolved aluminium oxide with cryolite is electrolysed in a graphite lined steel tank, which serves as a cathode. The anodes are also made of graphite. The aluminium ions are reduced to the metal at the cathode while oxygen, carbon monoxide and carbon dioxide are liberated at the anode.

Anode $2O^{2-}_{(l)} \longrightarrow O_{2(g)} + 4e^-$

Cathode $Al^{3+}_{(l)} + 3e^- \longrightarrow Al_{(l)}$

The cells run continuously. Since this bath is at a high temperature (about $950^0$C), the molten aluminium (m.p. $660^0$C) formed at the cathode is drained from the bottom of the cell (because it is heavier than salt) and cast into ingots for industrial use. The container used is called a Hall cell (Figure-1.1). After this process the aluminium is only 99% pure, because some impurities of copper, silicon and aluminium oxide still exist. Energy consumption is very high, and the process is only economic where there is a source of cheap electricity.

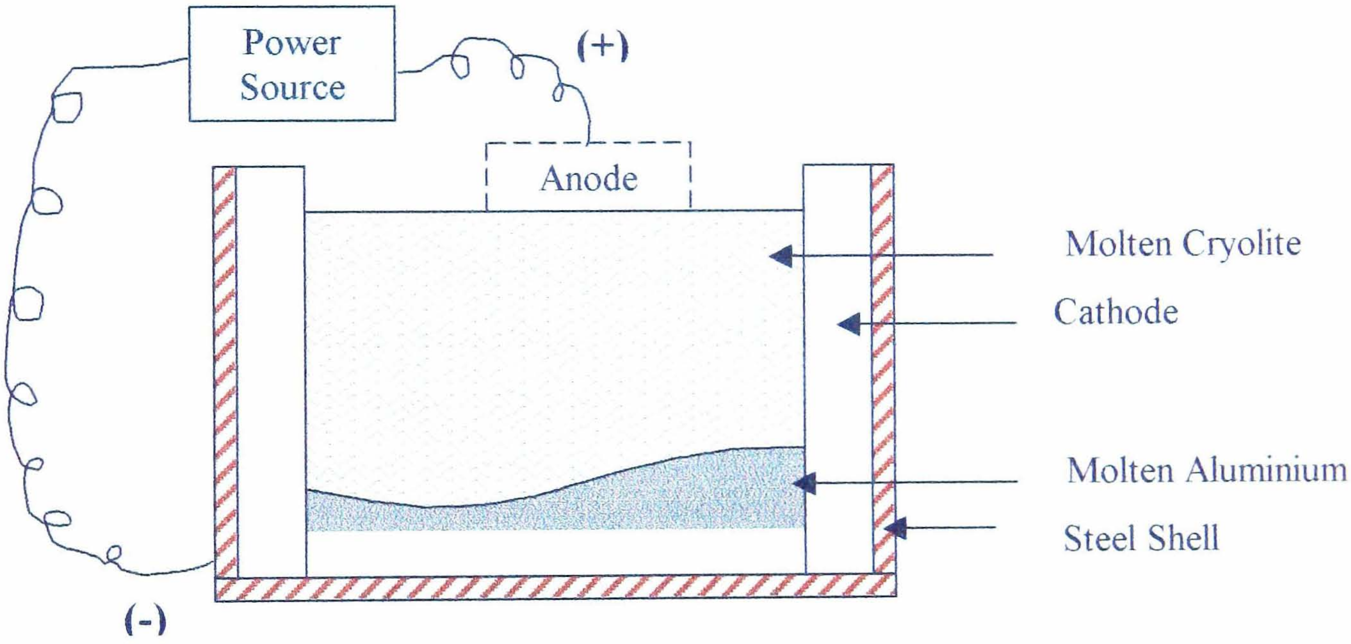

**Figure-1.1. Reduction of aluminium oxide to aluminium using Hall cell method.**

### 1.2.3 Aluminium Consumption[7]

More than 20 million tonnes of primary aluminium are presently used in the Western World per year. Western Europe (the 15 EU countries plus Norway, Switzerland and Turkey) accounts for approximately one third of primary aluminium use. Using about 5.8 million tonnes and producing 3.8 million tonnes, Western Europe presently imports around 2 million tonnes of primary aluminium per year. In addition approximately 2 million tonnes of aluminium are recycled every year.

Figure-1.2 illustrates the six main applications of aluminium in the western European countries in year 2000. The transport, building and packaging sectors are the most important markets for aluminium products. The remaining part goes into applications such as electrical and mechanical engineering, office equipment, domestic appliances, lighting, chemistry and pharmaceuticals.

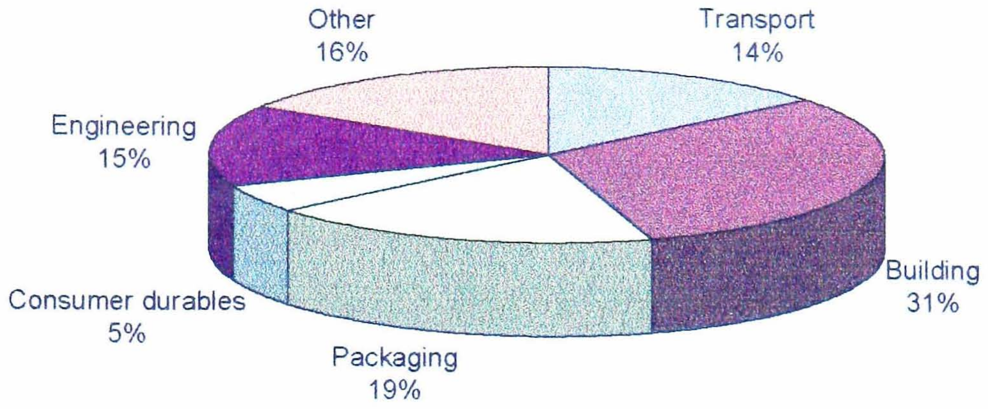

**Figure-1.2. The major western European markets for aluminium products in 2000[7].**

### 1.2.4 Aluminium Recycling

In 2000, the UK produced 1.17 million tonnes of aluminium ingot. Around 50% of this resulted from in-house fabrication recycling, 29% from primary aluminium smelting and the remaining 21% from old scrap[8]. Figure-1.3 shows the production of primary and secondary aluminium in UK from 1995-2000.

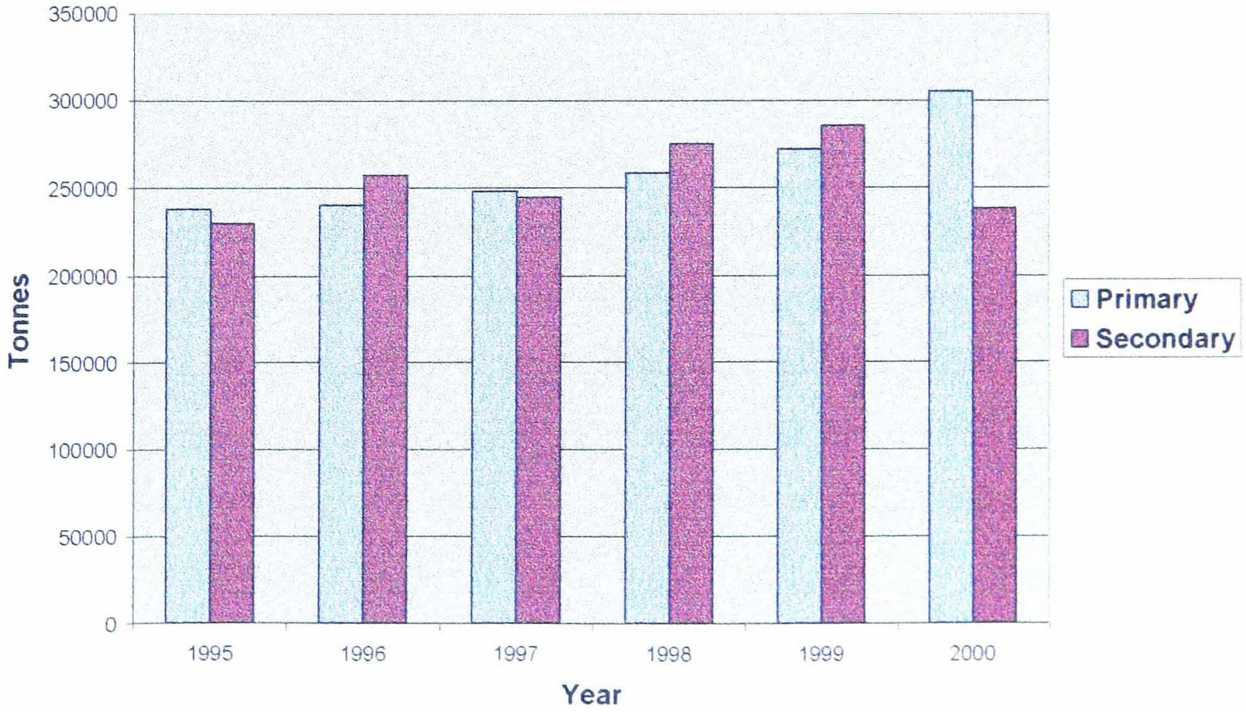

**Figure-1.3. UK primary and secondary aluminium production[5]**

Soon after the commercialisation of the Hall-Héroult process in the USA in 1886, recycling efforts started, driven by the high intrinsic value of aluminium. In the wake of the fast growing primary industry, a flourishing secondary industry developed, which initially handled all scrap types generated by the aluminium producers and manufacturers[9]. When in the mid-1960s primary metal production capacity could not keep up with the demand, the primary producers started to recycle their own production scrap, but later also purchased consumer (old) scrap. This set the stage for the development of the huge used beverage container (UBC) recycling industry, dominated by the primary producers. The infrastructure of the primary ingot plant changed dramatically and sophisticated scrap preparation and remelt technology was developed, which in turn stimulated a marketing strategy, coupling UBC return to price advantages for new can sheet sales[10]. The UK has the largest aluminium can recycling plant in Europe, operated by Alcan at Warrington[8]. Recycling became an integral part of the material loop, in which all participants had a stake. This holistic approach to managing materials flow of a specific product is neither limited to beverage cans nor to primary producers, but could, with proper adaptation, be applied to such diverse aluminium containing products as housing and automobiles.

Recycling of all old aluminium scrap is technically feasible, as aluminium can be repeatedly recycled into new products without loss of quality or properties. Primary smelting uses around 14kWh to produce 1kg of aluminium, whereas the secondary smelting consumes only around 5% of this energy. Also, the intrinsic high value of used aluminium products allows collection to be recovered by the scrap value, and covers all costs for processing, compacting and shipping to a remelt[10]. In every field where aluminium has been produced on an industrial scale, recycling has followed, provided that economic quantities of used metal have been available and subject to technology development capable of effecting economical recycling practices. Aluminium recycling is economically viable and not undertaken simply to counter environmental pressures. Used aluminium products represent an important metal source for the aluminium industry and demand will always be strong with prices remaining attractive. The value of aluminium scrap is around 10 times more than that of scrap steel.

Recycling is clearly of strategic importance to aluminium's major end use markets, and the aluminium industry aims to recycle as much of the available metal as possible into the same or equivalent products.

Return to the same product is known as closed loop recycling, and requires that a number of important conditions are satisfied[10]:

- collection logistics are satisfactory,
- composition can be met using available mixtures of manufacturing and post consumer metal, and prime metal if necessary,
- technology can be applied efficiently to maximise metal recovery and support the recycling economics.

Process scrap such as used beverage cans or scraps generated during manufacture are remelted in dedicated recycling centres[10]. Clean or bare metal may be melted using top loading gas fired furnaces, coreless electric induction furnaces or reverberatory melters. The choice of melting technology depends upon the gauge of the material to be melted and the capital and operating costs. Coated material may be remelted using furnaces with advanced emission control systems, such as the closed-well type, where products of combustion are recirculated and burned within a closed furnace of this type in one of its European operations. Alternatively, the coated metal may be passed into a decoating unit where the organic films and lacquers are removed. Decoating is an important step in the recycling process, because it improves both the economic and the environmental impact.

In 2001, business obligated under the UK's Packaging Regulations reported[8] 120,234 tonnes of aluminium packaging, of which 29,030 tonnes were recovered or recycled. This is equivalent to an aluminium packaging recycling rate of 24%. The requirement at present is 50% including the minimum of 24% recycling of each individual material, including aluminium. The UK Regulations have placed obligations on certain businesses in the packaging chain to ensure the recovery and recycling of packaging waste.

## 1.3. ALUMINIUM DROSS

### 1.3.1 Characterisation of Aluminium Drosses

Aluminium dross is a by-product of the aluminium production industry which contains significant quantities of recoverable metal (up to around 70%). Most drosses are a heterogeneous mixture of large lumps, fine oxides and small pieces of metal. Aluminium dross is a combination of free metal and non metallic substances (e.g. aluminium oxide and salts). Aluminium nitrides and carbides may also be present, as well as metal oxides derived from the molten alloy[11]. It has also been documented that dross should be stored in a dry environment since reactions of carbide or nitride of aluminium and calcium can form acetylene and ammonia[12].

Drosses may be classified by means of their metal content. Drosses with a high metal content (white, or wet, dross that is rich in free metal) typically occur as a compact material in large clotted lumps or blocks. A low metal content typically occurs when scrap is remelted with salts in an open hearth furnace. This black, or dry, dross is usually granular with a high metal content in the coarse fraction and chiefly oxides and salt in the fines[11].

Apart from melting samples, few chemical methods have been developed for determining the free metal content of drosses. However, more practical methods have been devised to determine the fines content after dross-grinding operations[13,14].

In order to simplify pre-analysis for recovery, aluminium dross can be characterised to produce a dross identity card to include such information as density data, particle size[15] analysis, distribution of elements in different fractions, composition, metal content of recovered alloys and gas evolution. To compile these dross identity cards Manfredi et al[11] examined six granular (black) and five compact (white) drosses from different smelters and foundries. After screening and weighing, samples of granular drosses were taken according to particle-size distribution. Each bulk density was measured by the weight of the dross put into a vessel of known volume. The sample was then melted at 1,023K with a mixture of 70% NaCl, 28% KCl, and 2% $CaF_2$ in a graphite crucible to determine the metal content and alloy composition. After cooling, crushing and washing, the spent salt flux was screened. Ingot and drops above 0.5mm diameter were assumed to be metal. Table-1.2 presents the dross identity card.

**Table-1.2. The range of physical and chemical properties measured[11].**

| Properties | Granular Dross | Compact Dross |
|---|---|---|
| Alloy Content (wt%) | | |
| Melt | 2.44-11.77 | 1.34-10.03 |
| Recovered Metal | 1.03-5.51 | 0.33-6.80 |
| Distribution function q($mm^{-1}$) | 0.08 (coarse)-0.452 (fine) | ---- |
| Density ($t/m^3$) | 0. 82 8-1.118 (bulk) | 2.396-2.528 (apparent) |
| Metal Content (% by mass) | 46.9-69.1 | 71-93 |
| Lixiviate (pH) | 9.52-10.14 | 9.03-9.48 |
| Salt Content (wt%) | 0.18-6.21 | 0.01-0.03 |
| Gas Evolution (l/kg dross) | 0.25-1.17 | No evolution |

The dross identity card provides details on the following:

1. origin and specifications and composition of the melt from which it was skimmed,
2. particle size analysis, characterised by distribution Q and distribution function q,
3. bulk density and metal content values,
4. the content of alloying metal and recovered metal,
5. results of a standard leaching test - 100g sample in 1 litre of distilled water (24 hours by open vessel, 24 hours turning by closed vessel), to determine salt content, conductivity of the lixiviate, salt content and gas evolution following addition to water[11].

Compact drosses (white) generally contain more than 70% metal, and have a different morphology compared to drosses containing less metal. Bulk density is known to decrease with increasing metal content because the specific weight of the aluminium alloy is lower than that of its oxide. In addition, the content of magnesium decreases with increasing particle size i.e. there is a higher content of magnesium in fine particles. The most important reason for metal losses is not the oxidation of aluminium, but the entrapment of liquid metals and agglomeration of oxide films. An increasing metallic aluminium content supports the growth of the dross granules. Theoretically, $Al_2O_3$ contains about 53% aluminium, so fractions with a lower aluminium content are predominantly oxide. If the aluminium content is above 53%, metallic aluminium is present in the dross fraction[11].

The quantity and quality of dross generation depends on the following factors[16]:

- the proportion of bath constituents contained during primary production,
- the quality of the scrap melted,
- the melting technique,
- movement of the metal to accelerate the melting, alloying and metal treatment,
- type of alloy and the metal treatment required for it,
- dross skimming method,
- frequency of skimming.

### 1.3.2. Dross Treatment

The free-metal content of the dross depends on how carefully skimming from the melt was executed, the composition of the molten alloy, the fluxing and the dross-cooling process[11]. Variability in processing techniques also varies the particle size of the materials found within the dross. Before smelting, white drosses must be upgraded to at least 50% aluminium to make recycling profitable. Upgrading is usually performed by grinding and screening. Metallic aluminium is concentrated in the coarser size fractions as the aluminium content has been shown to be greatest in the coarse fraction and decreases with decreasing particle size[15]. Dross fractions are said to be divided into three groups[15,17]:

1. fine fraction particles <1.5mm - almost zero aluminium recovery,
2. medium particle size <10mm - up to 90% aluminium recovery,
3. coarse particle size >10mm - over 96% aluminium recovery.

Two types of dross have been distinguished as a result of processing following skimming, virgin dross - still hot after skimming, and cooled dross[16]. If dross is cooled while open to the air, metallic aluminium decreases but weight increases since $Al_2O_3$ is formed. Besides, the size of the remaining aluminium particles changes due to partial oxidation. Up to 20% aluminium can be lost by oxidation and the metal yield of the cooled dross falls to less than 40%. Unfortunately all too often hot dross may ignite either while still inside the furnace or when skimmed off due to excess air and combustion of aluminium, magnesium and other alloying constituents may take place, resulting in the temperature rising up to $1200^0$C. Such dross is very difficult to cool. This can be avoided by covering the hot dross with a powder blanket named “Alcool” which smothers the combustion. “Alcool” is small hollow spheres of $Al_2O_3$ in a thin layer on the dross which extinguishes thermiting without introduction of salts. In addition, the dross can be cooled in an inert gas atmosphere which reduces combustion losses while leaving the particle size unaffected as well as the tendency to form dust.

The dross is then pressed (compacted). Bramley[18] treated dross further to collect trapped molten aluminium with a rocking press head system. Dross presses are used to press dross contained in a dross pot. The hot dross is extracted from a furnace and placed in the dross pot. The dross pot is then transferred to the press where the dross is pressed by a press head and the molten metal, usually aluminium, is collected in a sow mould positioned beneath the dross pot. The dross pot is provided with at least one drainage hole to allow the molten aluminium to flow into the sow mould. A problem with the present press head and skim box systems is that the liquid aluminium becomes trapped in the dross. In Bramley's work[18], an improved dross head movement system has been provided which increases the yield of metal from dross. In this system, the conical shape press head rocks slowly backward and forward by an upper hydraulic pressure generated by two hydraulic rams spaced apart on diametrically opposite sides of the press head. A control device is rigidly mounted on the top of head and therefore moves with the head. The rocking movement of the press head has a number of advantages. This movement creates a couple of cavities on two sides of the head. The cavities enable molten aluminium trapped on the inside surface of the dross skull to drain downwards. In addition, as the head moves, additional pressure is applied to the dross alternately on each side causing the dross to be further squeezed and thereby causing further release of aluminium. Figure 1.4 is shows a schematic diagram of the rocking press head system.

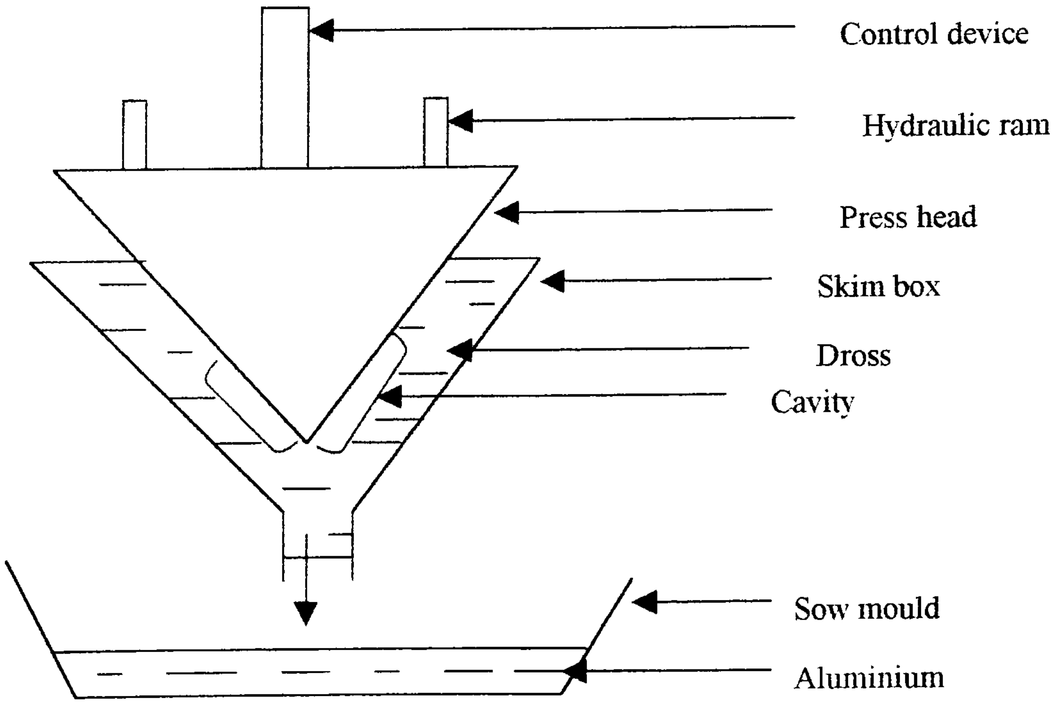

**Figure-1.4. Schematic diagram of a rocking press head system[18]**

The use of a press allows dross to be compacted very gently so that the relative velocity between the aluminium and, for example, a grain of oxide or nitride is so small that almost no such back-mixing can take place. Furthermore, the energy is quite sufficient to break up the oxide skin of millions of small droplets and squeeze metal out of pores of non-metallic compounds, so producing enough metal to drain and form massive aluminium plates. The cooling cycles of dross in this process are fast and efficient due to the high heat transfer rate (2-15 minutes). The heat from the compacted compressed dross passes quickly due to the heavy cast steel press head and skim box. The metallic surface of the pressed dross skull quickly drops well below melting point ($450^0$ C, where thermiting stops). Other cooling methods are less efficient because of the porous nature of the unpressed dross. Slower cooling cycles result in increased metal loss[11].

It was mentioned above that drosses must contain at least 50% (by mass) aluminium to make recycling profitable. Soto and Toguri[19] worked on aluminium recovery from primary dross containing only 25% (by mass) metallic aluminium without taking it back to the secondary furnace. In this study froth flotation was investigated as a means of upgrading the aluminium dross. A flotation test using the Hallimond tube indicated that metallic aluminium is not floatable within xanthate-type collectors. When the aluminium was conditioned with a copper solution however, cementation of the copper on the aluminium surface took place and the copper coated aluminium was readily floatable.

$$3Cu^{+2} + 2Al^0 \longrightarrow 3Cu^0 + 2Al^{3+}$$

This process is effective only for fine dross particles. The particle size larger than 298µm, the aluminium recovery drops drastically. Aluminium metal in secondary dross cannot be activated by copper, because the presence of soluble salts results in a powdery and non-adherent cement coating.

### 1.3.3. Black Dross Generation

The aluminium is recovered from waste materials, including the white dross generated from primary aluminium industries (salt free primary skim), scrap metals from manufacturing operations and post consumer products, and alloying elements. The primary white drosses are ground and screened in order to separate the metallic aluminium from the oxides and iron impurities. The oxide particles are manufactured in different metal industries for various purposes. Metallic aluminium along with the scrap and alloys are melted in the rotary furnace. During the melting process some aluminium is converted into oxides due to contact with the furnace's reactive atmosphere. A lot of metallic aluminium remains entrapped between the oxide particles (reasons of skim generation will be discussed later in this chapter). Almost all secondary aluminium industries however, use molten salts as a salt flux to minimise this metal loss. The salts with low melting points on the top of the molten metal provide a blanket which prevents the metallic aluminium being exposed in air and thus prevents oxidation. Some aluminium however, is still converted into oxides (i.e., molten aluminium trapped inside) and is removed by skimming before casting. Up to 10% of aluminium production can be lost to dross. All of this black dross is landfilled. In a joint research project with industry, Birmingham University and Centre for Environmental Research at Brunel University research was carried out to concentrate the aluminium content from the black dross using novel Eddy Current Separators (ECS) technology. Traditionally, small particles (<3mm) have not been successfully treated by this technology[1]. Part of the project (Birmingham University) was to improve the ECS technique and separate the fine particles (<3mm). Black dross is further successfully refined using the improved ECS, whereby the dross is passed over a rotating permanent magnetic linear motor. Induced currents repel the applied magnetic field with a force related to the specific conductivity, mass, size and shape of the particle. The process is capable of concentrating aluminium from the other materials, up to 65%. The recovered aluminium is recycled in the rotary furnace. The remaining black dross, which is known as black dross tailings (containing less than 5% aluminium) is the subject of this project. Figure-1.5 shows a schematic diagram of generation of secondary aluminium and black dross tailings. Typical input and output materials of the whole recycling process for industry are given below[20]:

**Inputs**

| | |
|---|---|
| White dross: | 14000 tons pa |
| Scrap aluminium & alloy: | 2000 tons pa |
| Salt (70% NaCl and 30% KCl by mass): | 3500 tons pa |

**Outputs**

| | |
|---|---|
| Aluminium metal | 8000 tons pa |
| White dross powder | 6000 tons pa (>80% sold; remainder to landfill) |
| Black dross | 5000 tons pa (all to landfill @ £35 per ton including transport, container, tax and fee) |

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### 1.3.4. Factors contributing to skim generation[21]

Metal loss through generation of dross has been the highest cost factor in metal production. Dross is generated during the skimming process. The layer of skim acts as an insulating blanket between the burner and the melt, thus severely reducing the thermal efficiency of the process. Skim floats on top of molten metal because a considerable amount of gas is trapped in the product. The ratio of gas, metal and oxide depend on the alloy, the atmosphere and the mass flow conditions during the formation.

Several researchers[21] are investigating the factors contributing to skim generation. There are three major metallurgical factors influencing skim generation during remelting scrap metals.

#### *(i) Oxide film on scrap*

Even if the scrap to be melted in a furnace is free of external contaminants, there will be an oxide film on the scrap which, depending on the total surface area, can be significant. Alfero[22] was interested in quantifying the contribution to melt loss by oxidation on the scrap. He determined that metal to oxide ratio is about 50:1. Freti et. al.[23] measured oxide films on foil directly and found the 50Å thick oxide film on capacitor foil to represent 0.11 wt%. A material with high surface area will be affected more by melt oxidation than the same material with a low surface area because high surface area is exposed to more oxidation.

#### *(ii) Molten metal oxidation*

In most remelt operations scrap is charged to entirely fill the furnace. The burners will strike the top and outside of the pile directly while the centre remains cold. As the metal in the top zone melts, it will drip down and solidify on the cold metal underneath until the entire scrap is liquid. Every time this happens, the oxide film will be broken and the exposed surface will form a new oxide skin. By the time the melting has been completed, the skim layer is a mass of randomly oriented oxide skins with trapped metal and gas floating on top of the melt. At this stage most of the oxide, trapping the metal inside the skim, will be in form of $\gamma$-$Al_2O_3$ films. If however, through excessive heat input the temperature of the skim rises and/or the residence time exceeds the incubation time for conversion to much denser $\alpha$-$Al_2O_3$, oxidation of the trapped metal will resume. A large surface area in the skim is exposed to the atmosphere and since the skim layer, with its trapped gases, is a poor conductor, dissipation of reaction heat is seriously impaired.

This paves the way for a rapid increase in the skim temperature. The heat of formation of the two main high temperature reactions is:

$$2Al + 3/2O_2 \longrightarrow Al_2O_3 + 399 \text{ kcal/mole}$$

and for $T>2000^0C$ $$2Al + N_2 \longrightarrow 2AlN + 131 \text{ kcal/mole}$$

Oxidation of metallic aluminium is exothermic. If 3% of a melt would be oxidised, the heat generated is sufficient to raise the temperature of the entire melt $1500^0$ C. Applying this to a skim layer containing 75% metal and assuming no heat loss to the surroundings, only 3% of the aluminium in the skim must burn to raise the temperature of the entire skim mass well above $2000^0$ C. At that point the nitride reaction will contribute to the continuation of this runaway situation until all the aluminium has been consumed. This molten metal oxidation is inevitable, but good management can minimise the problem. It suggests that in furnaces containing substantial amounts of skim, the residence time and the temperature should be as low as practically possible[21].

***(iii) Molten metal transfer***

Whenever the protective oxide film on molten metal is ruptured under the stress of moving metal during molten metal transfer, the freshly exposed metal will immediately start rebuilding it. The initially amorphous film has considerable flexibility. When it is ruptured and displaced (during filling and emptying of crucibles, mechanical stirring, pumping, siphoning, tapping and filling of furnaces), it has a tendency to wrinkle and trap metal as well as air[21].

### 1.3.5. Minimisation of skim[21]

Salt fluxes have long been known to facilitate metal recovery from skim in secondary aluminium processing. The purpose of the salt is 1) to protect the metal already melted from further oxidation, 2) to break up the oxide film around each aluminium drop - fluorides are very good for this purpose, and 3) to promote coalescence of aluminium droplets trapped in the skim.

Although salt fluxes are widely used in secondary aluminium processing, the mechanism is not well understood. Empirically a salt composition of an equimolar mixture of NaCl and KCl with an addition of 10% of a fluoride, often cryolite, has been established to be optimal for this multi-purpose task. It had been assumed that the addition of fluorides will provide limited solubility of alumina and other oxides in the salt, which will aid the stripping action. Fluorides also affect the surface tension of the salt, as well as – to a minor extent - the melting point and the viscosity of the salt. The fluxes have a finite life, because the build-up of suspended oxides affects the apparent viscosity. Unpublished work at Alcoa[24] determined that up to 5 wt% oxides in the salt can be tolerated before metal coalescence is affected. Since the suspension is very thixotropic, keeping the solution in proper motion will assist coalescence significantly.

Very little is known about the salt-oxide systems, and even less about the salt-metal-oxide three phase systems, yet, it seems that successful flux operation requires a combination of surface tension lowering of both salt-metal and salt-oxide, in order to promote oxide-metal separation as well as subsequent metal coalescence[21].

Since salts are added in the secondary furnace in order to minimise formation of skim, black dross contains a huge amount of mixtures.

No process can recover 100% of the aluminium within the white dross. Anywhere between 13-22% aluminium can be lost as result of 1) losses in fine dust, 2) oxidation and 3) incorporation of aluminium into salt-cake[25].

### 1.3.6. Recycling and uses of salt flux

The driving forces for salt extraction are: (1) there are problems with salt chlorides in the environment, in addition with, (2) the possible uses of recovered sodium and potassium salts in the secondary aluminium industry.

There are limited treatment and uses available for the spent salt flux. These are summarised as follows:

1. Washing and drying the salt flux and separating according to particle size (>0.5mm are metal drops, <0.5mm are considered residue). For the residue there is the possibility of recycling the ceramic material after washing and calcination. The residue contains <53% aluminium, which is predominantly oxide. Most of the magnesium is also obtained in fine fractions. Metal drops contain more aluminium. If this value is >80%, they can be added to the ingot metal[26].

2. In Germany, fine dross fractions are treated together with the salt cake to recycle the salt[27]. Although salt cake consists almost always of basically harmless ingredients, it

reacts with water with the evolution of ammonia. This reaction causes the pH in the salt cake to rise to a level where residual fine particles of aluminium can react and form aluminium hydroxide and hydrogen which, if allowed to build up to a critical concentration in a confined space, can cause an explosion. The oxide residue is used as a construction material[21].

3. Removal of salt slag by leaching methods has been investigated by Woehlk et al.[28] The salt is documented as being recovered from the slag as a mixed salt KCl/NaCl. The slag is comminuted, screened, and leached out at near boiling temperature to obtain gas-free and highly concentrated solutions. After a two stage solid removal system to remove the coarser metallic aluminium and the alumina, the resulting clear liquid overflow is fed into a single stage evaporative crystallisation unit where the solute is crystallised as a mixed salt.

4. There are currently two trial projects working towards recycling of salt cakes, in Germany and Australia[1]. The methodology used in both of these projects is based on dumping the black dross into large water filled lagoons, dissolving the dross and reclaiming the salt by evaporating water in large salt pans or by reverse osmosis in large scale desalination plants. After the recovery of only large aluminium particles, the remaining sludge (which accounts for around half of the mass of black dross) is then landfilled. These experimental projects have not been in operation for long enough to gauge the level of success achieved at this time. Due to the reliance on solar heat to evaporate the vast tonnages of salt water, this methodology would only be commercially viable in hot, dry climate countries, not in cold countries like the UK.

5. There is a patent that involves the desulphurisation/dechlorination concept to convert chloride-containing brine solution into carbonate/bicarbonate product stream[29]. The resin-based process is as follows:

   Carbonation

   $$\mathrm{ROH} + \mathrm{CO_2} \longrightarrow \mathrm{RHCO_3}$$

Dechlorination

$$RHCO_3 + NaCl/KCl \longrightarrow RCl + NaHCO_3/KHCO_3$$

Regeneration

$$RCl + NH_4OH \longrightarrow ROH + NH_4Cl$$

Ammonia recovery

$$NH_4Cl + H_2O \longrightarrow NH_4OH + HCl$$

or

(optional step)

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_4OH$$

where R represents the complex cation group present in the resin.

Potassium chloride and sodium chloride can be converted to respective hydroxides (and carbonates by subsequent carbonation) by electrolysis. Brine could be sold to chemical processors.

Salt-cake derived from brine solutions can be used in the manufacture of potassium carbonate by the electrodialysis process, provided there are acceptable levels of impurities. The main disadvantage is that most salt-cake fluxes use a mixture of sodium chloride and potassium chloride. Sodium causes problems in the processes. KCl is not obtained pure enough by evaporation (22% solids) to sell on[29].

The options for recovery of calcium and magnesium are listed as, chemical treatment, settling/filtration, and chelating ion-exchange resin. For aluminium, sorption, biological, cementation, pyrometallurgical, ion-exchange, magnetic separation, membrane separation, chemical precipitation and solvent extraction. For sodium, fractional crystallisation[29].

Chelating ion-exchange resin to reduce calcium and magnesium levels from brine used for electrodialysis is already in practice. Resin can be used to reduce the aluminium levels in brine based on successful application in the chloroalkali industry, in the purification of process streams containing trace heavy metal, electroplating industries and recovery of heavy metals from hydrometallurgical leach streams[29].

### 1.3.7. A new direction - research on salt free dross treatment

The conventional recycling process using a Salt Rotary Furnace (SRF) is thermally inefficient and environmentally unacceptable because of the production of salt slag. As the intention of the aluminium recyclers is to recycle 100% aluminium, recyclers are also very keen to solve the salt slag problems. For years researchers have been trying to develop a process that would either not require the use of salt for the treatment of white dross, or offer a method of transforming the black dross into landfillable or saleable products.

Researchers at the Arvida (Quebec, Canada) Research and Development Centre (ARDC) have tackled this problem using plasma energy technology where no salt is required to process white drosses[30].

In plasma heating, electricity dissociates and partially ionises a process gas to produce plasma. Superheated to a highly energised state, the ionised process gas conducts both heat and electricity. The plasma torch consists of two water-cooled internal electrodes separated by a small gap through which the process gas, such as air or nitrogen, is continuously injected. Application of high voltage initiates an electric arc between the electrodes; the arc heats the gas to a very high temperature, causing the gas to dissociate and partially ionise. The plasma ejects from the torch and can be used for heating within a controlled atmosphere.

In the dross treatment process the plasma torch is mounted on the charging door of a rotary furnace designed to maintain close control of atmosphere composition. The dross is charged, the door closed and the plasma turned on. The charge is heated to 700-800$^0$C while the furnace is rotated. Aluminium in dross is wrapped in oxide films. During heating of the dross by plasma operation with air or nitrogen as process gas, very little further oxide or nitride forms because these gases are much less reactive and used in small amounts. The rotation of the furnace provides mechanical stirring that ruptures the oxide film, freeing the molten metal and improving energy efficiency. When the final dross temperature is reached, the metal agglomerated in a pool separated from the oxide part of the dross is tapped away. No salt flux additions are required for any of the drosses originating from smelter or remelt operation. The oxide portion of the dross, termed nonmetallic product (NMP), is a greyish powder containing mostly alumina with variable quantities of aluminium nitride and magnesium oxide depending on the alloy composition. It does not flow through the tap hole with the metal, but is later discharged through the charging door by tilting the furnace forward (Figure-1.6). This process claims 80-90% process efficiency (defined as the percentage of aluminium recovered over the total aluminium content of the dross), and increases with the aluminium content. The process is currently under investigation at Alcan[30].

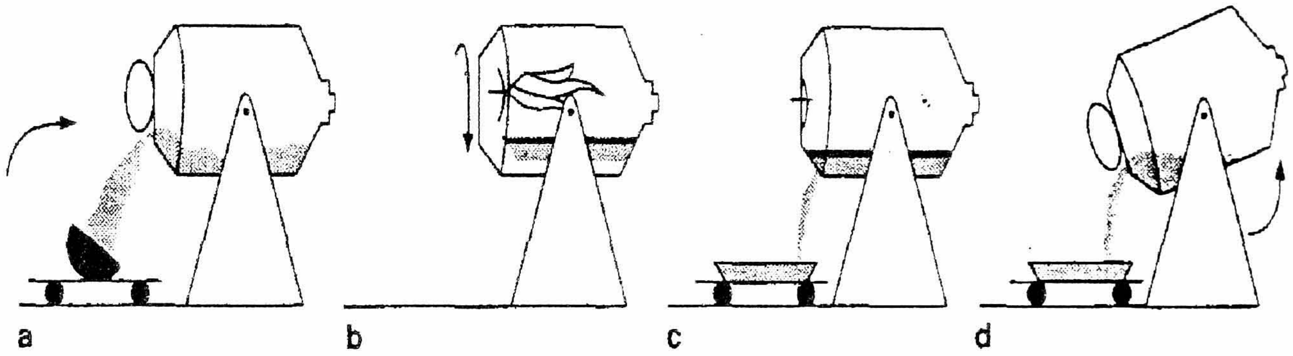


**Figure-1.6. The basic steps of the plasma dross treatment process. (a) charging the dross (b) plasma heating (c) recovery of aluminium (d)[30] removal of NMP[30].**

Further R&D led to the development of a much improved technology for the treatment of aluminium dross. Hydro-Quebec has developed a new technology using a rotary arc furnace with graphite electrodes. This process provides aluminium recovery rates of 80-90% using a highly energy efficient, environmentally sound production method[31].

Figure-1.7 shows a schematic diagram of the graphite electrode rotary arc dross treatment process. The rotary furnace is equiped with two graphite electrodes and has a charging capacity of four tonnes. The furnace rotates during heating of the dross to provide mechanical stirring. This breaks the oxide films on the droplets of aluminium present in the dross, and promotes agglomeration of the molten metal. The rotation also prevents formation of hot spots on the charge or refractories and improves energy transfer. On completion of heating, the metal is tapped from the furnace through a hole on the side. The solid residues remaining in the furnace form a greyish powder that does not flow through the tap hole. The residues are removed by tilting the furnace forward while slowly rotating it.

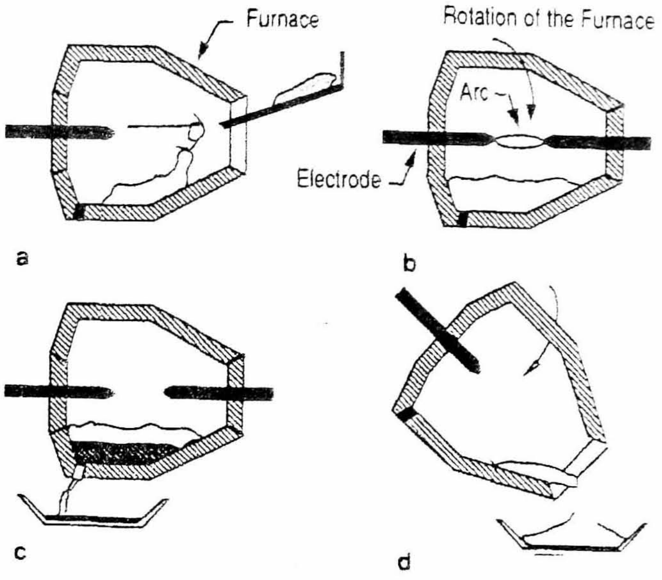


**Figure-1.7. Phases of dross treatment process in a rotary arc furnace (a)dross charging (b)heating (c)aluminium tapping (d)discharging solid residue[31].**

This technology claims more energy efficiency and higher aluminium recovery than conventional rotary salt furnace and plasma torch process. A comparision among the three process has been illustrated in Figure-1.8 and Figure-1.9. Commercializationn of this improved technology is in progress at the present.

American engineers at the Electric Power Research Institute (EPRI) in Palo Alto, California, and Process Engineering Dynamics in Grand Island, N.Y., have designed an electrically based aluminium melter that promises to reduce dross production by 60%[32]. The process is similar to the above plasma torch process, where it uses inert argon gas instead of air or nitrogen. The argon gas provides a stable, nonoxidising atmosphere that inhibits dross formation. The future step in this technique is to design and build an industrial plant to treat 10,000 pounds of scrap per hour.

### 1.3.8. Uses of aluminium slags.

Aluminium slag has been investigated as a replacement for aluminium powder in cellular concrete production[17]. 80-90% of all industrial buildings in European countries use cellular concrete because of its properties of low density, low thermal conductivity, high sound sorption and sound insulation and fire resistance.

The process for manufacturing cellular concrete involves reacting finely divided metallic aluminium powder with hydroxides to form minute bubbles of $H_2$ gas throughout the

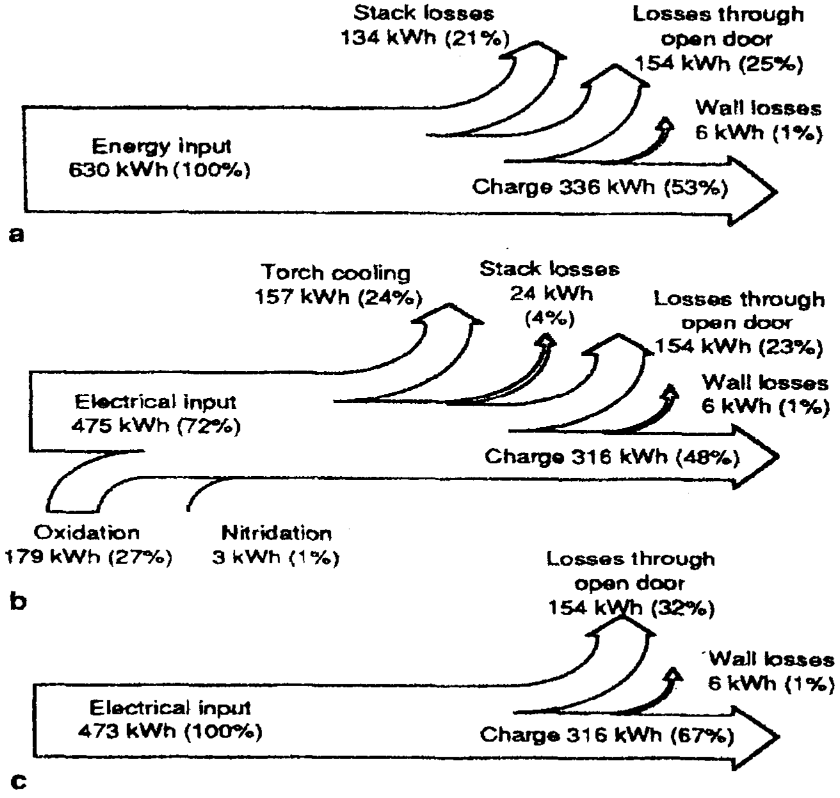


**Figure-1.8. Energy sources and utilization per tonne of dross input containing 50 wt% free Al. (a) Air/$O_2$/fuel-RSF (b) Air plasma torch (c) Graphite electrode process[31]**

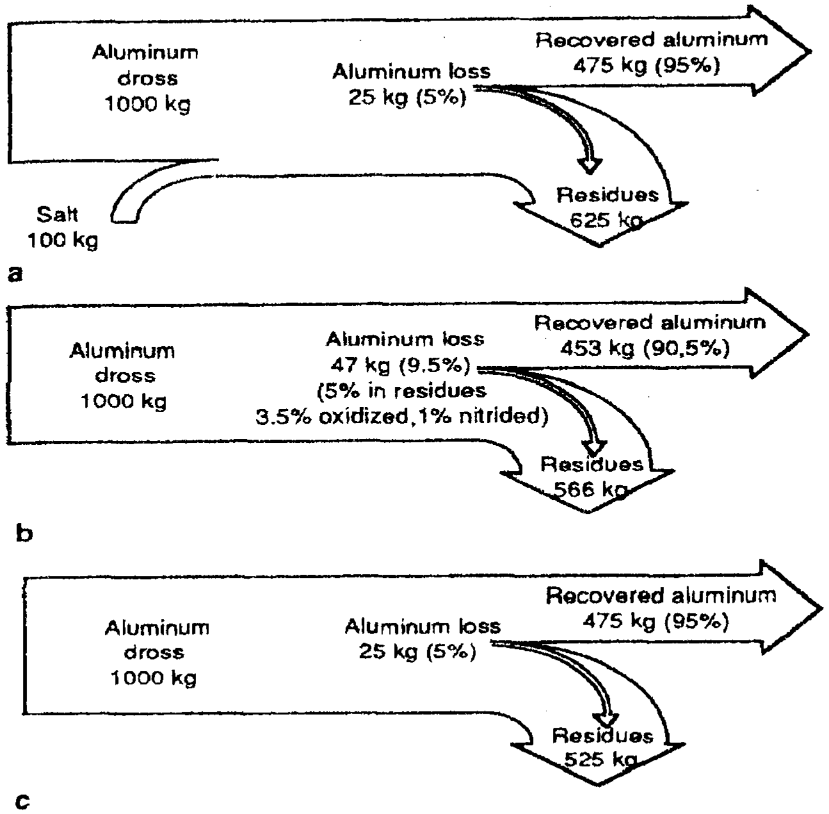


**Figure-1.9. Mass balance per tonne of dross input containing 50 wt% free aluminium. (a) Air/$O_2$/fuel-RSF (b) Air plasma torch (c) Graphite electrode process[31]**

mixture. Other additives include cement, sand, lime and fly ash. Pure Al powder is the most expensive component[33]. Therefore, in order to reduce the cost, the aluminium powder is reported as having been replaced with (1) powder produced from recycled scrap, and (2) aluminium processing wastes with <10% aluminium.

The aluminium surfaces in these processes are recycled aluminium foil and unrecoverable aluminium wastes which are oxidised via atmospheric exposure. This oxide layer prevents reaction between aluminium and hydroxides, necessary to generate hydrogen gas in cellular concrete. Hydroxyl groups are reacted with the alumina layer to form aluminate under alkaline conditions as follows:

$$Al_2O_3 + 2OH^- + 3H_2O \longrightarrow 2Al(OH)_4^-$$

Following removal of the alumina layer, the alkali dissolves aluminium forming aluminate with the release of hydrogen[17].

During the manufacture of cellular concrete, the aluminium residue does not have to be separated from the waste as the oxidised metal but can be used to replace fine aggregates. Slags generally contain a mixture of $Si_2O$, $Fe_2O$, $Al_2O_3$, CaO and NaCl, which, apart from NaCl and aluminium particles, has a chemical composition similar to silica sand and fly ash. Silica sand and fly ash are customarily used as fine aggregates in the manufacture of cellular concrete. Before use, the slags must be (1) crushed, (2) powdered, (3) ground to 100-mesh screen, (4) washed to remove NaCl, and (5) oven dried to low moisture content[17].

To produce cellular concrete, commercially produced Portland cement, hydrated lime, and additives are first mixed in a portable concrete mixer, then water is added to produce a slurry. Next, the slag powder is added and thoroughly mixed with the slurry. The mixture is transferred to a high-speed mixer before being poured into a mould. Each mould is filled to half of its depth. The gasification process begins and the mixture expands to fill the mould. The mould is then transferred into a setting room for precuring. The precured panel is cut into test samples and auto-claved under a pressurised steam environment to produce the final microstructure[17].

Average compression strength is not significantly different from pure aluminium powder cell concrete. Poor mechanical properties, however, have been obtained with this material. It is suggested that if the amount of pure aluminium were known, cellular concrete compositions could be altered to accommodate the differences. It was also recommended that a process control system be designed and developed to aid this[17].

Tayeb reports the use of some industrial wastes as energy storage media[34]. Solar energy is stored in different solid storage materials, both chemical and metallic industrial wastes. The materials tested in this report were paraffin wax, copper slag, aluminium slag, iron slag, cast iron slag and copper chips. Solar energy is stored in these materials, and the energy is then recovered with a water stream at different rates, and the storage capacity and period for different materials were compared. The same set of experiments was run on solid metallic materials mixed with wax. The results indicated that iron slag has the highest storage capacity followed by cast iron slag, the aluminium slag and copper chips and copper slag. It is also noted that the addition of paraffin wax to the solid metallic material greatly improves its storage capacity and duration.

Copper gave the highest fluid outlet temperatures because of high specific heat and high thermal conditions, however it cooled very quickly. Copper chips were similar. Iron slag cooled less rapidly. Aluminium slag does not have high outlet temperature at the beginning of storage, however it did not cool rapidly. This is because of the low specific heat and low thermal conductivity. It also had the longest time of energy storage. Cast iron slag gave the lowest temperatures and had a severe decline in energy storage over time[34].

Wax has very low thermal conductivity, and a very long energy storage time and can store a very high amount of energy. The increase in energy given by the wax is due to the latent heat of transformation.

The low thermal conductivity of the wax was overcome by mixing it with metallic materials in the ratio wax:material of 1:3. Only copper chips and cast iron were tested, and this reduced the cycle time i.e. melting and resolidifyinig in addition to increased energy storage. Further studies are required in this area[34].

### 1.3.9. Relevant slag processing techniques

#### *1.3.9.1. Ultrasound and leaching*

Leaching processes and the latest improvements using ultrasound have been studied by Narayana et al.,[35]. Ultrasound has been used to improve leaching rates, in the extractive metallurgy industry. However, below a critical particle size it had no effect. It has also been found that ultrasound assists in selective leaching.

#### *1.3.9.2. Leaching*

In the recovery of copper and tin from copper-fire refining slags[36], simply crushing samples and separating by particle size could improve the distribution of copper and tin in the slag. Flotation and leaching were used to refine the slag.

Reaction rate in leaching is said to be (i) proportional to reactive mineral surface area, and (ii) temperature dependant, but independent of (i) agitation providing there is enough agitation to keep particles in suspension. and (ii) solution concentration of products.

#### *1.3.9.3. Cleaning of slags*

Cleaning of slags containing base metals by injection of reducing gases to the electrode zone is documented with theory and the results of pilot studies by Rusakov et al[37]. Effective cleaning of the slag was achieved by creating simultaneous conditions ensuring intensive reduction of slag components, active coalescence or coagulation of fine-grained inclusions and the opportunity for the transition of the reduced and selected particles, containing base metals, in a phase collector.

### 1.3.10. Uses of other slags

Furnace slag has been documented as being used in subgrade roads (since the structural strength is too low for use in normal roads)[38]. Soil surfaced roads, forest roads or cycle tracks were recommended.

Waste slag from ferromanganese and silicomanganese furnaces has been utilised, by crushing and washing, in the production of concrete and other building aggregates[17]. It was stated that the slag conformed to all the requirements of an aggregate for the production of concretes, with the performance of the cured product being acceptable but with workability decreased. Slag was suggested for use in the construction of roads but caution was advised for use in surfacing[39].

The recycling of blast furnace slag and converter slag in brick manufacture has been documented by Elwan et al[40]. Blast furnace slag is said to be made up of $SiO_2$, $Al_2O_3$, CaO, MnO, and trace oxides of Fe, Ti, Mg, K, Na, S, and P. Converter slag is mainly $SiO_2$, $Al_2O_3$, $Fe_2O_3$, CaO, MnO and trace oxides of Ti, Mg, Na, S, and P. Up to 30% slag was added to the clay which was hand moulded. Firing was carried out at 800, 900 and 1000$^0$C at a rate of 2.5$^0$C/min up to the desired temperature for a duration of two hours. Increasing slag content was found to decrease the linear shrinkage during the drying process.

Substitution of 10% clay by blast furnace slag fired at 900$^0$C and 1000$^0$C improved the compressive strength and the bulk density but substitution by converter slag decreased these properties. Granulated slag was determined to be suitable for brickmaking whereas converter slag was unsuitable[40].

## 1.4. ANALYTICAL TECHNIQUES

In this section three main analytical instruments are described which were used throughout in this research work. The instruments are:

1) Atomic Absorption Sepctrophotometry
2) X-ray Diffractometer and
3) X-ray Fluorescence Spectroscopy.

### 1.4.1 Atomic Absorption Spectrophotometry[41]

Atomic absorption spectroscopy (AAS) can be used to determine most elements. In this method, a solution containing low concentrations of metallic elements is atomised into a vapour containing free atoms of the elements. A hollow cathode lamp (light source) emits radiation which is characteristic of the element to be determined and this radiation is directed through the vapour. The analyte atoms dispersed throughout the vapour absorb a proportion of the radiation resulting in a decrease in the radiation emerging from the vapour and it is this decrease in radiation which is measured by the detector. A monochromator is included in the system so that energy of the desired wavelength can be isolated from that of neighbouring wavelengths emitted from the light source. A schematic diagram of an Atomic Absorption Spectrophotometer is shown in Figure-1.10. The instrument used throughout the present study was a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer.

Sensitivity is defined as that concentration of an element, in ppm in aqueous solution which gives a 1% absorption signal.

No technique of chemical analysis is universally applicable. Figure-1.11 shows only those elements that can be analysed directly by atomic absorption. Of these shown osmium, wolfram, zirconium, hafnium, niobium, tantalum and the rare earth are better analysed by other techniques. These refractory elements present difficulties and exhibit poor sensitivity in flame atomizers. Alkali metals are easily analysed by flame emission and many workers still prefer this approach. For concentration levels below the parts per million (ppm) level, neutron activation and related nuclear techniques, when available, are considered more appropriate.

### Hollow-Cathode Lamp

Hollow-cathode lamps are the most common radiation sources for AAS. The hollow cathode lamp comprises a hollow cup cathode made from the element to be determined and a tungsten anode housed in a glass envelope containing an inert gas at low pressure (Figure-1.12). Ionisation of the inert gas occurs when a potential is applied across the electrodes, and a current of about 5 to 10 mA is generated as ions and electrons migrate to the electrodes. If the potential is sufficiently large, the gaseous cations acquire enough kinetic energy to dislodge some of the metal atoms from the cathode surface and produce an atomic cloud; this process is called sputtering. A portion of the sputtered metal atoms are in excited states and thus emit their characteristic radiation as they return to the ground state. Eventually, the metal atoms diffuse back to the cathode surface or to the glass walls of the tube and are redeposited. The cylindrical configuration of the cathode tends to concentrate the radiation in a limited region of the tube; this design also enhances the probability that redeposition will occur at the cathode rather than on the glass walls. The total light obtained is subsequently passed through a monochromator, usually a grating or prism, to separate the resonance line from other nearby spectral lines.

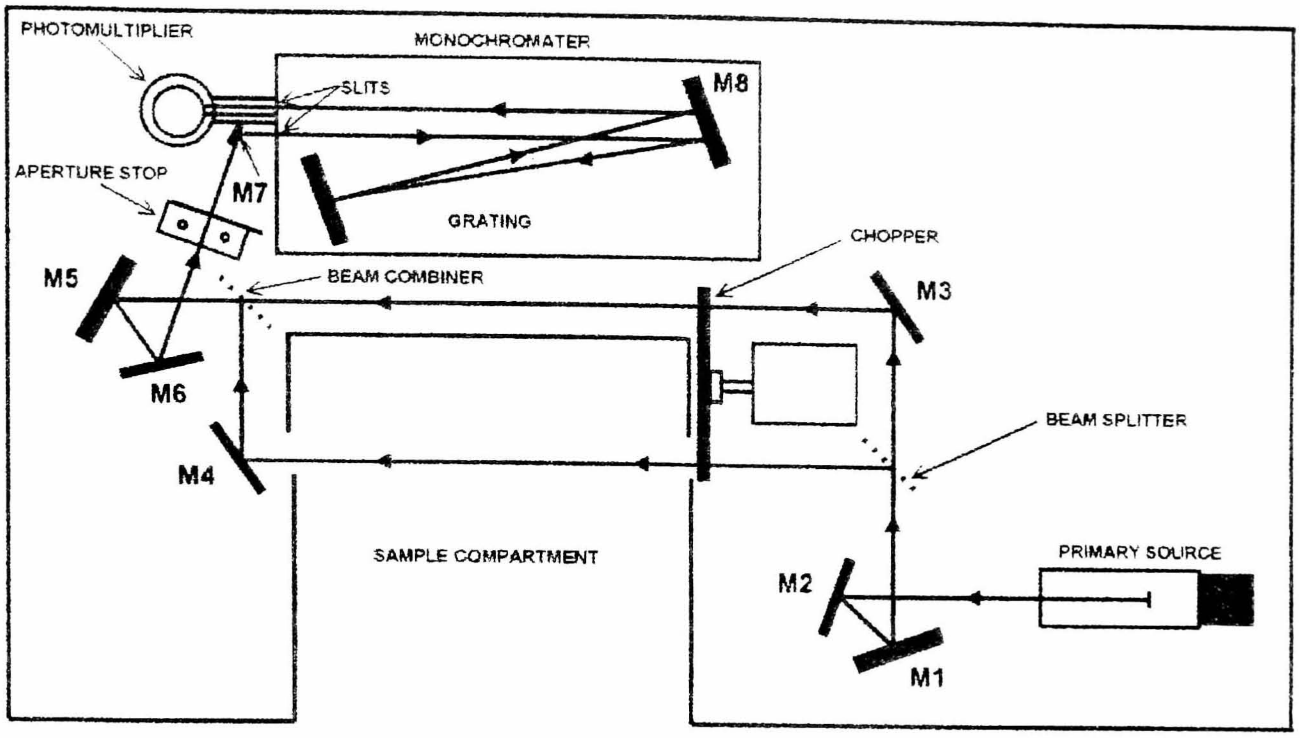
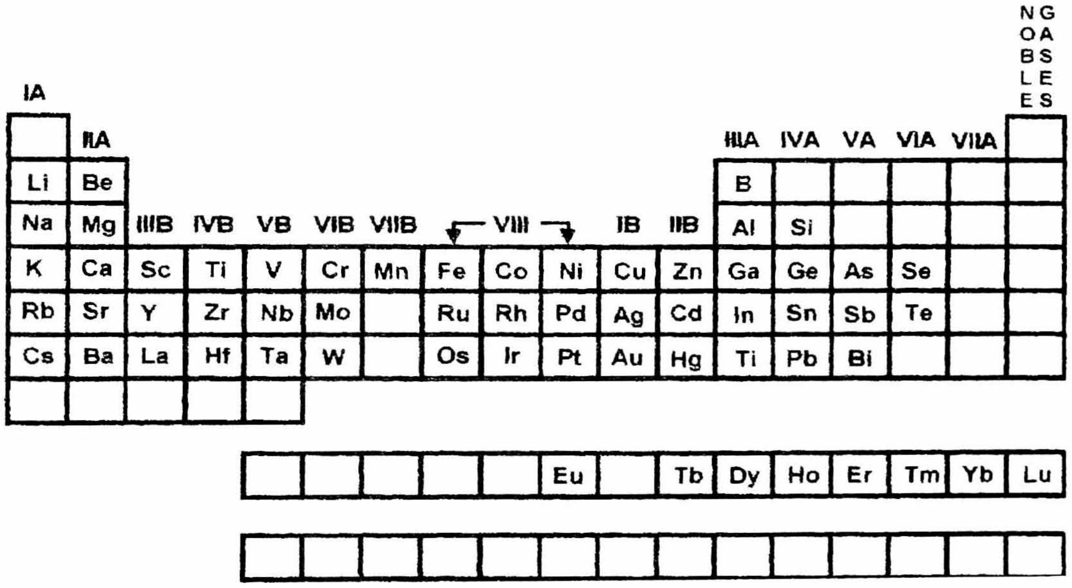


Figure-1.10. Schematic diagram of atomic absorotion spectrophotometer (Model 2380)[41]



| IA | IIA | IIIB | IVB | VB | VIB | VIIB | VIII | VIII | VIII | IB | IIB | IIIA | IVA | VA | VIA | VIIA | NOBLES GASES |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Li | Be |  |  |  |  |  |  |  |  |  |  | B |  |  |  |  |  |
| Na | Mg |  |  |  |  |  |  |  |  |  |  | Al | Si |  |  |  |  |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se |  |  |
| Rb | Sr | Y | Zr | Nb | Mo |  | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te |  |  |
| Cs | Ba | La | Hf | Ta | W |  | Os | Ir | Pt | Au | Hg | Ti | Pb | Bi |  |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  | Eu |  | Tb | Dy | Ho | Er | Tm | Yb | Lu |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

Figure-1.11. Periodic Table showing elements determinable by atomic absorption[41]

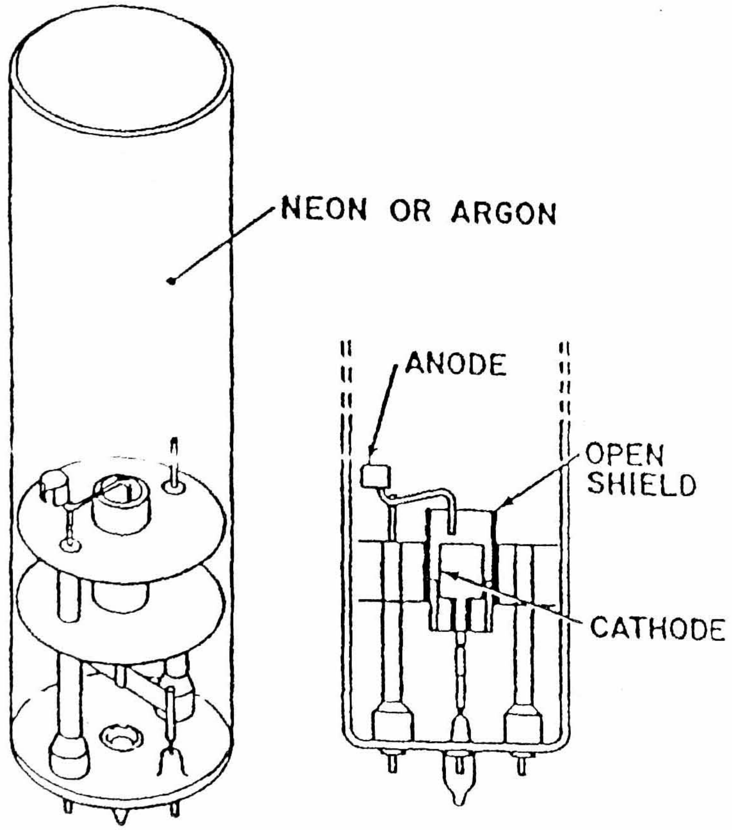


Figure-1.12. Diagram of a Hollow Cathode Lamp[41]

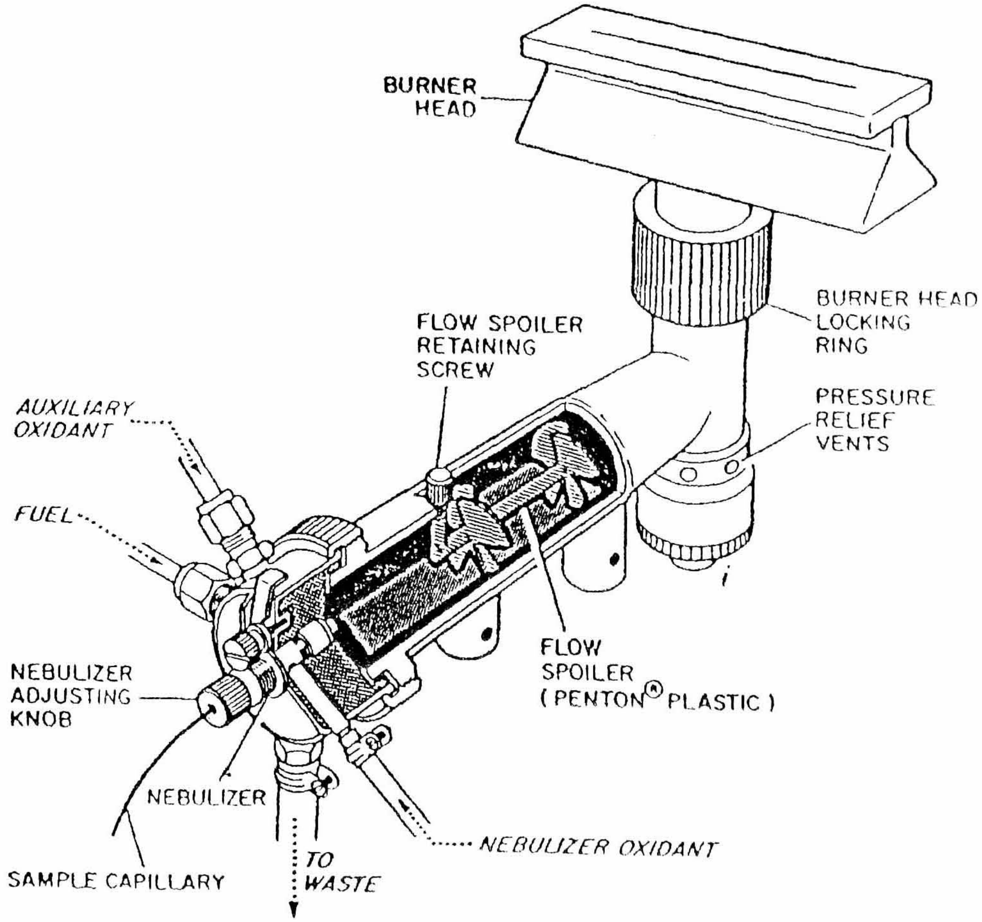


Figure-1.13. Burner nebulizer system[41]

### Atomisation Systems

The gas combination most often used to produce atomisation of vapours in AAS is air-acetylene and nitrous oxide-acetylene. Air-acetylene is the preferred flame for determination by AAS. Other rare combinations include air-hydrogen, argon-hydrogen, air-propane and air-natural gas. These cooler flames are often useful for specific determination but in general they are more susceptible to interference effects. The temperature of the air-acetylene flame is approximately $2300^0$C and it may be used as an oxidising lean blue flame. Nitrous oxide acetylene has a maximum temperature of about $2900^0$C and it is used for the determination of elements which form refractory oxides such as aluminium, tin etc. Light emission from the nitrous oxide/acetylene flame is very strong at certain wavelengths causing fluctuation in the analytical result at those wavelengths. However, it is unlikely to be a problem when using primary wavelengths of the elements but may occur when using a secondary wavelength.

### Burner-Nebuliser System

The laminar flow premix system is the only type of burner in general use for AAS. A liquid sample is introduced into a burner through the nebuliser by venturiaction of the nebuliser oxidant. Figure-1.13 shows a cross-section of the nebulizer premix burner assembly. As the sample passes through the nebuliser, the liquid stream is broken into a droplet spray. In addition to a nebuliser the premix burner contains a chamber and a burner head. Premix chambers are designed to mix the fuel, oxidant and sample.

Not all of the liquid entering a premix burner passes into the flame. The premix chamber allows large droplets; which are deleterious to the absorption processes to condense (aided by the flow spoiler system) and pass out of the chamber through the liquid drain tube. Rejection of these large drops helps to minimise light scattering effects in the flame.

### Optical System

In AAS the monochromator is placed after the atom reservoir to help diminish light-flux on the photo tube. Figure-1.10 is a schematic diagram of typical single and double beam instrument. The instrument used throughout the present study was a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer. It is a double beam model, where the beam from the hollow cathode source is split by a mirrored chopper, one half passing through the flame and the other half around it. The two beams are then recombined by a half-silvered mirror and passed into a grating monochromator; a photomultiplier tube serves as the transducer. The output from the latter is fed to a lock-in amplifier which is synchronised with the chopper drive. The ratio between the reference and sample signal is then amplified and fed to the readout which may be a meter or digital recorder. Double beam instruments lose a factor of 2 in the signal as a result of this process. The main purpose of this system is to cancel instabilities in the source by correcting for fluctations in lamp output. However, the more complex the optics, the greater the reduction in signal strength.

### 1.4.2. Powder X-ray Diffraction[42]

X-ray powder diffraction (XRD) is a physical technique used in the characterisation of solids. It has been in use since the early part of the last century for the identification of crystalline materials and for the determination of crystal structures. In this research Philips 1140/00 X-ray diffractometer was used.

X-rays are a form of electromagnetic radiation of very short wavelength, normally 0.1 to 100Å (Angstroms; 1Å being equal to $10^{-10}$m) that lie between gamma-rays and ultra-violet rays in the electromagnetic spectrum. They are produced by high energy collisions of charged particles with matter. Usually a beam of accelerated electrons is allowed to strike a metal target, such as copper, and this has sufficient energy to ionise some of the copper 1s electrons. An electron from an outer orbital (2p or 3p) immediately drops down to occupy the vacant 1s level and the energy released in the transition appears as X-radiation. The transition energies have fixed values, therefore a characteristic spectrum of X-rays results. For copper, the 2p $\rightarrow$1s transition called K$\alpha$, has wavelength 1.5418Å, and the 3p $\rightarrow$1s transition, K$\beta$, 1.3992Å. The K$\alpha$ transition is usually used in diffraction because it occurs more frequently and is more intense. In order to obtain a monochromatic X-ray beam, all other wavelengths can be filtered out.

A finely powdered sample, which ideally consists of randomly orientated crystals, has the power of scattering an X-ray beam incident on it because the separation of the atoms in a crystal sample is of the same order of magnitude as the wavelength of X-rays. In such a sample, the various lattice planes are also randomly orientated and will diffract the radiation in an analogous way to the refraction of light by an optical grating. Every crystalline substance scatters the X-rays in its own unique diffraction pattern producing a "fingerprint" of its atomic and molecular structure.

When crystals, which are regarded as being built of layers of planes, are struck by a monochromatic X-ray beam, some of the X-rays are reflected such that the angle of incidence equals the angle of reflection as shown in Figure-1.14. The rest are transmitted to be subsequently reflected by succeeding planes.

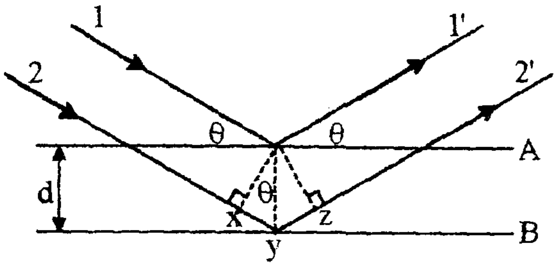


**Figure-1.14. Derivation of Bragg's law for X-ray diffraction.**

Two X-ray beams, 1 and 2, are reflected from adjacent planes, A and B, within the crystal. For the beams to be in phase, beam 22' has to travel the extra distance xyz compared to beam 11'. Therefore, for beams 11' and 22' to be in phase, the distance xyz must be equal to a whole number of wavelengths. The *d-spacing*, (*d* = perpendicular distance between pairs of adjacent planes) and the angle of incidence, or *Bragg angle*, $\theta$, are related to the distance *xy* by:

$xy \sim yz = d\sin\theta$

and $xyz = 2d\sin\theta$

and to be in phase $xyz = n\lambda$, (where n is an integer)

Therefore $2d\sin\theta = n\lambda$ Bragg's Law

It is only when Bragg's law is satisfied that the reflected beams are in phase and interfere constructively. At angles of incidence other than the Bragg angle, the reflected beams are out of phase and destructive interference occurs. Therefore, Bragg's law imposes stringent conditions on the angles at which reflection may occur. Diffracted beams are referred to as reflections and the angle between incident and diffracted beam is denoted by $2\theta$ and not simply $\theta$. The basic information required in crystal structure determination may be obtained from the intensity of each reflection. Each atom has a different number of electrons and the relative scattering will vary according to this. As a result, two identical crystal lattices differing only in atoms, will have different positions and intensities of refracted beams, and each crystal species will diffract X-rays in a characteristically different way[43].

Since a sample of powder contains many small crystallites that are randomly orientated, any one reflection at a particular Bragg angle will result in cones of reflection[44]. These are observed as lines or peaks on the detector rather than the single points seen with single crystals. A simplistic diagram of a powder x-ray diffractometer is shown in Figure-1.15

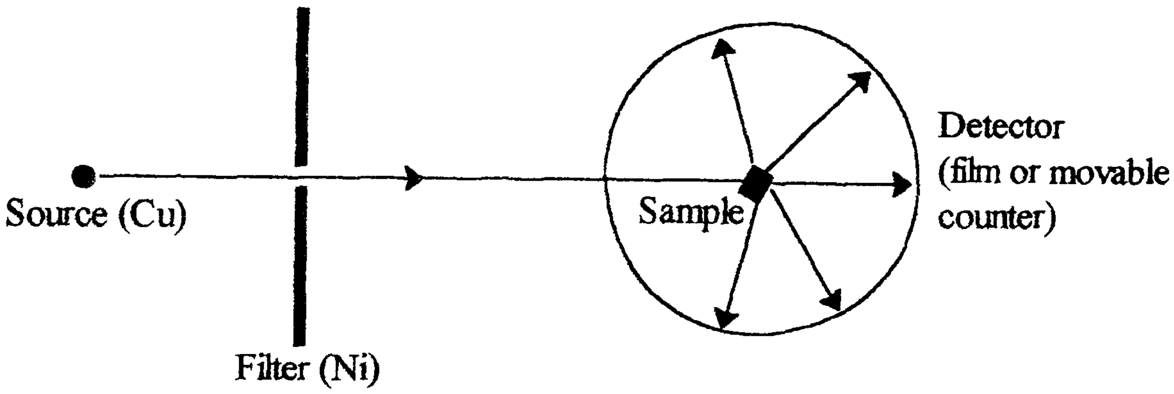


**Figure-1.15. A simplified Diffractometer arrangement.**

### Interpretation

The d-spacings and their intensities are the most important features of a powder pattern. The d-spacings (positions) of the lines in a powder pattern are governed by the values of the unit cell parameters (a, b, c, $\alpha$, $\beta$, $\gamma$). The intensities provide information on the types of atoms present in the sample. Intensities are recorded relative to the intensity of the strongest line of the pattern which is arbitrarily assigned 100. For a particular substance, the line positions are essentially fixed and are characteristic of that substance. Intensities may vary somewhat from sample to sample, depending on the method of sample preparation and instrument conditions.

The substance can be identified from its powder pattern either by the indirect method, visual comparison of the pattern of the unknown sample with those of likely substances, or by the direct method, where the key spacings are measured and examined against indices of known compounds. The powder method can be used for the quantitative analysis of crystalline phases.

It should be noted that in all x-ray diffractogram traces presented in this research work, the data recorded are expressed in a table as: angle (representing 2θ), D-space (representing d-spacing), relative intensity, peak identity (identified from the x-ray library of data files) and corresponding identity D-space (representing the d-spacing of the compound that has been identified).

### 1.4.3. X-Ray Fluorescence Spectroscopy

Energy dispersive X-ray fluorescence spectrometry (XRF) is an instrumental technique which provides elemental analysis for all elements with an atomic number of Na or greater[45,46,47]. X-rays are produced by in an X-ray tube by bombarding a rhodium plated copper anode with electrons. X-ray fluorescence is induced in elements by the bombardment of the sample by primary X-rays from the X-ray tube. In this work, an Oxford Instruments XR-300 X-Ray Fluorescence Spectrometer was used.

#### Fluorescence

When the atoms in a sample are bombarded by high energy X-ray photons, the energy carried by these photons is attenuated and partially transferred to the atoms of the specimen, exciting and ejecting bound electrons from their energy levels. If the energy of the impacting electron is great enough it may penetrate the atom structure through to an inner shell before this transfer of energy occurs. This leaves the atom in an ionised but unstable state. The laws of the atom mean that it will return to its most stable (lowest energy) ground state. This is achieved by electrons from higher energy electron shells dropping down to lower energy shells, with a free electron filling the gap.

When an electron moves from a higher to a lower energy level, the extra energy possessed by the electron is dissipated by the release of a photon of electromagnetic radiation (fluorescence), the energy of which is determined by the sharply defined quantum energy levels of the atom. These energy levels are unique to each element, and therefore the energy of the resulting photon is characteristic of the element from which it was produced, and is known as the characteristic radiation[48]. If the original electron was ejected from a K shell, the resultant radiation is known as a K line, with L or M shells likewise giving L or M lines.

**Detection**

The resultant secondary X-rays are analysed by an Energy Dispersive (ED) system, which consists of devices to detect the X-rays, measure their energy and compute the data. X-rays pass through a thin beryllium window into a cooled, reverse biased, lithium drifted silicon crystal. The crystal converts the X-ray energy into a pulse of electrical charge. The charge is converted into a voltage pulse by a pre-amplifier, which also amplifies the pulse to a high enough level to be passed along cables to the pulse processor. The pulse is then converted to a digital signal and put into a multi-channel analyser, from where it can be viewed and analysed radiation[48].

## 1.5. OBJECTIVES OF THIS RESEARCH

Stringent environmental regulations and the increased environmental concern will throw the secondary aluminium industry into chaos unless financially viable alternatives are found to deal with black and white dross, and diverting them from disposal in landfill site. Furthermore, a greater understanding is needed of the environmental impact of landfilling these residues. Other countries legislative and environmental authorities agree that pressure should be placed on the industry to find alternatives to landfill[2]. There are some secondary aluminium producers in UK who currently recycle white dross, but there is no recycler of black dross in the UK. The aluminium industries intend to transform the black dross tailings from landfill waste into a raw material source. The chief objectives of this project are to eliminate the practice of landfilling and to generate viable revenues.

## 1.6. SCOPE OF THIS THESIS

The purpose and objectives of the work described in this thesis and all the analytical techniques used throughout the work have been described in this introductory chapter. In Chapter 2 the black dross samples have been thoroughly characterised in order to understand the physical and chemical nature. Chapter 3 focuses on the environmental impact of the black dross. It provides a simulation analysis to understand the problems of landfilling. Chapter 4 examines the uses of black dross. It details research into converting the black dross into value-added products or material and the economic analysis. Finally, chapter 5 summarises the main findings of the research and draws the research together in a broader environmental and economic perspective.

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# CHAPTER TWO

# PHYSICAL AND CHEMICAL CHARACTERISATION OF ALUMINIUM BLACK DROSS

## 2.1. INTRODUCTION

Recycling of aluminium is one of the major successes in material recycling. The secondary aluminium industry has played a large part of this success. The punishment for recycling aluminium is the resulting black dross or salt cake residue remaining at the end of the process. It is well known that during aluminium recovery some part of the aluminium is converted into oxides that are removed by skimming before casting. During skimming however, a lot of aluminium remains entrapped between the oxide particles, although salts with low melting points are utilized to minimise metal loss. Up to ten percent of aluminium production can be lost to dross. Black dross consists of a heterogeneous mixture of aluminium oxides, metallic aluminium and chlorides and fluorides of potassium, calcium and sodium. It typically has a high salt content and is chemically active due to concentrations of various aluminium carbides and nitrides[1]. The total aluminium content in black dross is about five percent by mass and there is to date no commercially viable method of recovering this aluminium. World-wide, millions of tonnes of this dross dust is produced every year and almost all of this is landfilled by the dross reclamation industries, creating potential contamination problems. The research work described in this thesis seeks intends to process the black dross into harmless non-reactive soil material by recycling the high salt content and reclaiming the valuable aluminium.

In Chapter 1 it was reported that aluminium scrap is generally melted in a rotary furnace under low melting point salt fluxes, e.g., NaCl + KCl, with some fluorides and $CaCl_2$ to improve fluidity and separation of impurities from the melt to the slag. Therefore, the dross residue consists of a huge amount of salt mixture. Currently there is no viable method available to reclaim this salt.

Depending on the types of aluminium alloys used in the secondary recycling furnace, the occurrence of metals will differ from dross to dross. Some salty dross may not contain any other metals apart from aluminium and its compounds (e.g. oxide, nitride, carbide, silicate etc.), whereas other dross may contain a mixture of different elements. Sometimes during the remelting stage, alloying ingredients such as Mn, Ni, Zn, Ti, Cr etc., are also added to impart a specifically desired physical property to the metal (aluminium). Thus, trace or measurable amount of these elements can be found in the dross depending on the smelter.

There are a number of reports in the literature detailing the composition of black dross (discussed in Chapter 1), but there are no reports in the literature on the physical and chemical characteristics of black dross. In order to process the dross residue, it is extremely important to analyse its physical and chemical behaviour. In this chapter detailed research on the physical and chemical characteristics of black dross is presented.

## 2.2. METAL SEPARATION TECHNOLOGY

### 2.2.1.Particle Size Analysis[2]

Particle size analysis is used extensively in industries separating and processing minerals. It is of great importance in determining the quality of grinding and in establishing the degree of liberation of the values from the gangue at various particle sizes. In the separation stage, size analysis of the product is used to determine the optimum size of the feed to the process for maximum efficiency and to determine the size range at which any losses are occurring in the plant, so that they may be reduced.

#### *2.2.1.1. Particle size and shape*

The primary function of particle analysis is to obtain quantitative data about the size and size distribution of particles in the material. However, the exact size of an irregular particle cannot be measured. In this case, it is desirable to quote the size of a particle in terms of a single quantity, and the expression most often used is the "equivalent diameter". This refers to the diameter of a sphere that would behave in the same manner as the particle when submitted to some specified operation.

Several equivalent diameters are commonly encountered. For example, the Stokes' diameter is measured by sedimentation and elutriation techniques; the projected area diameter is measured microscopically and the sieve aperture diameter is measured by means of sieving. The last refers to the diameter of a sphere equal to the width of the aperture through which the particle just passes. If the particles under test are not true spheres and they rarely are in practice, this equivalent diameter refers only to their second largest dimension. In Table-2.1 more common methods of size analysis, together with their effective size ranges, are listed.

**Table-2.1. Some methods of particle-size analysis[2]**

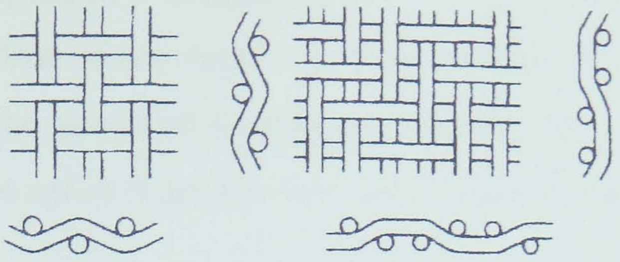
| Method | Approximate useful range (μm) |
|---|---|
| Test sieving | 100 000-10 |
| Elutriation | 40-5 |
| Microscopy (optical) | 50-0.25 |
| Sedimentation (gravity) | 40-1 |
| Sedimentation (centrifugal) | 5-0.05 |
| Electron microscopy | 1-0.005 |

In the current research work, test sieve analysis was undertaken. Test sieving is the most widely used method for particle size analysis. It covers a very wide range of particle size, this range being the one of the greatest industrial importance.

### *2.2.1.2. Test sieves*

Sieve analysis is one of the oldest methods of size analysis and is accomplished by passing a known weight of sample material successively through finer sieves and weighing the amount collected on each sieve to determine the percentage weight in each size fraction. Sieving is carried out with wet and dry materials and the sieves are usually agitated to expose all the particles to the openings.

Test sieves are designated by the nominal aperture size, which is the nominal central separation of opposite sides of a square aperture or the nominal diameter of a round aperture. A variety of sieve aperture ranges are currently used, the most popular being the German Standard, DIN 4188; ASTM standard, E11; the American Tyler series; the French series, AFNOR; and the British standard, BSS 410. Until relatively recently woven-wire sieves were designated by a mesh number, which referred to the number of wires per inch, which is the same as the number of square apertures per inch. Wire-cloth screens are woven to produce nominally uniform square apertures within required tolerance. Wire cloth in sieves with nominal aperture of 75 μm and greater are plain woven, while those in cloths with apertures below 63 μm may be twilled (Figure-2.1). Standard test sieves are not available with aperture sizes smaller than 37 μm. Micromesh sieves are available in aperture sizes from 5 μm to 150 μm, and are made by electroforming nickel in square and circular mesh.



(a) Plain weave (b) Twilled weave

**Figure-2.1. Weaves of wire cloth[2]**

### *2.2.1.3. Testing methods*

The general procedures for test sieving are comprehensively covered in BS 1796. Machine sieving is almost universally used as hand sieving is long and tedious, and its accuracy depends to a large extent on the operator.

The sieves chosen for the test are arranged in a stack, or nest, with the coarsest sieves on the top and the finest at the bottom. There is a pan attached to the finest sieve to receive the final undersize and a lid is placed on top of the coarsest sieve to prevent escape of the sample.

The material to be tested is placed in the uppermost, coarsest sieve, and the nest is then placed in a sieve shaker, which vibrates the material in a vertical plane (Figure-2.2), and, on some models, a horizontal plane. The duration of screening can be controlled by an automatic timer. During the shaking, the undersize material falls through successive sieves until it is retained on a sieve having apertures that are slightly smaller than the diameter of the particles. In this way the sample is separated into size fractions. One major problem with this technique is "blinding" in the finer mesh where the near size irregular particles get blocked during passing, which reduces the effective area of the sieving medium.

**Figure-2.2. Sieve shaker (Model- EFL 2000/2)**

After the required time, the nest is taken apart, and the amount of material retained on each sieve weighed. Most of the near-size particles which block the openings can be removed by inverting the sieve and tapping the frame gently, or may be brushed gently with a soft brass wire or nylon brush without damaging the nest.

### 2.2.2. Hydrometallurgical Process – Leaching[3]

Leaching is the process of extracting a soluble constituent from the solid by means of solvent. In extractive metallurgy, leaching is the process of dissolving a certain mineral from an ore or a concentrate, or dissolving certain constituents from metallurgical products such as calcines, mattes, scrap alloys, anodic slimes etc. In preparation for leaching, the sample is usually reduced to a small size by crushing and grinding; in some cases chemical treatment may be necessary to render the sample to its optimum state for recovery. For example, zinc sulphide and cobalt sulphide are insoluble in most solvents, but with an oxidising roast they can be converted to water-soluble sulphates, and roasting the ore with salt can convert the metallic material to a water soluble chloride. The material selected for a leaching process is usually a low-grade ore, but in some instances may be concentrates, calcines, sulphide, scrap alloys etc.

The leaching of low-grade ore is a large scale operation and requires large volumes of solvent and great quantities of ore. The solvent must be inexpensive and capable of being cheaply regenerated. If the ore is concentrated, the solvent or reactant costs are not too significant because of the high metallic yield of the concentrate, and more expensive leachants can be used.

Leaching is an extensive and a cheap method employed by industry for the extraction of metals, and was applied in this work as the method to determine leachability of black dross.

#### *2.2.2.1. Leaching Agents*

The choice of leaching agent depends upon many factors:

- Chemical and physical character of the material to be leached.
- Cost of the reagent.
- Corroding action of the reagent and consequently the materials of construction.
- Selectivity for the desired constituent to be leached.

- Ability of leaching agent to be regenerated.

The selectivity of a leaching agent towards a particular mineral in an ore depends on[3]:

*1. Concentration of leaching agent:* In some cases, little is to be gained in leaching a mineral by increasing the concentration of the leaching agent. For example, in acid leaching of copper oxide ores, acidity control is used to prevent the dissolution of undesirable minerals.

*2. Temperature:* Sometimes an increase in temperature has little effect on increasing the leaching efficiency of the desired mineral, but has a marked effect on increasing the level of impurities. In leaching copper oxide ores at Weed Heights, Nevada during the summer, the leach solution is circulated over a cooling tower to keep the solution temperature at $29.5^0$C. Very little increase in copper leaching efficiency is noted above this temperature, but there is a marked increase in impurity level.

*3. Contact time:* Extended contact period between the solvent and the ore may also result in an increased percentage of impurities in solution. For example, copper oxide mineral are usually dissolved first from an ore when contacted with dilute sulphuric acid but in iron and aluminium minerals dissolution increases with contact time

*4. Agitation:* Leachability of solid material in solution may increase with agitation. Appropriate agitation allows better contact between solid and liquid and therefore, better reaction. Agitation may occur by mechanical force such as stirring or by material force where liquid moves into different stationary solid phases, or the both phases may occur at the same time.

The following leaching agents are in common use[3]:

**Water**

Water alone is used to leach calcines produced by sulphating or chlorodising roasting, such as the leaching of zinc sulphate or treated pyrite cinder, and in the leaching of $Re_2O_7$ from flue dusts in $MoS_2$ roasting. Water in the presence of air or oxygen under pressure and at about $150^0$C can dissolve sulphides, converting them to sulphates.

**Aqueous Salt Solutions**

A number of solutions of inorganic compounds have been used in leaching. These include:

1. Ferric sulphate for leaching sulphide minerals
2. Sodium carbonate for leaching uranium ores
3. Sodium chloride for leaching $PbSO_4$
4. Sodium cyanide for leaching gold and silver from their ores.
5. Sodium sulphide for leaching sulphide minerals, forming soluble polysulphide
6. Sodium thiosulphate for leaching silver chloride produced by salt roasting of ores
7. $NH_3/NH_4CO_3$ for leaching Co concentrates
8. Sodium cyanide for leaching gold ores

**Acids**

Sulphuric acid is an important leaching agent. It is the cheapest acid, with only minor corrosion problems encountered with its use, and it is effective in solubilising ores. It is used either dilute, concentrated, or sometimes mixed with hydrofluoric acid. In many cases, spent acid from electrolytic processes is adjusted to the required concentration and used. Oxidised ores are readily soluble in dilute sulphuric acid.

In concentrated hydrochloric acid, the majority of metals can exist as soluble anionic chloride complexes. Separation of one metal from another is achieved by utilising the variations in stability of each metal complex and its solubility with varying acid concentration.

Sulphurous acid is finding new applications for leaching some ores, including low - grade manganese types. Aqua regia is used for leaching native platinum ores, and in the refining of gold and silver.

**Bases**

Sodium hydroxide is used for dissolving aluminium from bauxite, for opening monazite sand, and for leaching wolframite and scheelite ores. Ammonium hydroxide is used for extracting metals such as copper and nickel that form soluble amines from their ores.

Leaching by bases has the following advantages; (a) negligible corrosion problems; (b) suitability for ores containing carbonate gangue; (c) more selectivity, since iron oxides will not be leached.

#### *2.2.2.2. Types of leaching*[4]

(i) Basic leaching – where solid is leached (dissolved) in appropriate aqueous media with temperature control and proper agitation.

(ii) Countercurrent leaching – where solvent and solid are mixed, allowed to approach equilibrium, and the two phases are separated. Liquid and solid move countercurrently to the adjacent stages. The solvent phase called the extract, becomes more concentrated as it contacts in a stagewise fashion the increasingly solute-rich solid. The raffinate becomes less concentrated in soluble material as it moves toward the fresh solvent stage. Countercurrent stagewise leaching processes are frequently used in industrial leaching because they can deliver the highest possible concentration in the extract and can minimise the amount of solvent needed.

(iii) Heap leaching – where the solid is in a stationary heap and the solvent percolates through the solid. It is also a type of countercurrent leaching which occurs in nature, eg., the impurities dissolved by percolating rainwater from the naturally enriched bauxite deposits. Landfilling toxic waste material is hazardous due to heap leaching. Heap leaching is also used in recovering metals from their ores. Bacterial leaching is first used to oxidise sulphide minerals. Cyanide solution is then used to leach the metal from the mineral heap.

## 2.3. EXPERIMENTAL PROCEDURE

A selection of 15 different black dross tailing samples, produced from different secondary aluminium furnaces, were used in this research work. Differences (particle size; content of salt, aluminium, alumina and other impurities) between the dross samples were negligible. Therefore, in this chapter, the results will be presented as general black dross in order to minimise the extensive list of results. To test the reproducibility, all experiments were repeated three times, and the results are presented as an average. Standard deviation (written as *sdv*) was calculated for the dominant elements present within the washed black dross.

## 2.3.1. Chemical Composition of Aluminium Dross

XRF and XRD techniques were used to determine qualitatively the distribution of metals and the compounds in the black dross.

## 2.3.2. Quantification and characterisation of salts in black dross

### *2.3.2.1. Batch Washing*

In this washing procedure black dross was washed three times.

First wash - 500g of black dross was placed in a 3-litre plastic vessel. One litre of de-ionised water was introduced and the mixture stirred slowly using a plastic spatula at room temperature, continuously, for 15min. At the end of stirring the dross solution was filtered using a filter paper (Whatman 2, medium/fine retention and medium flow rate, 320mm) and the brine solution (the filtrate) was collected in a 1-litre Pyrex glass beaker. The Pyrex beaker containing the filtrate was then placed on a hot plate and the brine solution was evaporated to obtain crystalline salt. The salt was left in an oven at $100^0$C overnight to dry completely. After drying, the hot salt was cooled and weighed.

Second wash - The wet black dross from the filtration above was replaced in the same plastic vessel and a further 500ml de-ionised water was introduced to the dross for a second wash. The dross was washed and the salt was collected and weighed using the procedure described above.

Third wash- The wet dross was washed again using the procedure described above, for the third time with 500ml de-ionised water to make sure that there was no salt present in the dross. The salt was weighed and collected for a third time. At the end of washing, the wet black dross was dried in the oven at $100^0$C overnight. After drying the dross was allowed to cool and then weighed. XRF and XRD analyses of the three salt samples and the washed black dross were made.

The sodium and potassium contents in the salt were determined. 2g of salt was dissolved in 250ml de-ionised water. After complete dissolution, the solution was analysed by AAS.

### *2.3.2.2. Countercurrent washing (leaching)*

The above batch washing procedure is a very simple and reliable method to wash black dross and remove the salt content. The major problem with this method is that it needs too much heat and water and therefore, is very expensive and energy intensive. As Great Britain has a temperate climate, it is not possible to evaporate the large amounts of salt water using natural solar heating; so heat needs to be generated in other ways.

The aim of this experiment is to design a method to wash black dross that uses no heat to evaporate the brine solution, and also to minimise water consumption.

The counter-current washing or leaching process required four sinter-glass filter columns, operating in series. The columns were held by clamps fixed to retort stands. Figure-2.3 shows a schematic diagram of a complete set up of a single column and Figure-2.4 shows the set up of the whole procedure in the laboratory. The four columns are labelled as A, B, C and D in Figure-2.5a. Each column was filled with 500g of black dross. The taps at the base of the columns were closed. One litre of de-ionised water was introduced to the first column A and the contents in the column were stirred for 15 minutes using a mechanical stirrer (Figure-2.3). The resulting solution was removed from the column A through the sinter-glass filter (porosity-1). The solution was then introduced into the second column B, and the contents in the column were stirred for 15 minutes. The solution was again removed from the base of the second column B. This process was repeated with the remaining two columns C and D.

After passing the solution through the four columns, the resulting solution was well saturated with salt and crystallised at room temperature over a period of two weeks. Unlike the batch washing procedure (Section2.3.2.1), there was no need for the oven-drying process in order to dry the salt product in the counter-current method.

A second aliquot of 1 litre of distilled water was introduced to the column A, and the leaching process was repeated. The final salt solution was again saturated. It had been established during the batch washing process (Section-2.3.2.1) that 2 litres of distilled water was sufficient to remove the salt from a 500 g sample of dross. Therefore, column A was completely washed after the second leaching phase, but column B, C and D were receiving solutions that were already concentrated with salt from the previous columns, they were not completely washed after the second stage.

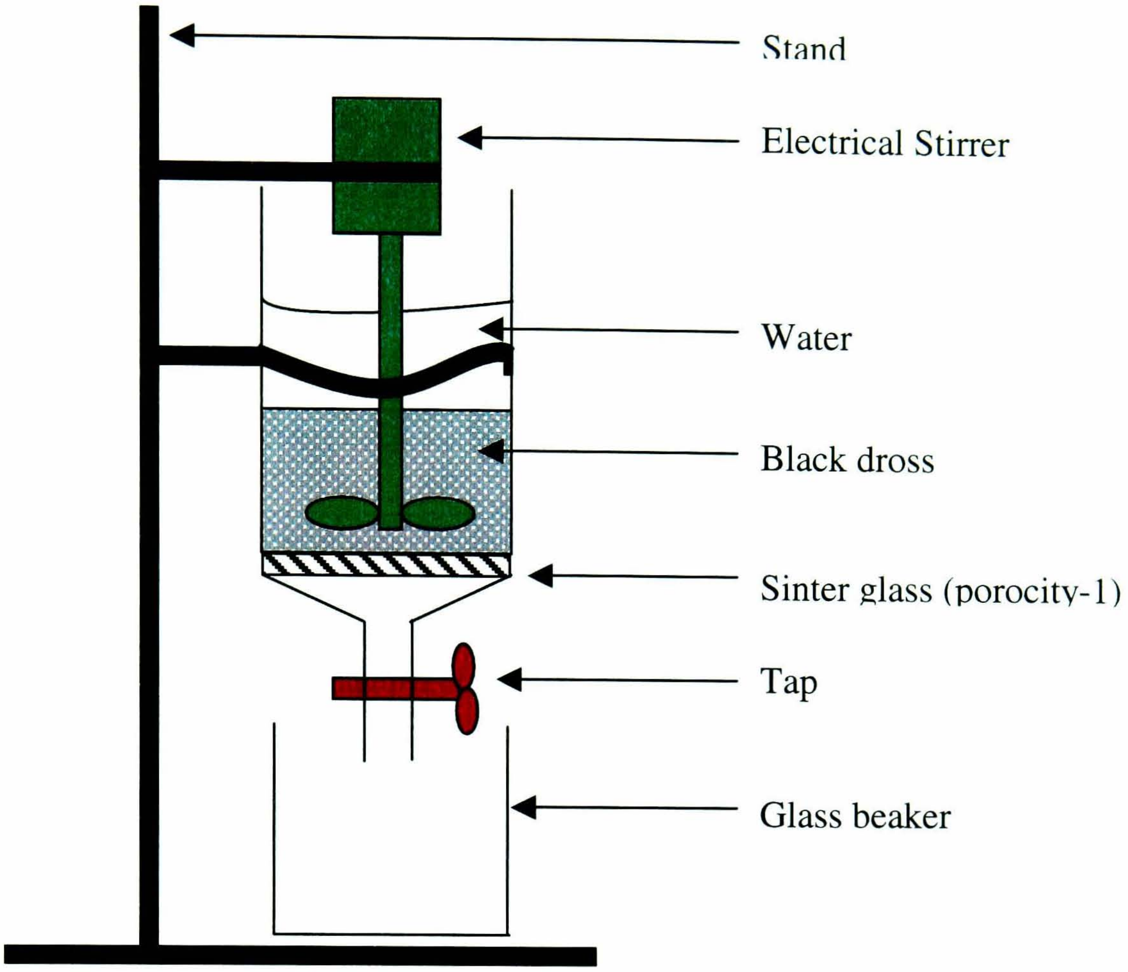


Figure-2.3. A schematic diagram of complete set up of a column.

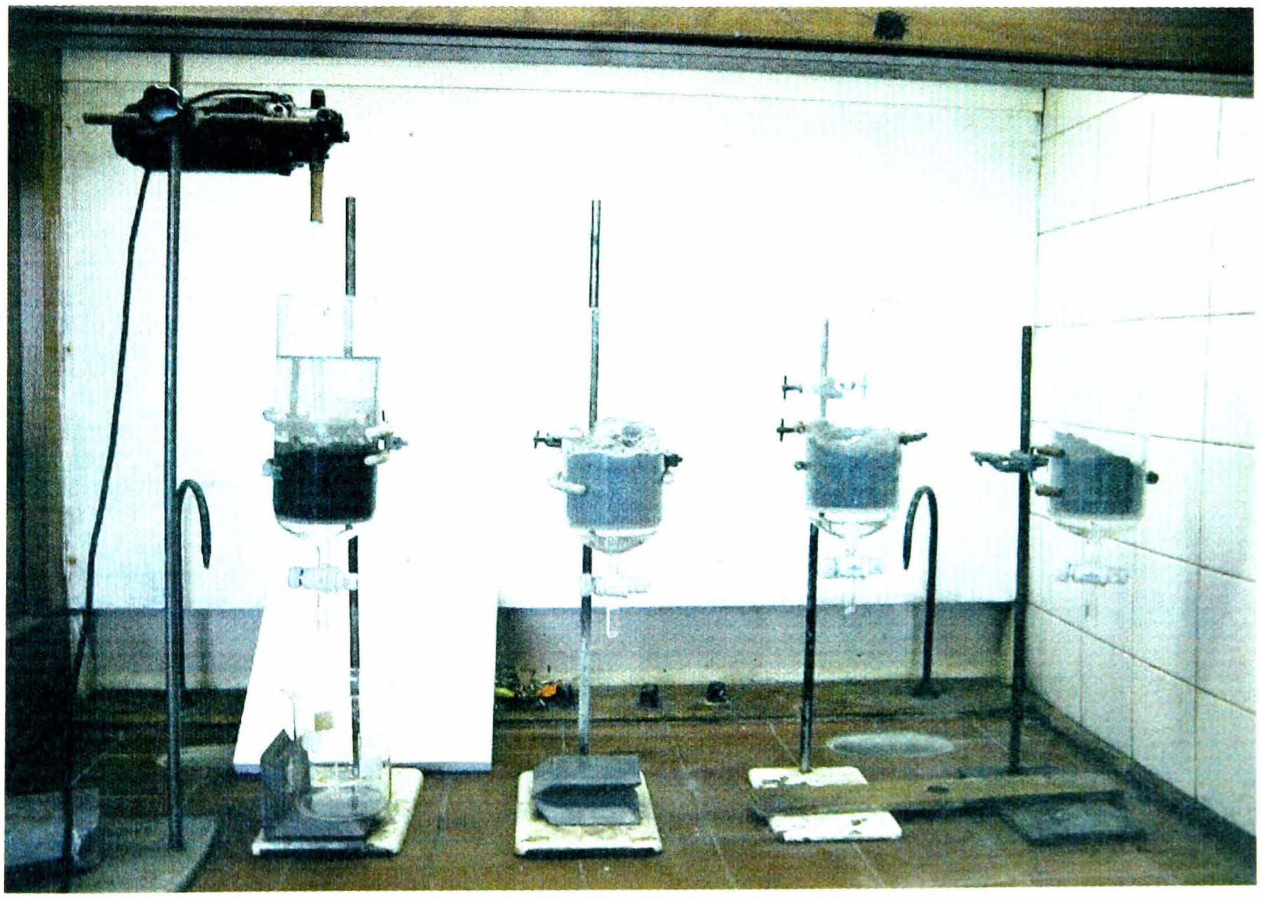


Figure-2.4. A laboratorial set up of countercurrent leaching process.

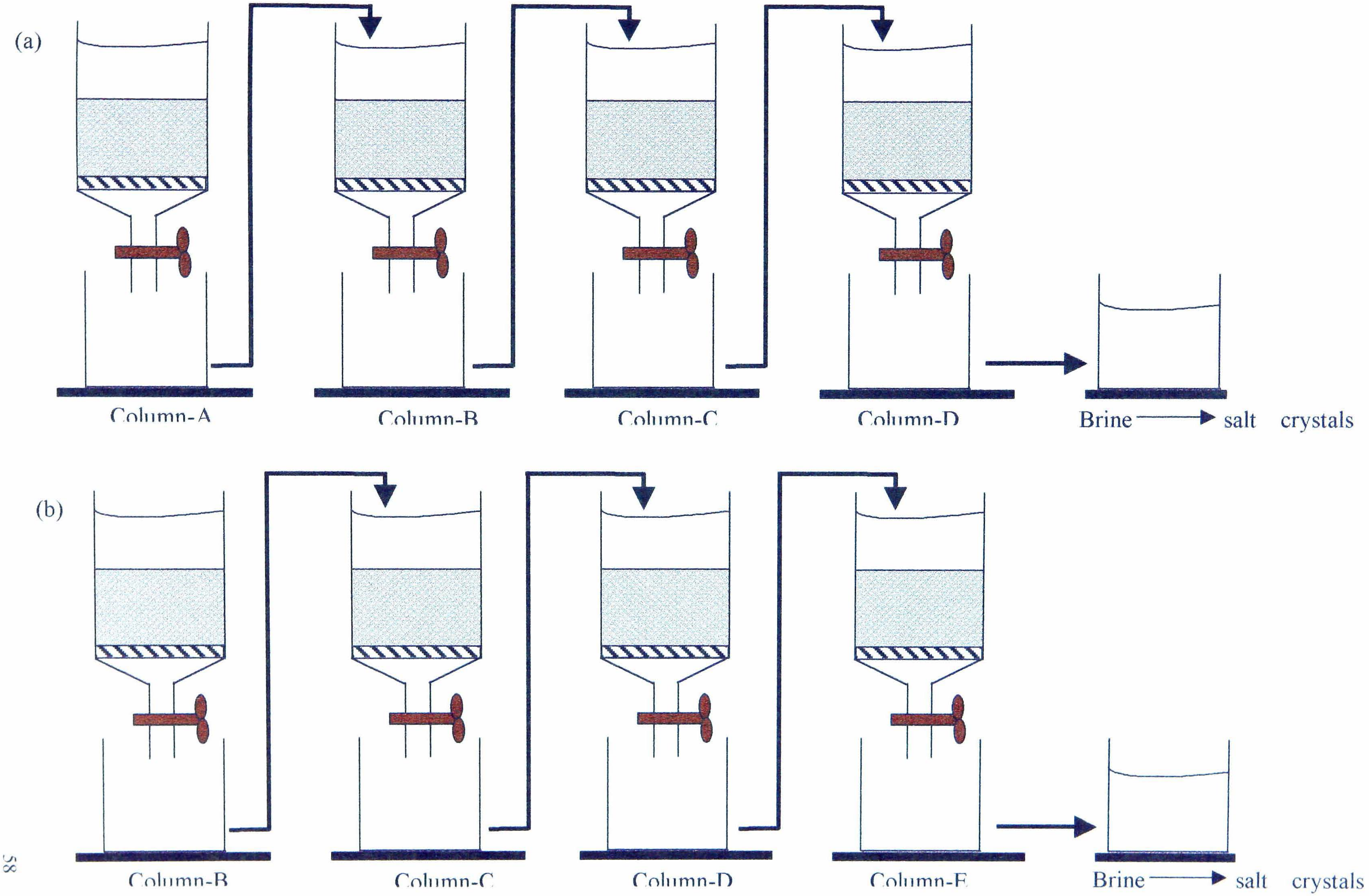


**Figure-2.5. (a) A schematic diagram of countercurrent leaching procedure. (b) Replacement of Column-A to Column-B and added a new Column-E**

The next step was to remove the washed dross from the column A. This column was then filled with 500 g of unwashed black dross. Column B, C and D, which contained dross with increasing amounts of salt, were promoted so that column B was placed at the head of the leaching chain (Figure-2.5b). The column containing the fresh (unwashed) dross was placed at the end of the leaching process and labelled as column E.

The washing process was repeated, with the first column removed each time. The dross from the first column was dried and weighed to check the final dry weight. It was also analysed by XRD to confirm the amount of salt remaining. Dry weights of the salts collected from every wash were also recorded and analysed by XRF and XRD.

### 2.3.3. Leachability studies to assess the solubility of the Black Dross

All experimental work was carried out in a fume cupboard and was done in triplicate. Washed black dross, i.e., no salt content, was used in these experiments as the salt may have been saturated in the solution and interfered with the experiments.

#### *2.3.3.1. De-ionised water*

2g of black dross sample was introduced to each of four 500ml flange flasks followed by 100ml of de-ionised water. The mixtures were stirred at 4-5rpm on a magnetic stirrer at room temperature ($23^0$C), $40^0$C, $80^0$C, and $100^0$C for 3 hours. Figure-2.6a shows a schematic diagram of the set up of a flange flask and Figure-2.6b shows a set up of the flange flask as used in the laboratory. At the end of leaching, the solutions were gravity filtered (Filter paper- Whatman 542, hardened, ashless, 150mm) and the residue was washed and dried in an oven at $100^0$C overnight. After drying the residue was weighed to determine the percentage solubility of black dross and characterised by XRF. The solutions were analysed using AAS to determine the concentration of the aluminium metal and to assess the degree of leachability.

#### *2.3.3.2. Hydrochloric acid*

The above procedure was repeated using 1M, 2M, 3M and 4M hydrochloric acid as the leaching media in place of de-ionised water.

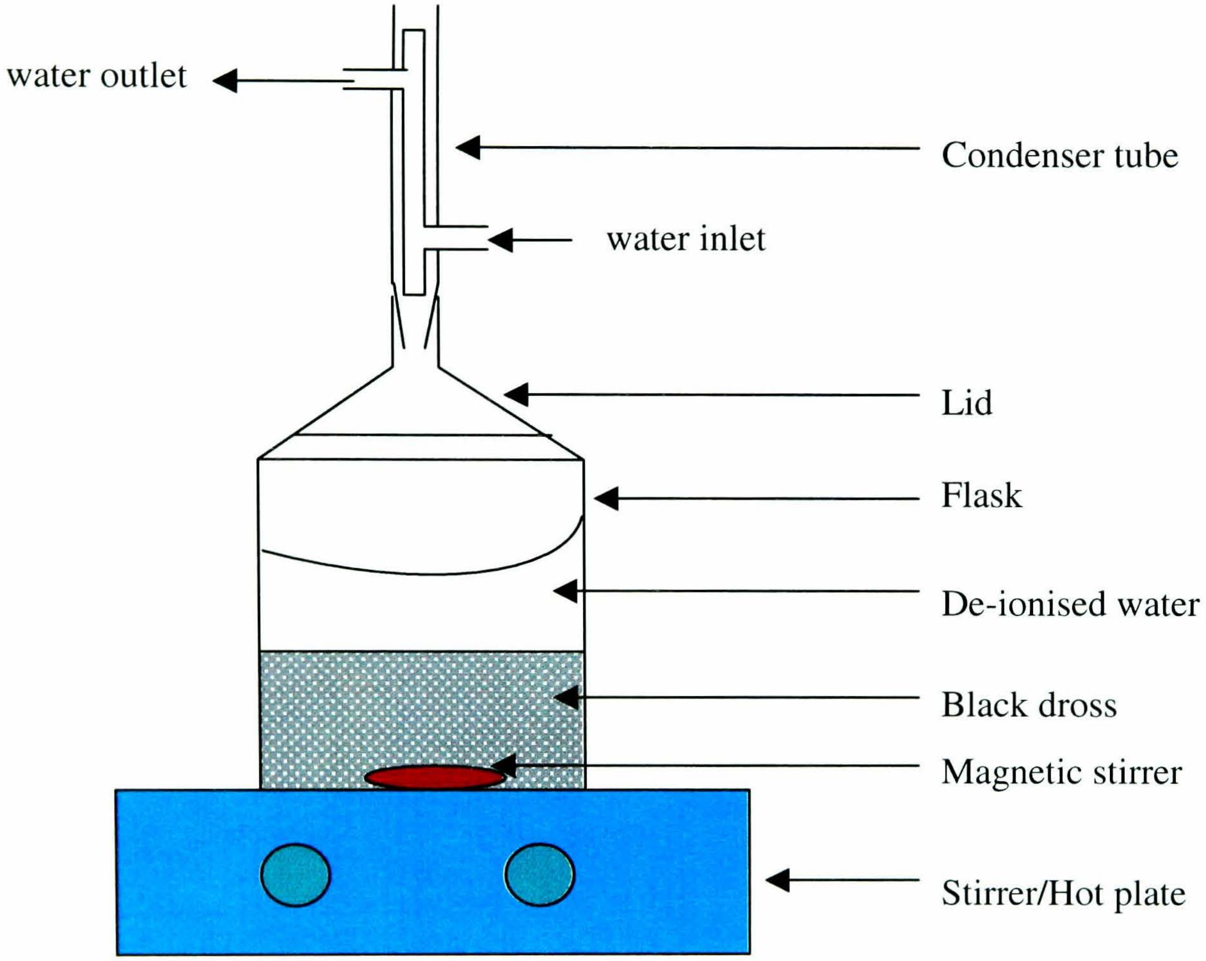
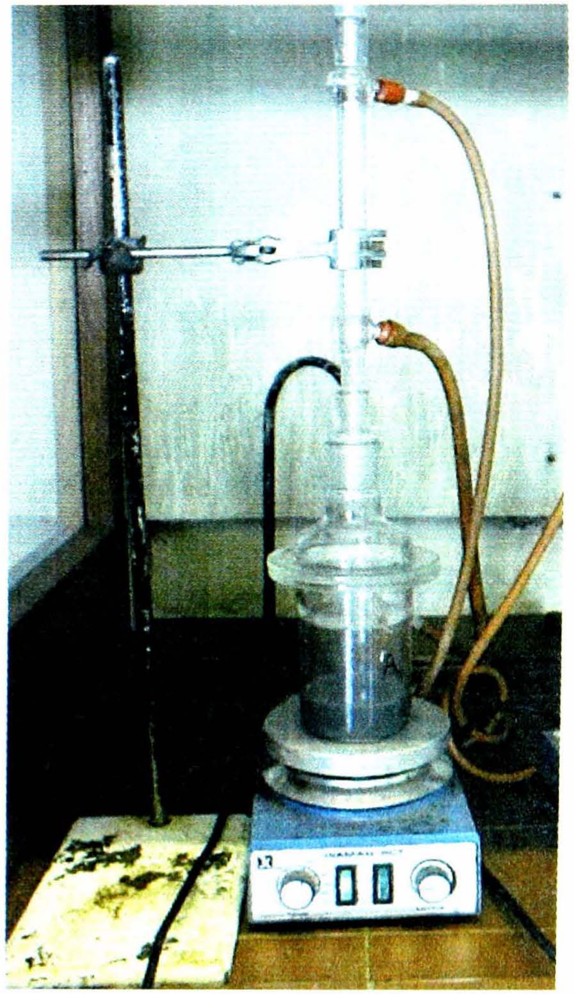


Figure-2.6 (a). A schematic diagram of a flange flask set up



(b) A laboratorial set up of flange flask

#### *2.3.3.3. Nitric acid*

The above procedure was repeated with 1M, 2M, 3M and 4M Nitric acid as the leaching media.

#### *2.3.3.4. Sulphuric acid*

The above procedure was repeated with 1M, 2M, 3M and 4M sulphuric acid as the leaching media.

#### *2.3.3.5 Sodium hydroxide*

The above procedure was repeated with 1M, 2M, 3M and 4M sodium hydroxide as the leaching media.

### 2.3.4. Screening test

#### *2.3.4.1. Determination of particle size distribution*

Unwashed black dross or as received black dross was used in these experiments.

Black dross is a mixture of different particle sizes. Six different mesh size sieves (Endecotts Ltd.) were used for screening the black dross to determine the different particle size distributions. The descriptions of the sieves are given below in Table-2.2.

**Table-2.2. The description of sieves used.**

| Aperture | Mesh # | Frame metal | Mesh metal |
|---|---|---|---|
| 4,000 μm | 4 | Brass | Brass |
| 2,360 μm | 7 | Brass | Brass |
| 1,180 μm | 16 | Brass | S/Steel |
| 850 μm | 20 | Brass | S/Steel |
| 600 μm | 30 | Brass | S/Steel |
| 500 μm | 35 | Brass | S/Steel |

100g of as supplied (unwashed) black dross was sieved for half an hour. After sieving each particle size was collected and weighed to determine the particle size distribution.

#### *2.3.4.2. Determination of aluminium and salt distribution in each particle size*

In four different flange flasks, 2g of black dross from each particle size distribution was introduced into 100ml of 3M hydrochloric acid. The solution was refluxed for 3 hours at

$100^0$C. At the end of leaching, the solutions were gravity filtered (Filter paper-Whatman 542, hardened, ashless, 150mm) and the residue was washed and dried in an oven at $100^0$C overnight. After drying, the residue were weighed to determine the percentage of solubility of black dross and characterised by XRF. The solutions were analysed using AAS to determine the concentration of the aluminium, sodium and potassium.

## 2.4. RESULTS AND DISCUSSION

### 2.4.1. Chemical Composition of Aluminium Dross (as supplied)

The sample of black dross was analysed by X-ray fluorescence and X-ray diffraction to determine the sample compositions. The X-ray fluorescence spectrum of as supplied black dross shows (Figure-2.7) the presence of aluminium along with the following major impurities: Ca, Cl, Cr, Cu, Fe, K, P, Ti and Zn. These impurities and aluminium are not exposed but entrapped in the salt (NaCl) particles. The XRF spectrum does not show the presence of sodium because the machine cannot detect elements with atomic number below 13.

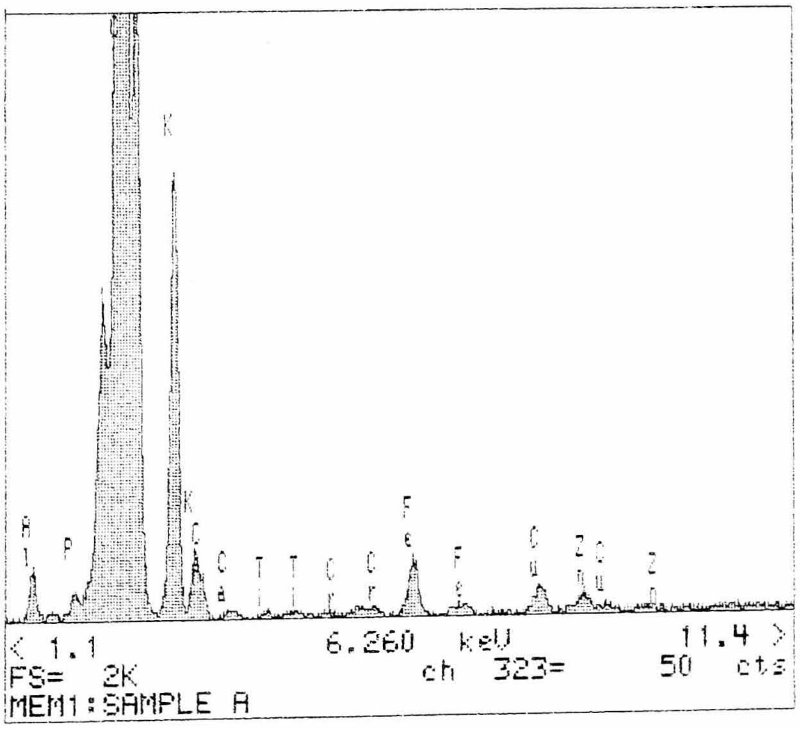
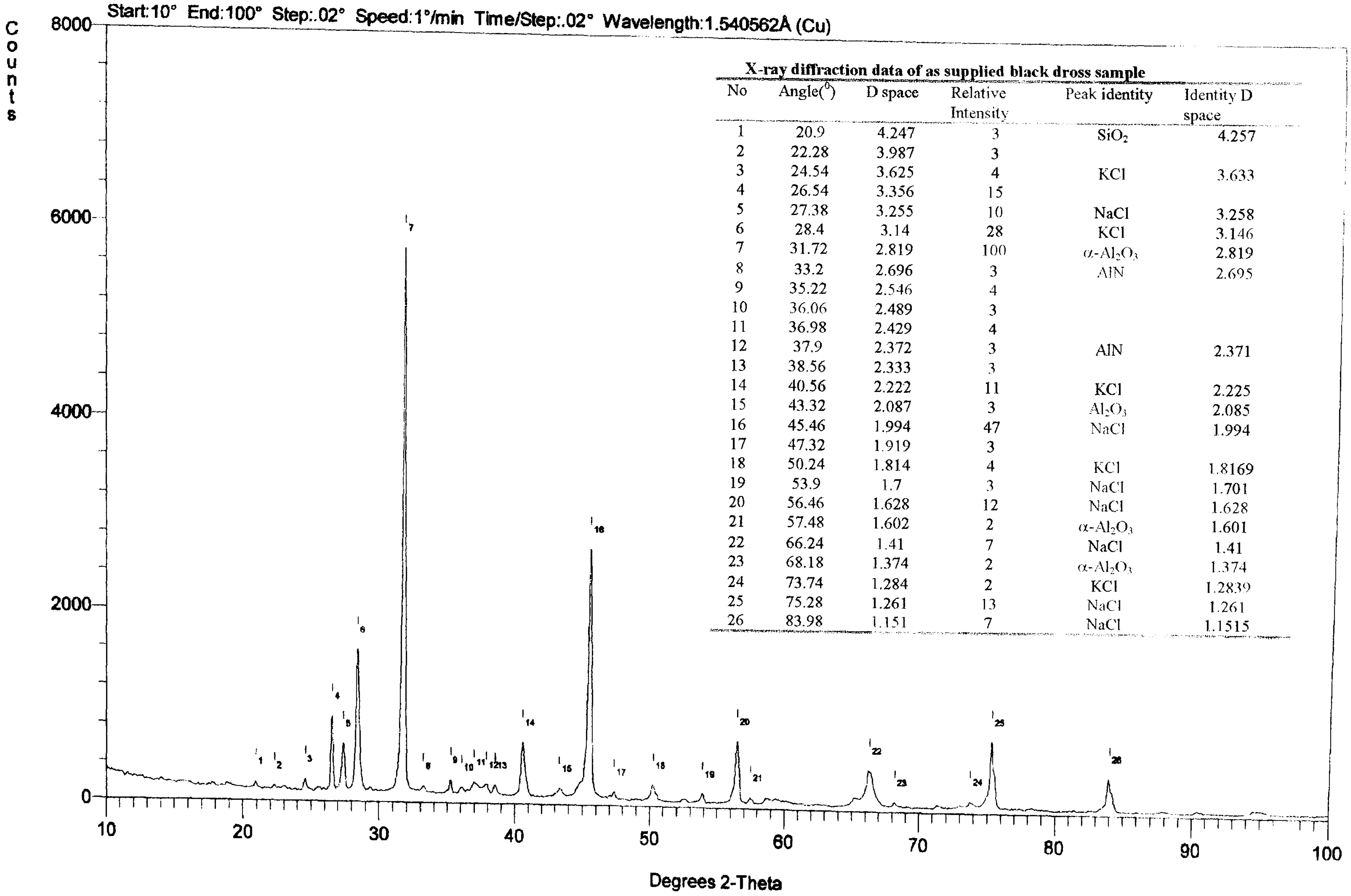


**Figure-2.7. X-ray fluorescence spectrum of as supplied black dross sample.**

Figure-2.8 shows the X-ray diffraction spectrum of the as supplied black dross. The data of the spectrum have been analysed and confirms the presence of the following major compounds:- alumina ($\alpha$-$Al_2O_3$), aluminium nitride (AlN), quartz silica ($SiO_2$), sodium chloride (NaCl) and potassium chloride (KCl). Both XRF and XRD techniques are used



**X-ray diffraction data of as supplied black dross sample**

| No | Angle($^0$) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 20.9 | 4.247 | 3 | $SiO_2$ | 4.257 |
| 2 | 22.28 | 3.987 | 3 | | |
| 3 | 24.54 | 3.625 | 4 | KCl | 3.633 |
| 4 | 26.54 | 3.356 | 15 | | |
| 5 | 27.38 | 3.255 | 10 | NaCl | 3.258 |
| 6 | 28.4 | 3.14 | 28 | KCl | 3.146 |
| 7 | 31.72 | 2.819 | 100 | $\alpha$-$Al_2O_3$ | 2.819 |
| 8 | 33.2 | 2.696 | 3 | AlN | 2.695 |
| 9 | 35.22 | 2.546 | 4 | | |
| 10 | 36.06 | 2.489 | 3 | | |
| 11 | 36.98 | 2.429 | 4 | | |
| 12 | 37.9 | 2.372 | 3 | AlN | 2.371 |
| 13 | 38.56 | 2.333 | 3 | | |
| 14 | 40.56 | 2.222 | 11 | KCl | 2.225 |
| 15 | 43.32 | 2.087 | 3 | $Al_2O_3$ | 2.085 |
| 16 | 45.46 | 1.994 | 47 | NaCl | 1.994 |
| 17 | 47.32 | 1.919 | 3 | | |
| 18 | 50.24 | 1.814 | 4 | KCl | 1.8169 |
| 19 | 53.9 | 1.7 | 3 | NaCl | 1.701 |
| 20 | 56.46 | 1.628 | 12 | NaCl | 1.628 |
| 21 | 57.48 | 1.602 | 2 | $\alpha$-$Al_2O_3$ | 1.601 |
| 22 | 66.24 | 1.41 | 7 | NaCl | 1.41 |
| 23 | 68.18 | 1.374 | 2 | $\alpha$-$Al_2O_3$ | 1.374 |
| 24 | 73.74 | 1.284 | 2 | KCl | 1.2839 |
| 25 | 75.28 | 1.261 | 13 | NaCl | 1.261 |
| 26 | 83.98 | 1.151 | 7 | NaCl | 1.1515 |

Figure-2.8. X-ray diffraction spectrum of as supplied black dross for qualitative, not quantitative analysis. The concentrations of these elements were determined by atomic absorption spectrometry after leaching with acid and base (Section-2.3.3.).

## 2.4.2. Quantification and characterisation of salts in black dross

### *2.4.2.1. Batch Washing*

The data in Table-2.3 shows that the black dross sample contains 47.6% of salt mixture. Almost half of the black dross is salt.

**Table-2.3. Recovery and recycling of salt by washing with distilled water**

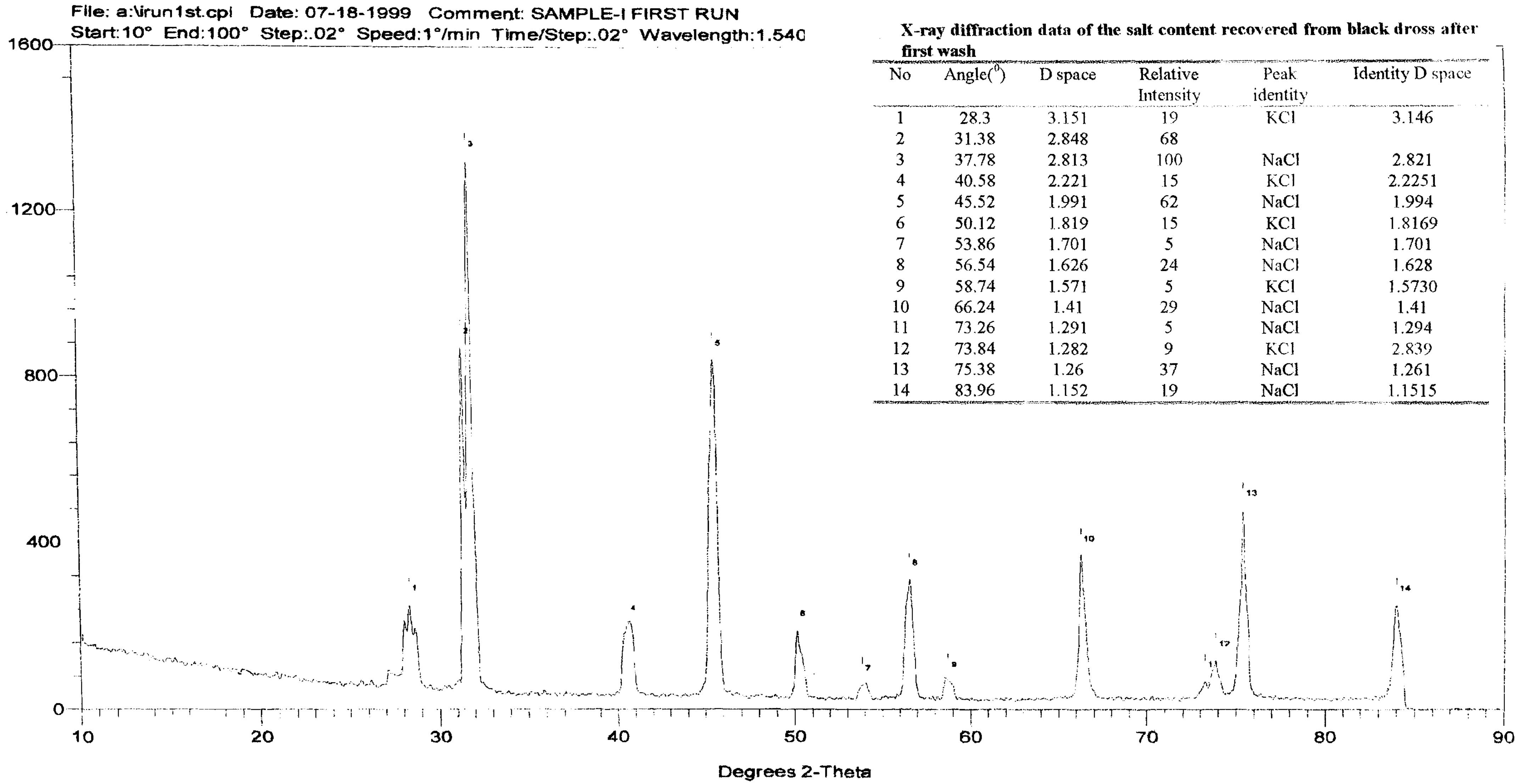
| Weight of black dross(g) | Weight of salt recovered(g) | | | Total weight of salt(g) | Total weight of residue(g) |
|---|---|---|---|---|---|
| | 1st wash | 2nd wash | 3rd wash | | |
| 500 | 188 | 39 | 11 | 238 | 262 |

XRD patterns of the salt recovered from black dross in the three different stages show that this salt is a mixture of sodium and potassium chloride (Figure-2.9a-c). The patterns do not show presence of any other compounds, which confirms the salt is a pure mixture of sodium chloride and potassium chloride without any other impurities. AAS analysis showed that the salt is a mixture of 74% sodium and 26% potassium, (Table-2.4) which is almost the exact amount of salt flux mixture used in the smelter during remelt of the scrap metals (Section 1.3.3). Therefore, the recovered salt can be used in a rotary furnace to recycle white dross.

**Table-2.4. Percentage composition of sodium and potassium in the salt**

| Elements | Sodium | Potassium |
|---|---|---|
| Concentration (mg/l) | 3000 | 1740 |
| moles/l | 0.13 | 0.044 |
| % | 74 | 26 |

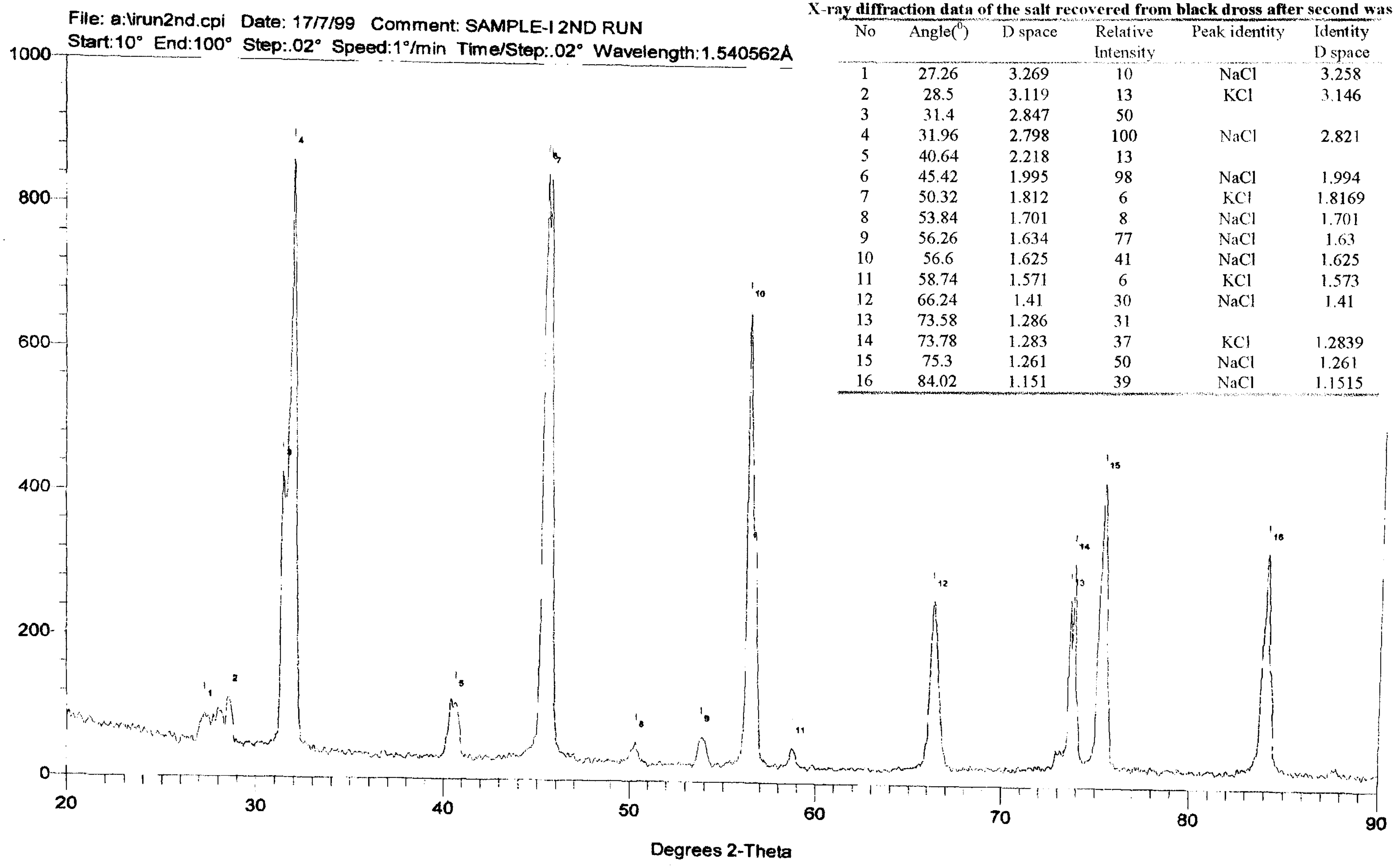
XRF pattern of the washed black dross (Figure-2.10) gives no evidence of the presence of chloride and potassium elements, which confirms that the washing step will remove almost 100% salt content. These results were also confirmed in the XRD pattern of the washed black dross (Figure-2.11). Comparison of the XRD pattern of the unwashed black dross sample (Figure-2.8), and the washed black dross residue (Figure-2.11)



**X-ray diffraction data of the salt content recovered from black dross after first wash**

| No | Angle($^0$) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 28.3 | 3.151 | 19 | KCl | 3.146 |
| 2 | 31.38 | 2.848 | 68 | | |
| 3 | 37.78 | 2.813 | 100 | NaCl | 2.821 |
| 4 | 40.58 | 2.221 | 15 | KCl | 2.2251 |
| 5 | 45.52 | 1.991 | 62 | NaCl | 1.994 |
| 6 | 50.12 | 1.819 | 15 | KCl | 1.8169 |
| 7 | 53.86 | 1.701 | 5 | NaCl | 1.701 |
| 8 | 56.54 | 1.626 | 24 | NaCl | 1.628 |
| 9 | 58.74 | 1.571 | 5 | KCl | 1.5730 |
| 10 | 66.24 | 1.41 | 29 | NaCl | 1.41 |
| 11 | 73.26 | 1.291 | 5 | NaCl | 1.294 |
| 12 | 73.84 | 1.282 | 9 | KCl | 2.839 |
| 13 | 75.38 | 1.26 | 37 | NaCl | 1.261 |
| 14 | 83.96 | 1.152 | 19 | NaCl | 1.1515 |

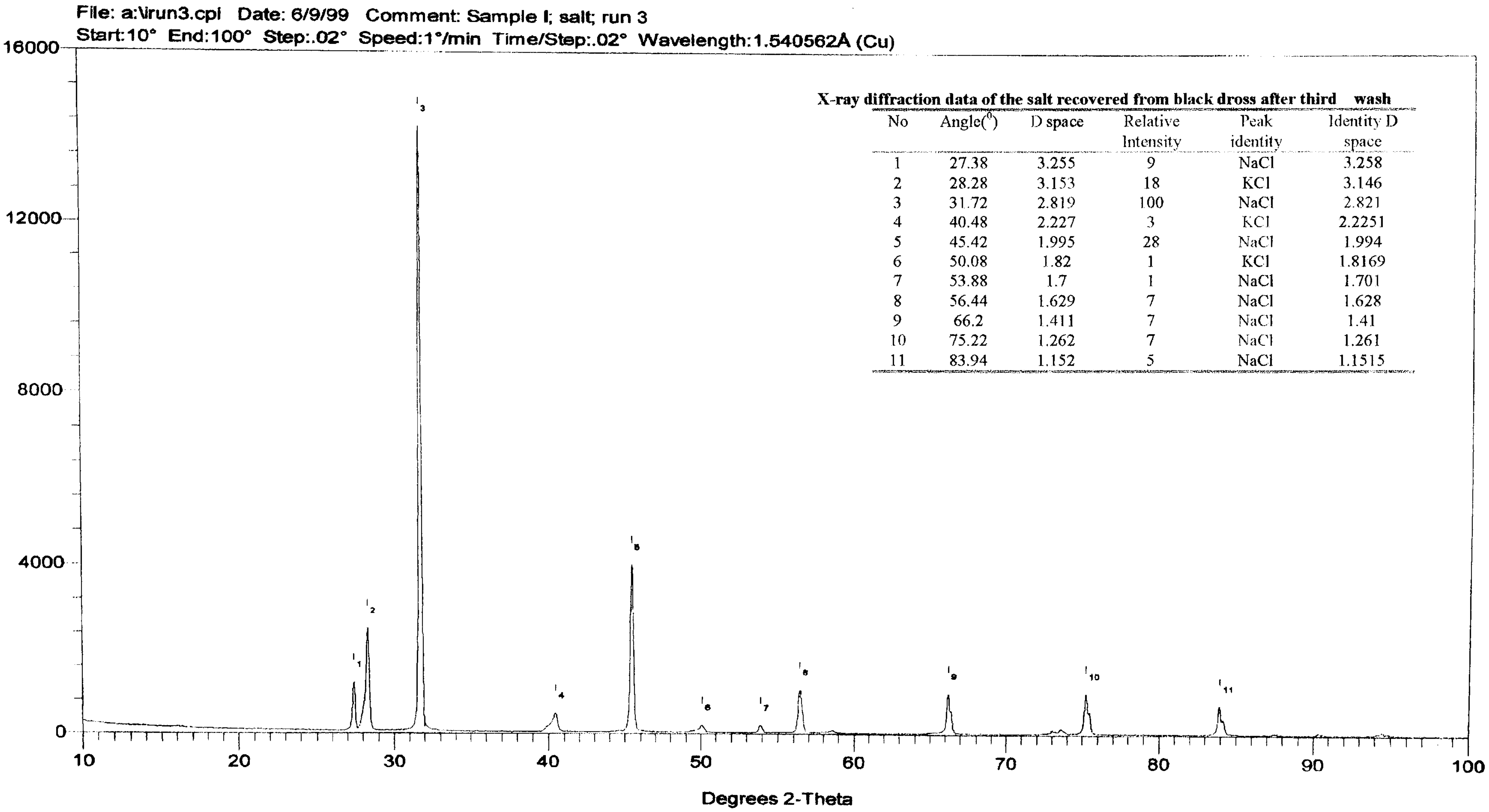
Figure-2.9.a. X-ray diffraction spectrum of the salt recovered from black dross after first wash



**X-ray diffraction data of the salt recovered from black dross after second wash**

| No | Angle($^0$) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 27.26 | 3.269 | 10 | NaCl | 3.258 |
| 2 | 28.5 | 3.119 | 13 | KCl | 3.146 |
| 3 | 31.4 | 2.847 | 50 | | |
| 4 | 31.96 | 2.798 | 100 | NaCl | 2.821 |
| 5 | 40.64 | 2.218 | 13 | | |
| 6 | 45.42 | 1.995 | 98 | NaCl | 1.994 |
| 7 | 50.32 | 1.812 | 6 | KCl | 1.8169 |
| 8 | 53.84 | 1.701 | 8 | NaCl | 1.701 |
| 9 | 56.26 | 1.634 | 77 | NaCl | 1.63 |
| 10 | 56.6 | 1.625 | 41 | NaCl | 1.625 |
| 11 | 58.74 | 1.571 | 6 | KCl | 1.573 |
| 12 | 66.24 | 1.41 | 30 | NaCl | 1.41 |
| 13 | 73.58 | 1.286 | 31 | | |
| 14 | 73.78 | 1.283 | 37 | KCl | 1.2839 |
| 15 | 75.3 | 1.261 | 50 | NaCl | 1.261 |
| 16 | 84.02 | 1.151 | 39 | NaCl | 1.1515 |

Figure-2.9.b. X-ray diffraction spectrum of the salt recovered from black dross after second wash



**X-ray diffraction data of the salt recovered from black dross after third wash**

| No | Angle($^0$) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 27.38 | 3.255 | 9 | NaCl | 3.258 |
| 2 | 28.28 | 3.153 | 18 | KCl | 3.146 |
| 3 | 31.72 | 2.819 | 100 | NaCl | 2.821 |
| 4 | 40.48 | 2.227 | 3 | KCl | 2.2251 |
| 5 | 45.42 | 1.995 | 28 | NaCl | 1.994 |
| 6 | 50.08 | 1.82 | 1 | KCl | 1.8169 |
| 7 | 53.88 | 1.7 | 1 | NaCl | 1.701 |
| 8 | 56.44 | 1.629 | 7 | NaCl | 1.628 |
| 9 | 66.2 | 1.411 | 7 | NaCl | 1.41 |
| 10 | 75.22 | 1.262 | 7 | NaCl | 1.261 |
| 11 | 83.94 | 1.152 | 5 | NaCl | 1.1515 |

**Figure-2.9.c. X-ray diffraction spectrum of the salt recovered from black dross after third wash**

shows the presence of additional compounds. This is because, in the unwashed black dross, aluminium and the other impurities are entrapped in the salts, forming coarse particles. After washing thoroughly with de-ionised water, the coarse particles are broken as the salts are dissolved in water and the entrapped compounds consequently released.

The XRD pattern in Figure-2.11 shows the presence of alumina, aluminium nitride, iron oxides and silica.

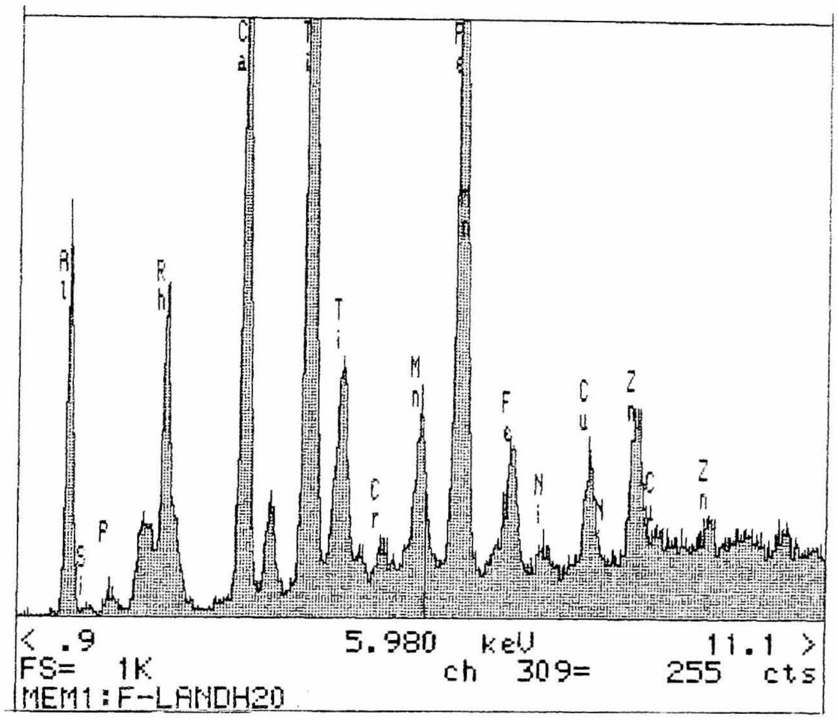


**Figure-2.10. X-ray fluorescence spectrum of washed black dross residue.**

In Industry the conventional recovery of aluminium from white dross is carried out at high temperature in a rotary furnace[5]. During the process, some part of aluminium is converted into oxide that is removed by skimming. However, during skimming a lot of aluminium remains entrapped between the oxide particles. A large surface area of skimming is exposed to the atmosphere and this leads to the following high temperature reactions:

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

at $200^0$C $$2Al + N_2 \longrightarrow 2AlN$$

During the washing of black dross, aluminium nitride reacts with water to produce alumina and ammonia gas. No measurable temperature change was noticed during contact between the dross and water.

$$2AlN + 3H_2O \longrightarrow Al_2O_3 + 2NH_3\uparrow$$

**X-ray diffraction data of washed black dross residue**

| No | Angle($^0$) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 19.04 | 4.657 | 44 | $Fe_3O_4$ | 4.67 |
| 2 | 20.66 | 4.296 | 31 | $SiO_2$ | 4.257 |
| 3 | 25.56 | 3.482 | 43 | $\alpha$-$Al_2O_3$ | 3.479 |
| 4 | 26.62 | 3.271 | 30 | | |
| 5 | 27.24 | 3.138 | 31 | | |
| 6 | 28.42 | 2.827 | 55 | $SiO_2$ | 2.88 |
| 7 | 31.62 | 2.696 | 54 | AlN | 2.695 |
| 8 | 33.2 | 2.552 | 35 | $\alpha$-$Al_2O_3$ | 2.552 |
| 9 | 35.14 | 2.487 | 59 | AlN | 2.490 |
| 10 | 36.08 | 2.433 | 84 | $Fe_3O_4$ | 2.439 |
| 11 | 36.92 | 2.38 | 100 | $\alpha$-$Al_2O_3$ | 2.379 |
| 12 | 37.76 | 2.336 | 67 | $Fe_3O_4$ | 2.335 |
| 13 | 38.5 | 2.222 | 57 | | |
| 14 | 40.56 | 2.087 | 23 | $Fe_2O_3$ | 2.0779 |
| 15 | 43.32 | 2.012 | 54 | $Fe_3O_4$ | |
| 16 | 45.02 | 1.921 | 69 | | |
| 17 | 47.28 | 1.87 | 34 | $SiO_2$ | 1.86 |
| 18 | 48.64 | 1.826 | 22 | AlN | 1.829 |
| 19 | 49.9 | 1.74 | 20 | $\alpha$-$Al_2O_3$ | 1.74 |
| 20 | 52.54 | 1.638 | 28 | $Fe_2O_3$ | 1.6367 |
| 21 | 56.12 | 1.602 | 25 | $\alpha$-$Al_2O_3$ | 1.601 |
| 22 | 57.48 | 1.555 | 45 | AlN | 1.5559 |
| 23 | 59.38 | 1.543 | 41 | $\alpha$-$Al_2O_3$ | 1.546 |
| 24 | 62.28 | 1.49 | 19 | $\alpha$-$Al_2O_3$ | 1.483 |
| 25 | 65.72 | 1.42 | 63 | $SiO_2$ | 1.4189 |
| 26 | 66.48 | 1.405 | 53 | $\alpha$-$Al_2O_3$ | 1.404 |
| 27 | 68.16 | 1.375 | 31 | $\alpha$-$Al_2O_3$ | 1.374 |
| 28 | 71.56 | 1.317 | 16 | AlN | 1.3194 |
| 29 | 78.22 | 1.221 | 17 | $SiO_2$ | 1.2285 |
| 30 | 88.06 | 1.108 | 12 | | |
| 31 | 95.16 | 1.043 | 18 | AlN | 1.0461 |

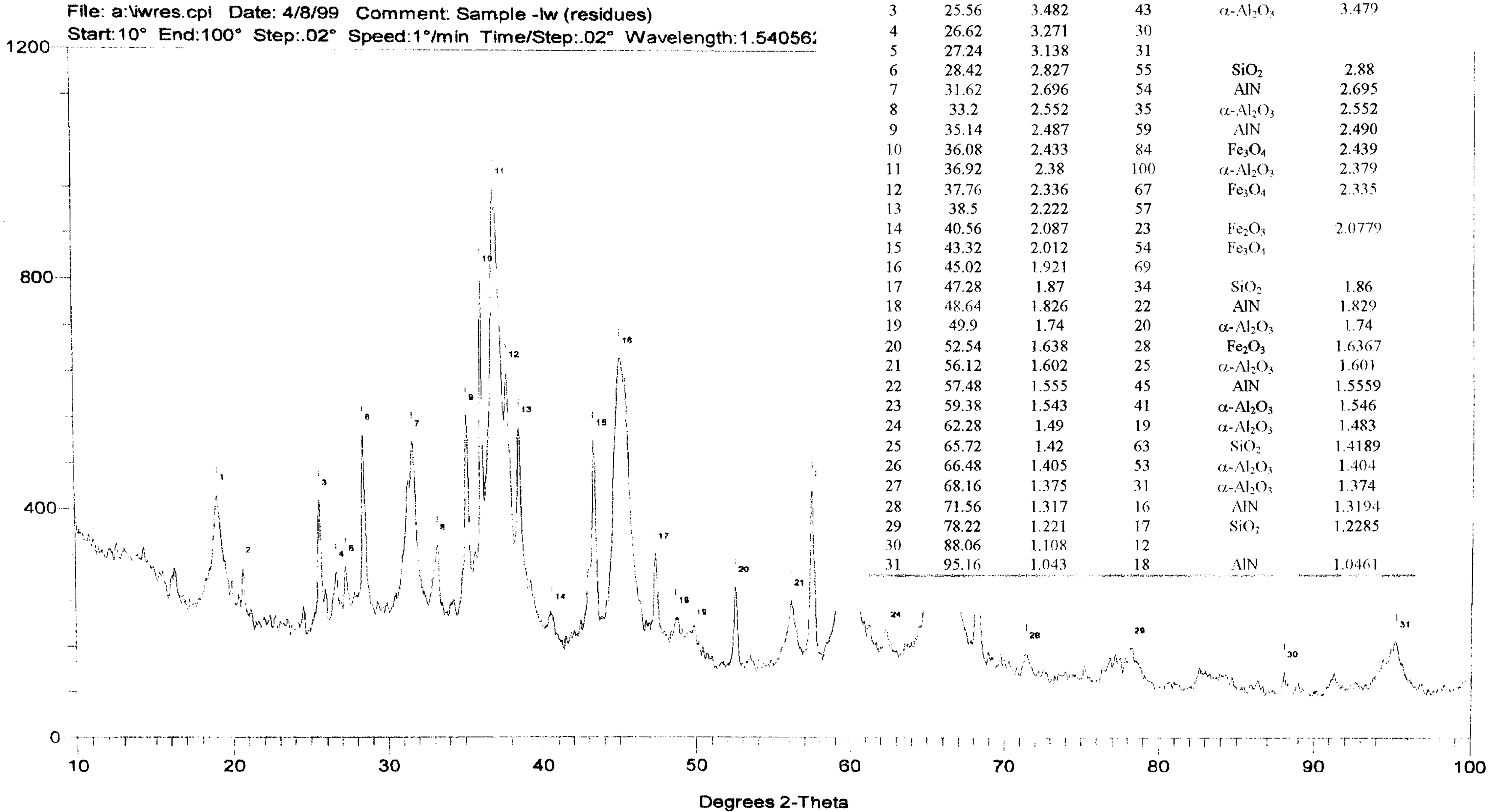


Figure-2.11. X-ray diffraction spectrum of the (washed) black dross residue after third wash

### *2.4.2.2. Countercurrent Leaching*

The results described in the previous section show that almost half of the black dross is a mixture of sodium and potassium chloride. All of this black dross is currently landfilled without any previous treatment. Sodium and potassium chloride are easily dissolved in water. This vast amount of salt in black dross would easily leach out in the landfill, consequently mixing with the fresh water sources i.e. rivers, lakes; so disturbing the natural environment. It is essential to remove this salt from the black dross, as this would not only avoid environmental pollution, but also offers an economically viable solution for its reuse (recycle) within the aluminium industry.

If electric heating system is used for salt recovery, the process would be very costly. In order to minimise heat consumption, countercurrent leaching or washing process has been developed in this project. The results from this study ( Section-2.3.2.2) are presented in Table-2.5.

**Table-2.5. Countercurrent leaching process**

| Series of wash | De-ionised water (l) | Wt of dry black dross residue after washing (g)* | | | | Wt of dry salt (g) | Weeks taken to dry (salt) |
|---|---|---|---|---|---|---|---|
| | | Column-A | Column-B | Column-C | Column-D | | |
| 1 | 1 | - | - | - | - | 116 | 2 |
| 2 | 1 | 255 | - | - | - | 125 | 2 |
| | | Column-B | Column-C | Column-D | Column-E | | |
| 3 | 1 | 260 | - | - | - | 180 | 2 |
| | | Column-C | Column-D | Column-E | Column-F | | |
| 4 | 1 | 260 | - | - | - | 178 | 2 |

*Wt. of as supplied (unwashed) black dross in each column: 500g.

It can be seen that in the first series of wash, one litre of de-ionised water was used to wash four different sinter-glass filter columns (Column A-D), each contained 500g of as supplied (unwashed) black dross. At the end of the washing of all four columns, the salt water was highly concentrated and crystallised within 2 weeks at room temperature. Figure-2.12 shows (a) a beaker containing salt water collected after the first series wash and (b) crystallised salt around the beaker after being left for two weeks. Figure-2.13 shows the XRD pattern of the crystallised salt, which contains a mixture of sodium chloride and potassium chloride.

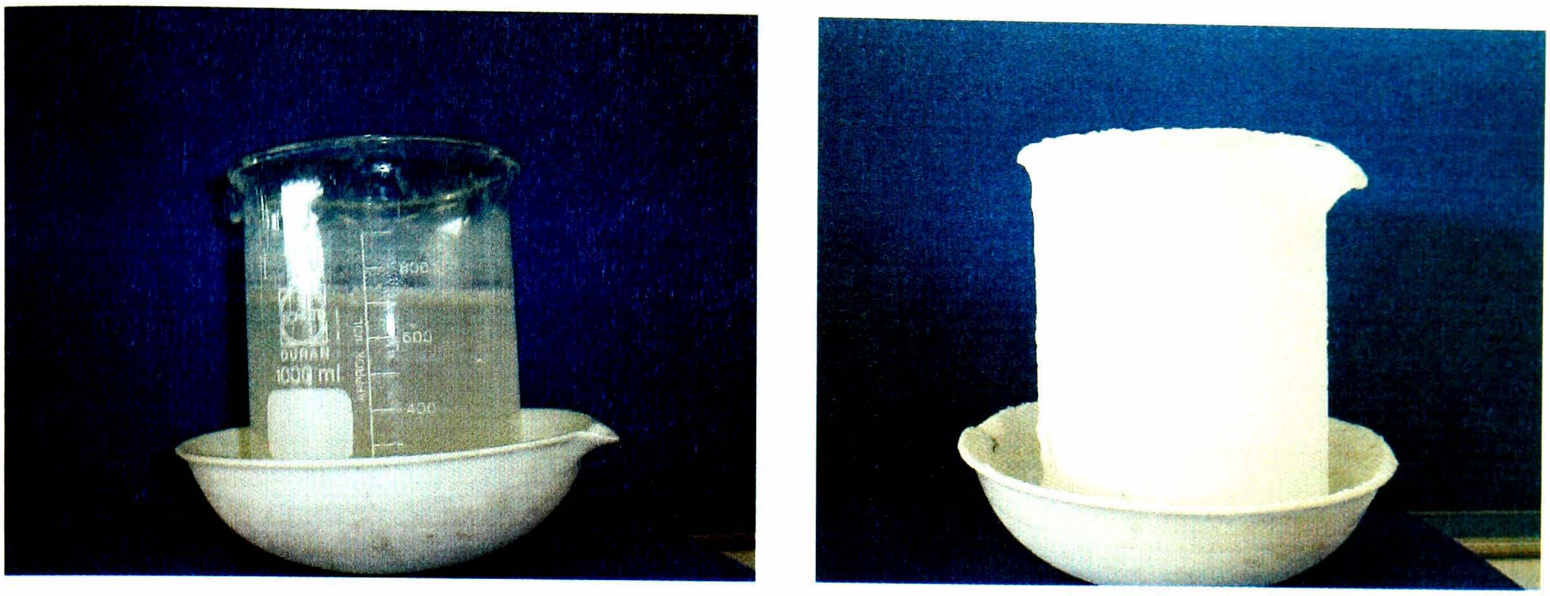


**Figure-2.12 (a) Salt water collected after the 1st series of countercurrent leaching process**

**(b) Salt crystals around the glass beaker after two weeks**

**X-ray diffraction data of the crystallised salt collected from countercurrent leaching process**

| No | Angle($^0$) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 27.44 | 3.248 | 3 | NaCl | 3.258 |
| 2 | 28.46 | 3.134 | 57 | KCl | 3.146 |
| 3 | 31.8 | 2.812 | 100 | NaCl | 2.812 |
| 4 | 40.68 | 2.216 | 25 | KCl | 2.2251 |
| 5 | 45.52 | 1.991 | 16 | NaCl | 1.994 |
| 6 | 50.32 | 1.812 | 2 | KCl | 1.8169 |
| 7 | 53.92 | 1.699 | 1 | | |
| 8 | 56.52 | 1.627 | 4 | NaCl | 1.628 |
| 9 | 58.78 | 1.57 | 2 | KCl | 1.573 |
| 10 | 66.28 | 1.409 | 4 | NaCl | 1.410 |
| 11 | 66.5 | 1.405 | 5 | KCl | 1.4071 |
| 12 | 73.08 | 1.294 | 1 | NaCl | 1.294 |
| 13 | 73.84 | 1.282 | 1 | KCl | 1.2839 |
| 14 | 75.32 | 1.261 | 4 | NaCl | 1.261 |
| 15 | 75.52 | 1.258 | 2 | | |
| 16 | 84.0 | 1.151 | 2 | NaCl | 1.1515 |
| 17 | 84.24 | 1.148 | 1 | | |
| 18 | 87.84 | 1.11 | 1 | | |
| 19 | 94.7 | 1.047 | 1 | KCl | 1.0485 |

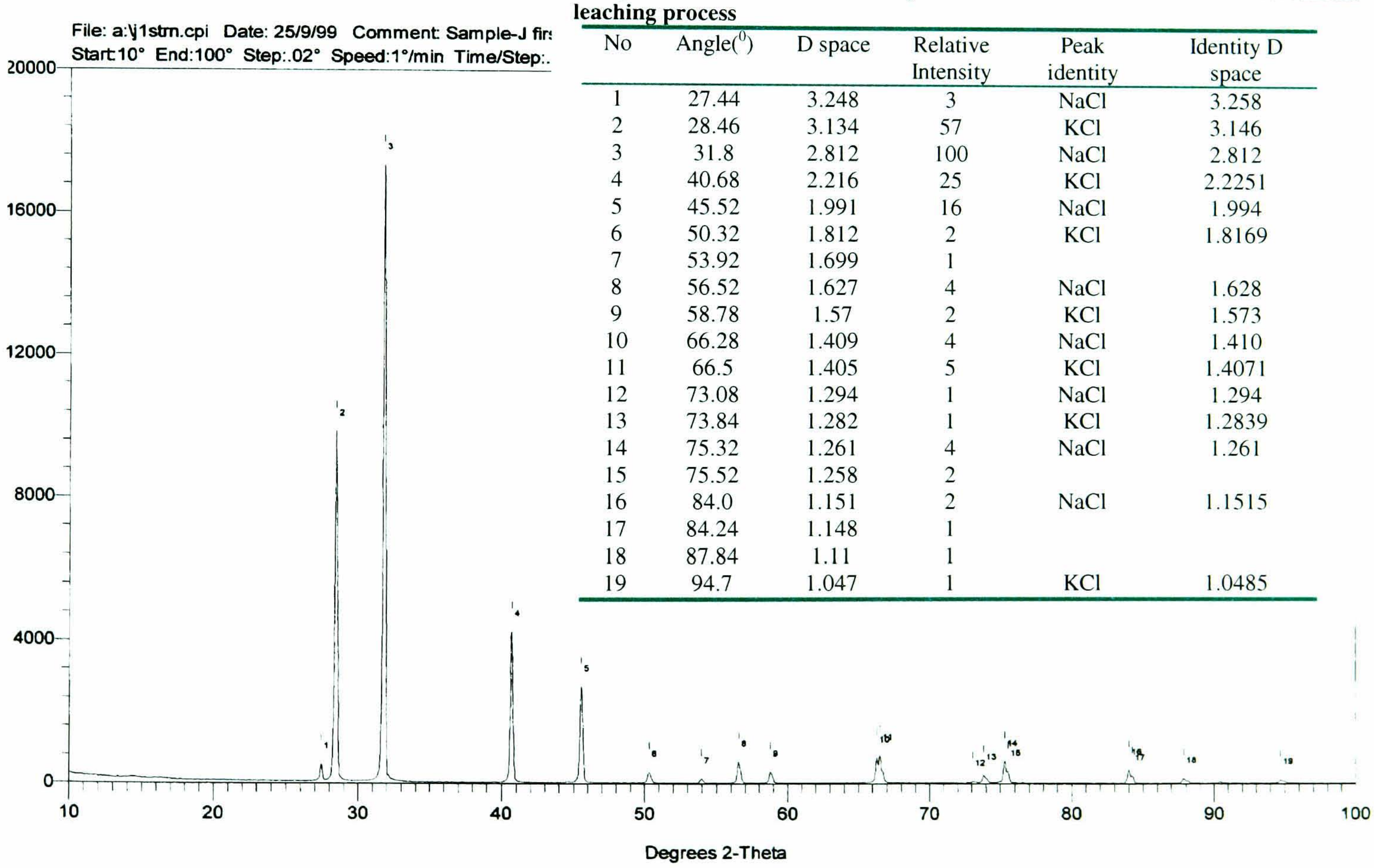


**Figure-2.13. X-ray diffraction spectrum of the crystallised salt collected from countercurrent leaching process**

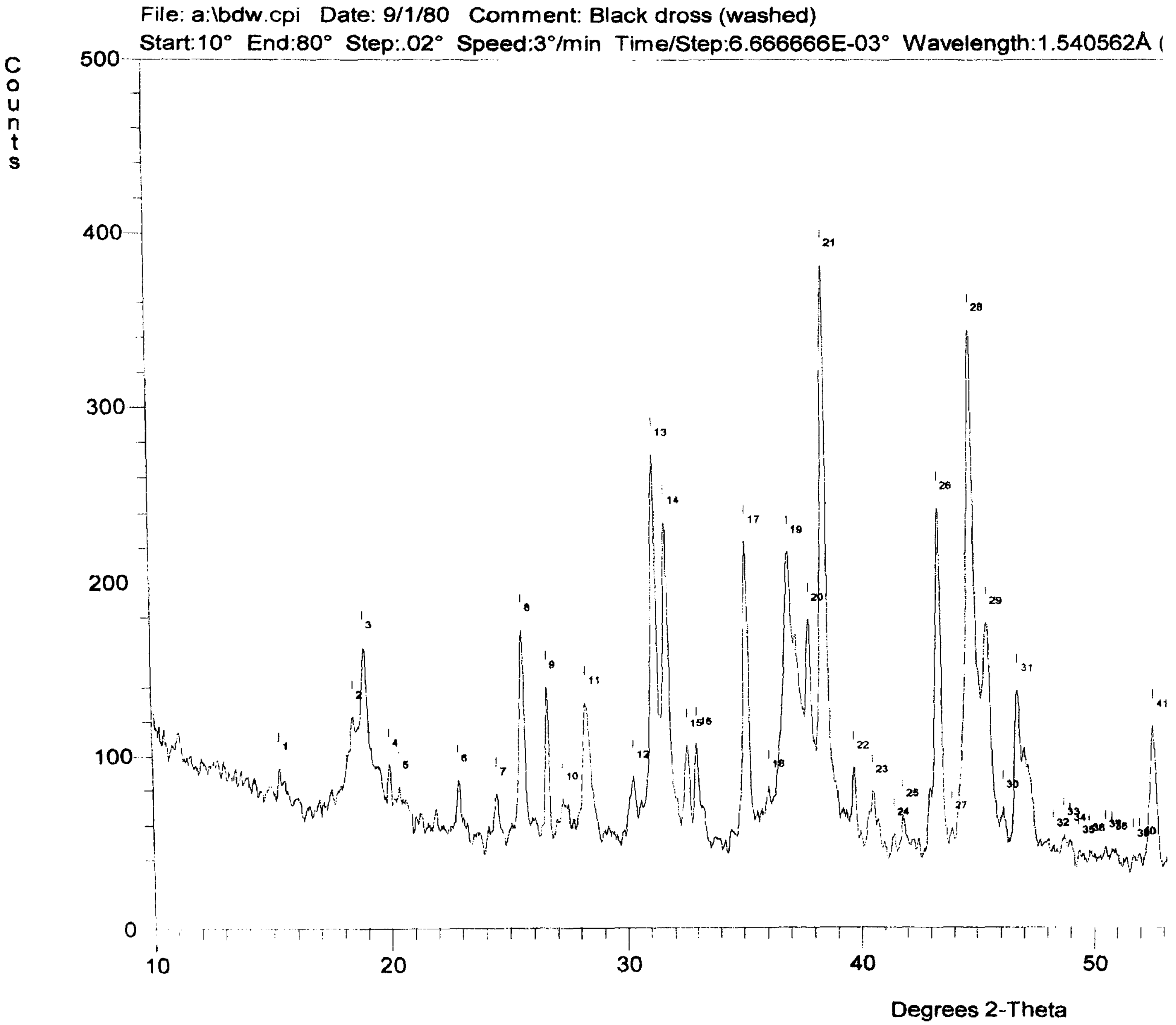
In the batch washing process (Section 2.4.2.1) it was established that two litres of water was sufficient to wash 500g of black dross in order to remove the salt content from it. Therefore, after the second series of washing procedure, the residue in Column-A was removed as it was washed thoroughly with two litres of water. Weight of the dried residue from Column-A was noted and the column was filled with new unwashed black dross and labelled as Column-E (Table-2.5). The XRD pattern (Figure-2.14) of the dried residue from Column-A also confirms the absence of any salt.

In each series of the washing procedure, the fresh water becomes more concentrated with salt as it contacts the salt richer black dross in the respective columns. At the end of each washing series, black dross from first column is removed and replaced with unwashed black dross and placed at the end of the leaching process. The collected brine is highly concentrated and crystallises within two weeks. However, if the salt water does not evaporate into salt crystals after more than two weeks, the remaining salt water can be added to the fresh water to make up the volume to one litre and to be used in the new washing series.

In summary, since black dross contains a large amount of salt, to concentrate the aluminium content, it is necessary to wash this dross. The batch washing procedure can be very simple but it requires heat, whilst, the countercurrent washing procedure is very straight forward and more economically viable as this procedure requires no heating to evaporate water from the salt solution. The whole procedure takes place at room temperature (~ $23^0$C), leaving a salt free black dross and allowing the recovered salt to be recycled into the smelter. Furthermore, this process minimises the use of water.

### 2.4.3. Leachability studies to assess the solubility of the black dross

The presence of metal impurities in the aluminium dross suggests that acid leaching could be the type of treatment that will dissolve aluminium along with other metals from the sample. Different leaching media were used at different concentrations and at different temperatures to determine the best leaching media, to dissolve the maximum amount of black dross, and determine the concentrations of the metals. The black dross was washed before the experiment to remove the salt content, as the presence of a high amount of salt would interfere with this leaching procedure.



**X-ray diffraction spectrum washed black dross residue collected from countercurrent leaching process**

| No | Angle(°) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 15.32 | 5.779 | 24 | | |
| 2 | 18.44 | 4.807 | 32 | α-$Al_2O_3$ | 4.8 |
| 3 | 18.92 | 4.687 | 43 | $Fe_3O_4$ | 4.67 |
| 4 | 19.98 | 4.44 | 25 | $SiO_2$ | 4.45 |
| 5 | 20.38 | 4.354 | 21 | $SiO_2$ | 4.38 |
| 6 | 22.86 | 3.887 | 23 | | |
| 7 | 24.5 | 3.63 | 20 | | |
| 8 | 25.58 | 3.479 | 45 | α-$Al_2O_3$ | 3.479 |
| 9 | 26.6 | 3.348 | 37 | $SiO_2$ | 3.342 |
| 10 | 27.26 | 3.269 | 20 | | |
| 11 | 28.24 | 3.157 | 34 | | |
| 12 | 30.28 | 2.949 | 23 | | |
| 13 | 31.18 | 2.866 | 71 | $Fe_3O_4$ | 2.86 |
| 14 | 31.68 | 2.882 | 62 | α-$Al_2O_3$ | 2.8 |
| 15 | 32.56 | 2.748 | 28 | | |
| 16 | 32.98 | 2.14 | 28 | $Fe_3O_4$ | 2.7 |
| 17 | 35.12 | 2.553 | 59 | | |
| 18 | 36.08 | 2.487 | 21 | | |
| 19 | 36.92 | 2.433 | 57 | $Fe_3O_4$ | 2.439 |
| 20 | 37.78 | 2.379 | 47 | α-$Al_2O_3$ | 2.379 |
| 21 | 38.44 | 2.34 | 100 | α-$Al_2O_3$ | 2.3 |
| 22 | 39.68 | 2.27 | 24 | $SiO_2$ | 2.28 |
| 23 | 40.5 | 2.225 | 21 | $SiO_2$ | 2.237 |
| 24 | 41.4 | 2.179 | 14 | $SiO_2$ | 2.19 |
| 25 | 41.8 | 2.159 | 17 | α-$Al_2O_3$ | 2.165 |
| 26 | 43.3 | 2.088 | 64 | α-$Al_2O_3$ | 2.085 |
| 27 | 43.9 | 2.061 | 15 | | |
| 28 | 44.7 | 2.026 | 90 | $Fe_3O_4$ | 2.023 |
| 29 | 45.42 | 1.995 | 46 | $SiO_2$ | 1.98 |
| 30 | 46.12 | 1.967 | 18 | α-$Al_2O_3$ | 1.964 |
| 31 | 46.74 | 1.942 | 36 | $Fe_2O_3$ | 1.938 |
| 32 | 48.26 | 1.884 | 13 | | |
| 33 | 48.72 | 1.867 | 14 | | |
| 34 | 48.98 | 1.858 | 13 | | |
| 35 | 49.34 | 1.845 | 12 | $Fe2O_3$ | 1.84 |
| 36 | 49.8 | 1.829 | 12 | $SiO_2$ | 1.83 |
| 37 | 50.5 | 1.806 | 12 | | |
| 38 | 50.78 | 1.796 | 12 | $SiO_2$ | 1.79 |
| 39 | 51.72 | 1.766 | 11 | | |
| 40 | 51.98 | 1.758 | 11 | | |
| 41 | 52.54 | 1.74 | 31 | α-$Al_2O_3$ | 1.74 |
| 42 | 53.74 | 1.704 | 9 | | |
| 43 | 54.44 | 1.684 | 9 | $SiO_2$ | 1.69 |
| 44 | 54.74 | 1.675 | 13 | $SiO_2$ | 1.67 |
| 45 | 56.4 | 1.63 | 17 | | |
| 46 | 57.46 | 1.602 | 52 | α-$Al_2O_3$ | 1.601 |
| 47 | 58.72 | 1.571 | 19 | | |
| 48 | 59.82 | 1.545 | 21 | α-$Al_2O_3$ | 1.546 |

**Figure-2.14. X-ray diffraction spectrum of washed black dross residue from Column-A**

### *2.4.3.1. Distilled water*

Black dross was leached with distilled water at four different temperatures. Solubility of the black dross in distilled water is low at any temperature. The results (Table-2.6) show that a maximum solubility of 10% is achieved at 100$^0$C. Table-2.7 shows that only trace amounts of metals have been recovered. As this black dross was previously washed to remove the salt content, most of the water soluble compounds were already removed from it. Therefore, distilled water is not a good leaching medium to recover the metals.

**Table-2.6. Solubility of black dross in distilled water at different temperatures**

| Temp ($^0$C) | Room temp | 40 | 80 | 100 |
|---|---|---|---|---|
| Weight (g) | 2.05 | 2.03 | 2.05 | 2.04 |
| dry residue (g) | 1.90 | 1.83 | 1.84 | 1.80 |
| %Solubility | 7.15 | 9.65 | 10.1 | 10.33 |

**Table-2.7. Concentrations of metals extracted from black dross using distilled water at different temperatures.**

| Temp ($^0$C) | Room temp | 40 | 80 | 100 |
|---|---|---|---|---|
| Metals | Concentration (mg/g) | | | |
| Al | 0.06 | 0.4 | 0.45 | 0.6 |
| Ca | 0.12 | 0.013 | 0.04 | 0.012 |
| Cr | 0.0 | 0.0 | 0.0 | 0.0 |
| Cu | 0.0 | 0.0 | 0.0 | 0.0 |
| Fe | 0.013 | 0.02 | 0.02 | 0.02 |
| Mn | 0.01 | 0.004 | 0.01 | 0.01 |
| Ni | 0.013 | 0.013 | 0.023 | 0.03 |
| Ti | 0.0 | 0.0 | 0.0 | 0.0 |
| Zn | 0.002 | 0.002 | 0.002 | 0.003 |

### *2.4.3.2 Hydrochloric acid*

Four different concentrations of hydrochloric acid (1-4M) at four different temperatures (room temperature, 40$^0$C, 80$^0$C and 100$^0$C) were used to leach the washed black dross, to determine the best conditions for the dross to dissolve totally. The Figure-2.15 shows that the black dross is most soluble in 3M HCl at 100$^0$C. Under these conditions 80% of black dross dissolved. The XRF analysis of the washed and oven dried residue (Figure-

2.16) shows the presence of silicon, aluminium, titanium, manganese and iron (the presence of rhodium is due to the emission of x-ray source in the machine). The XRD analysis (Figure-2.17) confirms the presence of alumina ($\alpha$-$Al_2O_3$ or corundum), silica ($SiO_2$), and iron oxide ($FeFe_2O_4$) compounds.

Data given in Table-2.8 are the concentrations of the different metals in different strengths of HCl under different conditions. The results show that apart from aluminium, the sample also contains iron and copper and some other metals as trace impurities. Figure-2.18 summarises the concentration of aluminium in different concentration of hydrochloric acid at different temperatures. It can be seen that the optimum conditions to leach most aluminium from black dross samples are 3M HCl at $100^0$C temperature.

### *2.4.3.3. Nitric acid*

Leaching experiments were carried out under same conditions as described above, using $HNO_3$ in place of HCl. Figure-2.19 shows that maximum solubility 77% is achieved by using 4M nitric acid at $100^0$C. The XRF (Figure-2.20) analysis shows that the 23% undissolved residue is aluminium, silica, titanium, chromium, manganese and iron. The XRD analysis (Figure-2.21) confirms the presence of alumina ($\alpha$-$Al_2O_3$ or corundum), silica ($SiO_2$), and iron oxides ($FeFe_2O_4$, $Fe_2O_3$). Data presented in Table-2.9 are the concentrations of the different metals in the different strengths of $HNO_3$ acid and at different temperatures. It can be seen from the Figure-2.22 that the optimum conditions to dissolve maximum amount of aluminium are 2M $HNO_3$ at $100^0$C temperature for 3 hours. Moreover, an increase in nitric acid concentration and temperature does not provide more effective leaching conditions.

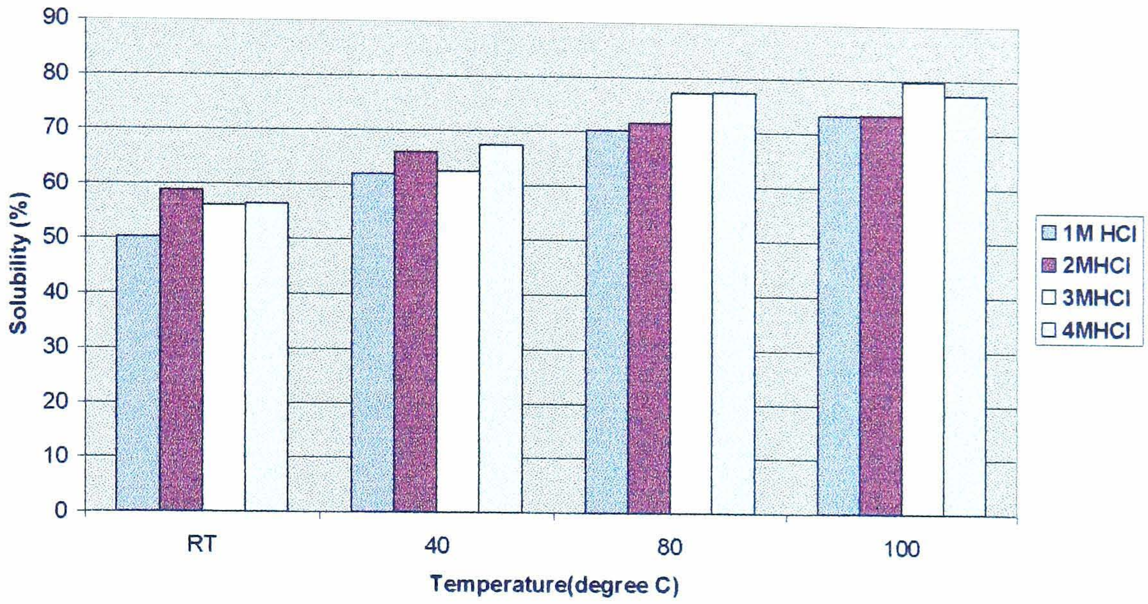


**Figure-2.15. %Solubility of washed black dross using different concentration of HCl at different temperatures.**

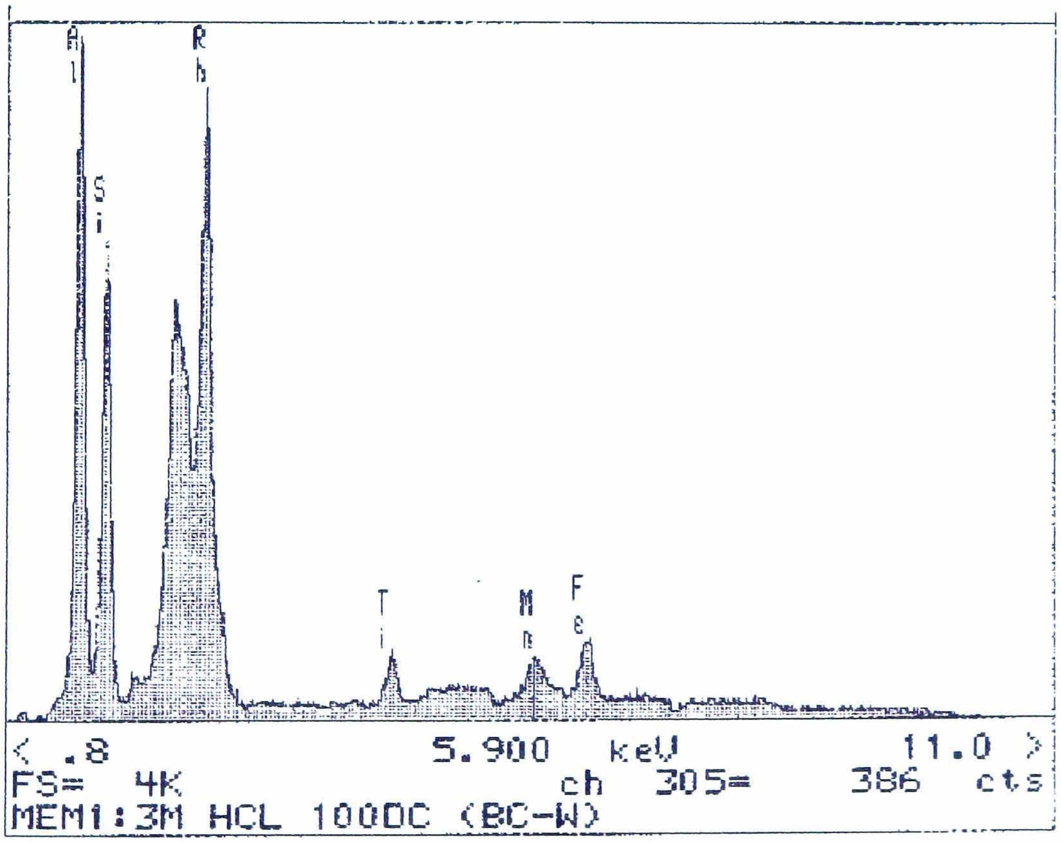


**Figure-2.16. XRF spectrum of black dross residue leached by 3M HCl at 100$^0$C.**

**X-ray diffraction data of black dross residue leached by 3M at 100$^0$C temperature.**

| No | Angle($^0$) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 18.1 | 4.897 | 10 | | |
| 2 | 18.98 | 4.672 | 13 | $FeFe_2O_4$ | 4.67 |
| 3 | 20.86 | 4.255 | 13 | $SiO_2$ | 4.257 |
| 4 | 25.58 | 3.479 | 62 | $\alpha$-$Al_2O_3$ | 3.479 |
| 5 | 26.6 | 3.348 | 59 | $SiO_2$ | 3.342 |
| 6 | 28.46 | 3.134 | 47 | $SiO_2$ | 3.13 |
| 7 | 30.4 | 2.938 | 5 | | |
| 8 | 31.3 | 2.855 | 12 | $FeFe_2O_4$ | 2.86 |
| 10 | 35.14 | 2.552 | 100 | $\alpha$-$Al_2O_3$ | 2.552 |
| 12 | 36.88 | 2.435 | 30 | $FeFe_2O_4$ | 2.439 |
| 13 | 37.78 | 2.379 | 47 | $\alpha$-$Al_2O_3$ | 2.379 |
| 14 | 39.5 | 2.279 | 6 | | |
| 15 | 42.48 | 2.126 | 6 | $SiO_2$ | 2.127 |
| 16 | 43.34 | 2.086 | 94 | $\alpha$-$Al_2O_3$ | 2.085 |
| 17 | 44.84 | 2.02 | 19 | $SiO_2$ | 2.02 |
| 18 | 47.32 | 1.919 | 24 | | |
| 19 | 50.12 | 1.819 | 6 | | |
| 20 | 52.52 | 1.741 | 40 | $\alpha$-$Al_2O_3$ | 1.74 |
| 21 | 56.12 | 1.638 | 11 | $FeFe_2O_4$ | 1.651 |
| 22 | 57.48 | 1.602 | 85 | $\alpha$-$Al_2O_3$ | 1.601 |
| 23 | 59.34 | 1.556 | 18 | $SiO_2$ | 1.555 |
| 24 | 59.9 | 1.543 | 13 | $\alpha$-$Al_2O_3$ | 1.546 |
| 25 | 61.24 | 1.512 | 10 | $\alpha$-$Al_2O_3$ | 1.514 |
| 26 | 65.38 | 1.426 | 17 | $FeFe_2O_4$ | 1.43 |
| 27 | 66.48 | 1.405 | 29 | $\alpha$-$Al_2O_3$ | 1.404 |
| 28 | 68.18 | 1.374 | 46 | $\alpha$-$Al_2O_3$ | 1.374 |
| 29 | 69.18 | 1.357 | 6 | | |
| 30 | 71.3 | 1.322 | 8 | | |
| 31 | 74.28 | 1.276 | 4 | $\alpha$-$Al_2O_3$ | 1.276 |
| 32 | 76.36 | 1.246 | 7 | | |
| 33 | 76.84 | 1.24 | 17 | $\alpha$-$Al_2O_3$ | 1.239 |

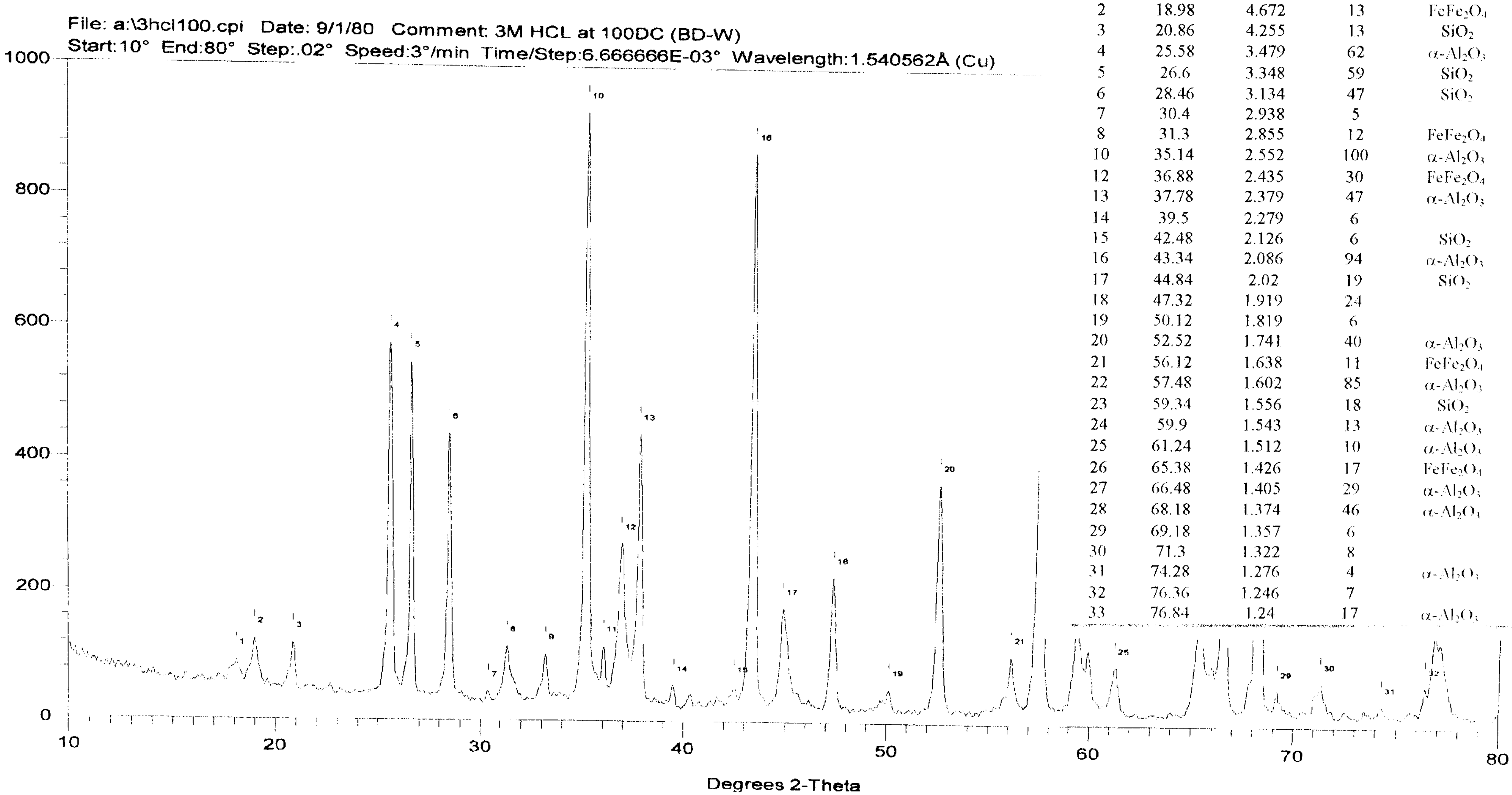


Figure-2.17. X-ray diffraction spectrum of black dross residue leached by 3M HCl at 100$^0$C.

**Table-2.8. Leaching of black dross using different concentrations of hydrochloric acid and temperatures**

**1M HCl**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| | Concentration (mg/g) | | | |
| Al | 132.81<br>*sd 4.3* | 157.47<br>*sd 4.5* | 200.32<br>*sd 4.2* | 239.86<br>*sd 4.5* |
| Ca | 0.73 | 1.40 | 1.93 | 2.24 |
| Cr | 0.68 | 0.61 | 0.77 | 0.82 |
| Cu | 2.43<br>*sd 4.5* | 3.28<br>*sd 4.2* | 3.44<br>*td 5.1* | 3.66<br>*sd 4.3* |
| Fe | 7.57<br>*sd 4.3* | 8.42<br>*sd 4.8* | 7.94<br>*sd 5.3* | 7.87<br>*sd 5.0* |
| Mn | 0.67 | 0.67 | 0.72 | 1.02 |
| Ni | 0.43 | 0.44 | 0.57 | 0.55 |
| Ti | 1.29 | 1.62 | 1.78 | 1.34 |
| Zn | 0.96 | 0.79 | 0.86 | 1.02 |

**2M HCl**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| | Concentration (mg/g) | | | |
| Al | 140.08<br>*sd 5.3* | 185.50<br>*sd 5.1* | 200.50<br>*sd 8.3* | 259.46<br>*sd 6.3* |
| Ca | 1.78 | 1.68 | 2.20 | 2.35 |
| Cr | 1.01 | 1.08 | 1.16 | 1.41 |
| Cu | 3.97<br>*sd 5.6* | 4.08<br>*sd 5.1* | 4.07<br>*sd 7.3* | 4.15<br>*sd 6.2* |
| Fe | 7.85<br>*sd 5.4* | 10.44<br>*sd 5.8* | 10.52<br>*sd 7.4* | 12.97<br>*sd 6.4* |
| Mn | 0.78 | 0.91 | 0.85 | 0.98 |
| Ni | 0.22 | 0.24 | 0.25 | 0.25 |
| Ti | 1.05 | 1.71 | 1.77 | 1.57 |
| Zn | 1.81 | 1.60 | 1.61 | 1.73 |

**3M HCL**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| | Concentration (mg/g) | | | |
| Al | 169.73<br>*sd 6.9* | 193.45<br>*sd 4.2* | 255.21<br>*sd 4.3* | 267.97<br>*sd 4.5* |
| Ca | 1.42 | 1.69 | 1.87 | 2.66 |
| Cr | 0.69 | 1.15 | 1.13 | 1.14 |
| Cu | 3.96<br>*sv 5.3* | 3.70<br>*sd 4.2* | 3.58<br>*sd 4.6* | 3.90<br>*sd 4.2* |
| Fe | 8.05<br>*sd 4.8* | 9.79<br>*sd 4.0* | 9.75<br>*sd 3.6* | 9.87<br>*sd 4.0* |
| Mn | 0.88 | 0.87 | 0.87 | 1.00 |
| Ni | 0.20 | 0.23 | 0.24 | 0.23 |
| Ti | 1.73 | 1.64 | 1.54 | 1.50 |
| Zn | 1.61 | 1.59 | 1.69 | 1.71 |

**4M HCl**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| | Concentration (mg/g) | | | |
| Al | 136.43<br>*sd 4.3* | 172.15<br>*sd 4.0* | 218.04<br>*sd 1.8* | 231.21<br>*sd 2.6* |
| Ca | 1.41 | 1.94 | 2.65 | 2.58 |
| Cr | 0.63 | 0.99 | 1.05 | 1.02 |
| Cu | 3.57<br>*sd 5.8* | 3.78<br>*sd 5.6* | 3.80<br>*sd 7.3* | 3.93<br>*sd 5.8* |
| Fe | 8.04<br>*sd 5.3* | 9.58<br>*sd 5.8* | 9.04<br>*sd 7.0* | 10.77<br>*sd 6.3* |
| Mn | 0.79 | 0.84 | 0.89 | 0.83 |
| Ni | 0.60 | 0.53 | 0.63 | 0.71 |
| Ti | 1.25 | 1.50 | 2.42 | 1.52 |
| Zn | 0.90 | 0.88 | 0.95 | 1.08 |

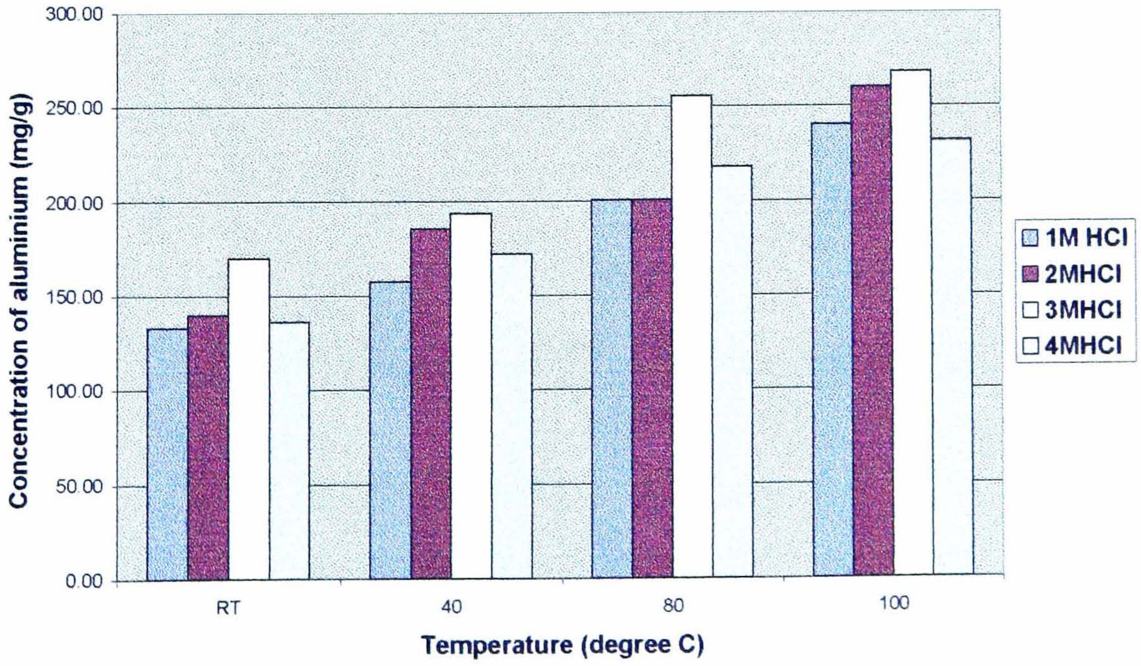


**Figure-2.18. Concentration of aluminium in washed black dross leached with HCl**

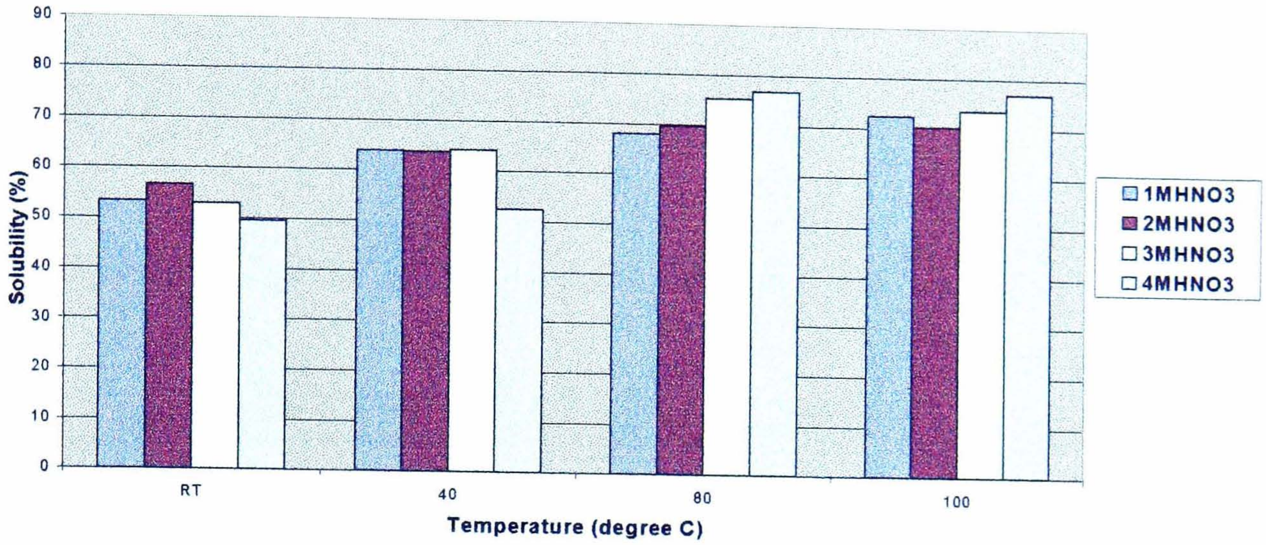


Figure-2.19. %Solubility of washed black dross using different concentration of $HNO_3$ at different temperatures.

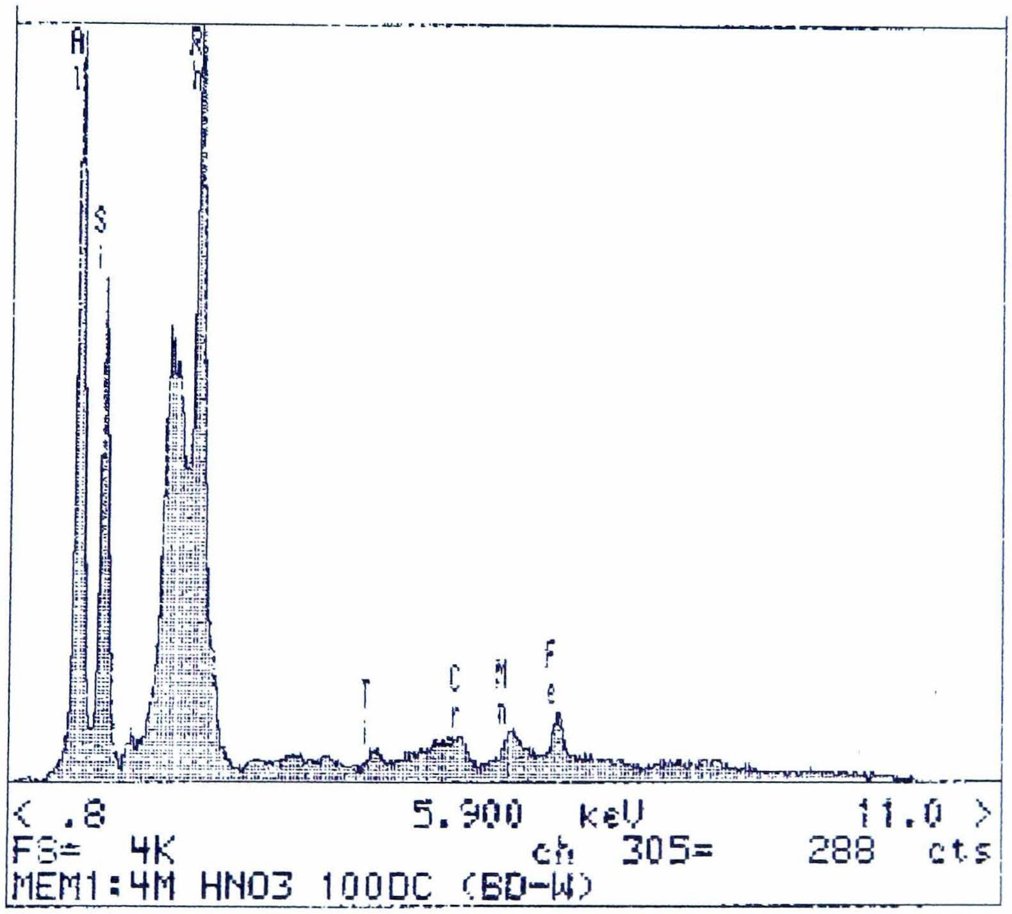


Figure-2.20. XRF spectrum of black dross residue leached by 4M $HNO_3$ at $100^0C$.

**X-ray diffraction data of black dross residue leached by 4M $HNO_3$ at $100^0C$ temperature.**

| No | Angle($^0$) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 17.98 | 4.929 | 9 | | |
| 2 | 18.98 | 4.672 | 12 | $FeFe_2O_4$ | 4.67 |
| 3 | 20.84 | 4.259 | 22 | $SiO_2$ | 4.257 |
| 4 | 25.54 | 3.485 | 65 | $\alpha$-$Al_2O_3$ | 3.479 |
| 5 | 26.6 | 3.348 | 31 | $SiO_2$ | 3.342 |
| 6 | 28.44 | 3.136 | 44 | | |
| 7 | 31.26 | 2.859 | 10 | $FeFe_2O_4$ | 2.86 |
| 8 | 33.1 | 2.704 | 11 | $Fe_2O_3$ | 2.7 |
| 9 | 35.1 | 2.555 | 100 | $\alpha$-$Al_2O_3$ | 2.552 |
| 10 | 35.98 | 2.494 | 7 | | |
| 11 | 36.86 | 2.436 | 24 | $FeFe_2O_4$ | 2.439 |
| 12 | 37.74 | 2.382 | 45 | $\alpha$-$Al_2O_3$ | 2.382 |
| 13 | 39.46 | 2.282 | 5 | $SiO_2$ | 2.282 |
| 14 | 41.66 | 2.166 | 4 | $\alpha$-$Al_2O_3$ | 2.165 |
| 15 | 42.44 | 2.128 | 5 | $SiO_2$ | 2.127 |
| 16 | 43.3 | 2.088 | 98 | $\alpha$-$Al_2O_3$ | 2.085 |
| 17 | 44.84 | 2.02 | 15 | $SiO_2$ | 2.02 |
| 18 | 47.26 | 1.922 | 22 | | |
| 19 | 50.02 | 1.822 | 5 | $SiO_2$ | 1.83 |
| 20 | 50.52 | 1.805 | 5 | $SiO_2$ | 1.802 |
| 21 | 52.5 | 1.742 | 43 | $\alpha$-$Al_2O_3$ | 1.74 |
| 22 | 56.08 | 1.639 | 13 | | |
| 23 | 57.46 | 1.602 | 87 | $\alpha$-$Al_2O_3$ | 1.601 |
| 24 | 59.38 | 1.555 | 10 | $SiO_2$ | 1.555 |
| 25 | 59.62 | 1.549 | 10 | $SiO_2$ | 1.546 |
| 26 | 59.88 | 1.543 | 9 | $\alpha$-$Al_2O_3$ | 1.541 |
| 27 | 61.24 | 1.512 | 9 | $\alpha$-$Al_2O_3$ | 1.514 |
| 28 | 65.24 | 1.429 | 13 | | |
| 29 | 66.46 | 1.406 | 30 | $\alpha$-$Al_2O_3$ | 1.404 |
| 30 | 68.14 | 1.375 | 49 | $\alpha$-$Al_2O_3$ | 1.374 |
| 31 | 76.84 | 1.24 | 19 | $\alpha$-$Al_2O_3$ | 1.239 |

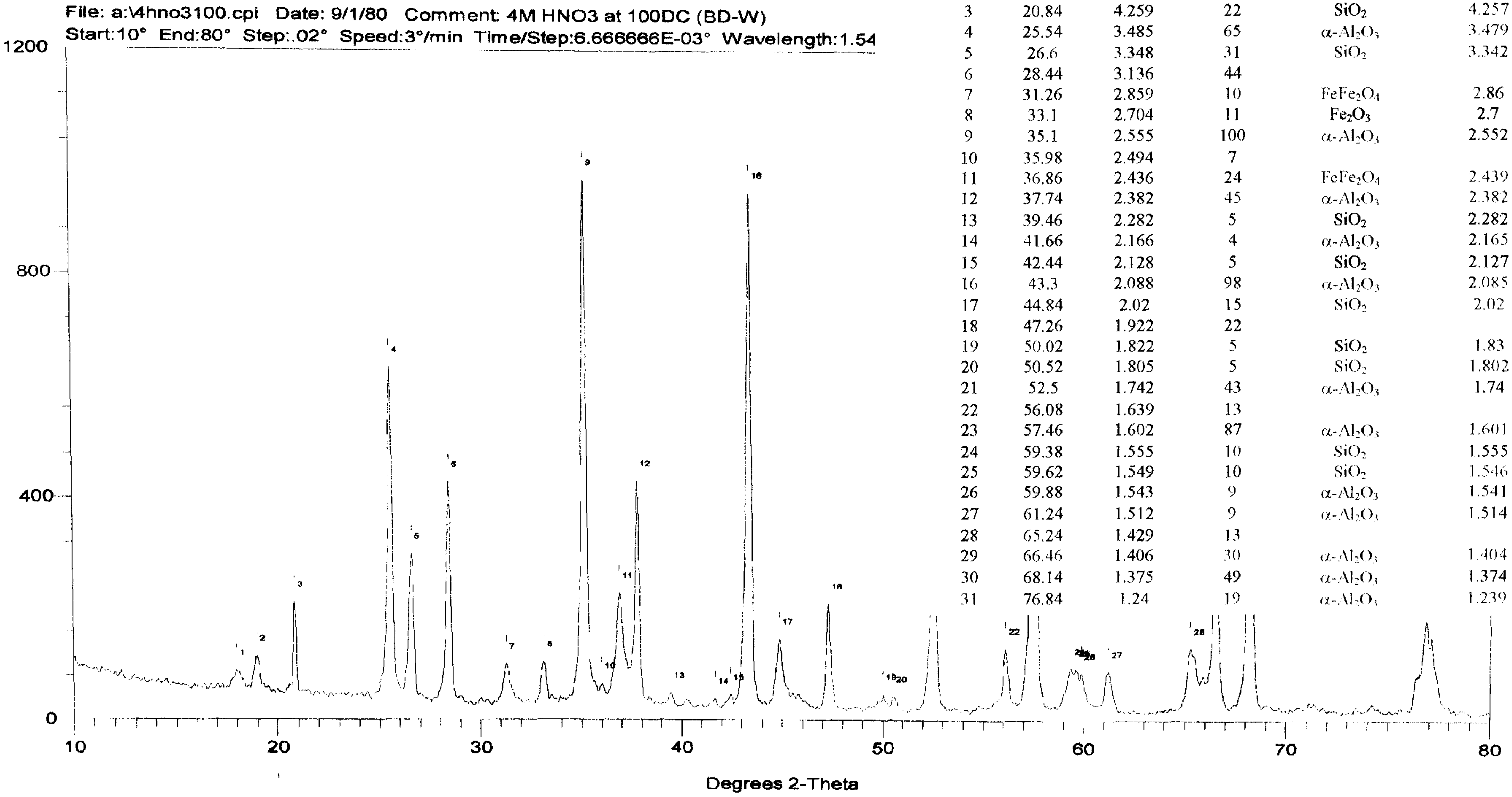


Figure-2.21. X-ray diffraction spectrum of black dross residue leached by 4M $HNO_3$ at $100^0C$.

**Table-2.9. Leachability studies of black dross using different concentration of nitric acid and temperatures.**

**1M $HNO_3$**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 121.02<br>*sd 3.5* | 151.05<br>*sd 2.9* | 193.70<br>*st 1.63* | 190.49<br>*sd 7.9* |
| Ca | 0.19 | 3.71 | 0.39 | 0.40 |
| Cr | 0.87 | 0.85 | 0.86 | 0.88 |
| Cu | 3.28<br>*sd 4.0* | 3.43<br>*sd 2.3* | 4.53<br>*sd 2.0* | 7.67<br>*sd 7.3* |
| Fe | 10.04<br>*sd 3.5* | 8.35<br>*sd 2.0* | 8.47<br>*sd 1.9* | 9.28<br>*sd 6.9* |
| Mn | 0.59 | 0.66 | 0.82 | 0.74 |
| Ni | 0.00 | 0.00 | 0.00 | 0.00 |
| Ti | 1.27 | 1.42 | 1.43 | 1.74 |
| Zn | 0.80 | 0.85 | 1.94 | 1.73 |

**2M $HNO_3$**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 158.22<br>*sd 2.6* | 198.20<br>*sd 2.1* | 245.43<br>*sd 4.7* | 249.21<br>*sd 4.1* |
| Ca | 0.17 | 0.36 | 0.33 | 0.40 |
| Cr | 0.84 | 0.98 | 0.91 | 0.99 |
| Cu | 3.01<br>*sd 2.5* | 4.30<br>*sd 2.6* | 4.32<br>*sd 4.0* | 4.37<br>*sd 4.0* |
| Fe | 9.13<br>*sd 2.8* | 8.86<br>*sd 2.7* | 8.74<br>*sd 4.3* | 9.58<br>*sd 4.5* |
| Mn | 0.73 | 0.85 | 0.98 | 0.83 |
| Ni | 0.21 | 0.20 | 0.24 | 0.22 |
| Ti | 1.11 | 1.58 | 1.56 | 1.80 |
| Zn | 1.46 | 1.72 | 2.04 | 1.80 |

**3M $HNO_3$**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 141.70<br>*sd 3.3* | 187.70<br>*sd 2.9* | 235.15<br>*sd 4.3* | 225.54<br>*sd 8.2* |
| Ca | 0.31 | 0.37 | 0.41 | 0.43 |
| Cr | 1.07 | 1.89 | 1.17 | 0.43 |
| Cu | 3.83<br>*sdv 3.5* | 4.95<br>*sdv 2.5* | 4.15<br>*sdv 4.6* | 4.43<br>*sdv 8.0* |
| Fe | 8.87<br>*sd 3.5* | 15.11<br>*sd 2.6* | 13.67<br>*sd 4.3* | 11.58<br>*sd 8.2* |
| Mn | 0.80 | 1.10 | 0.82 | 0.87 |
| Ni | 0.00 | 0.00 | 0.00 | 0.00 |
| Ti | 1.60 | 1.71 | 1.99 | 1.57 |
| Zn | 0.95 | 1.58 | 1.72 | 1.58 |

**4M $HNO_3$**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 103.29<br>*sd 6.4* | 149.39<br>*sd 7.6* | 187.63<br>*sd 3.5* | 194.01<br>*sd 2.5* |
| Ca | 0.40 | 0.52 | 0.49 | 0.55 |
| Cr | 0.78 | 0.91 | 1.07 | 1.07 |
| Cu | 3.16<br>*sd 6.2* | 3.39<br>*sd 7.3* | 0.49<br>*sd 3.4* | 3.57<br>*sd 2.6* |
| Fe | 8.46<br>*sd 6.4* | 9.21<br>*sd 7.3* | 9.13<br>*sd3.4* | 9.76<br>*sd 2.6* |
| Mn | 0.70 | 0.72 | 0.77 | 0.80 |
| Ni | 0.00 | 0.00 | 0.00 | 0.00 |
| Ti | 1.26 | 1.82 | 1.56 | 1.41 |
| Zn | 0.82 | 0.87 | 0.89 | 1.02 |

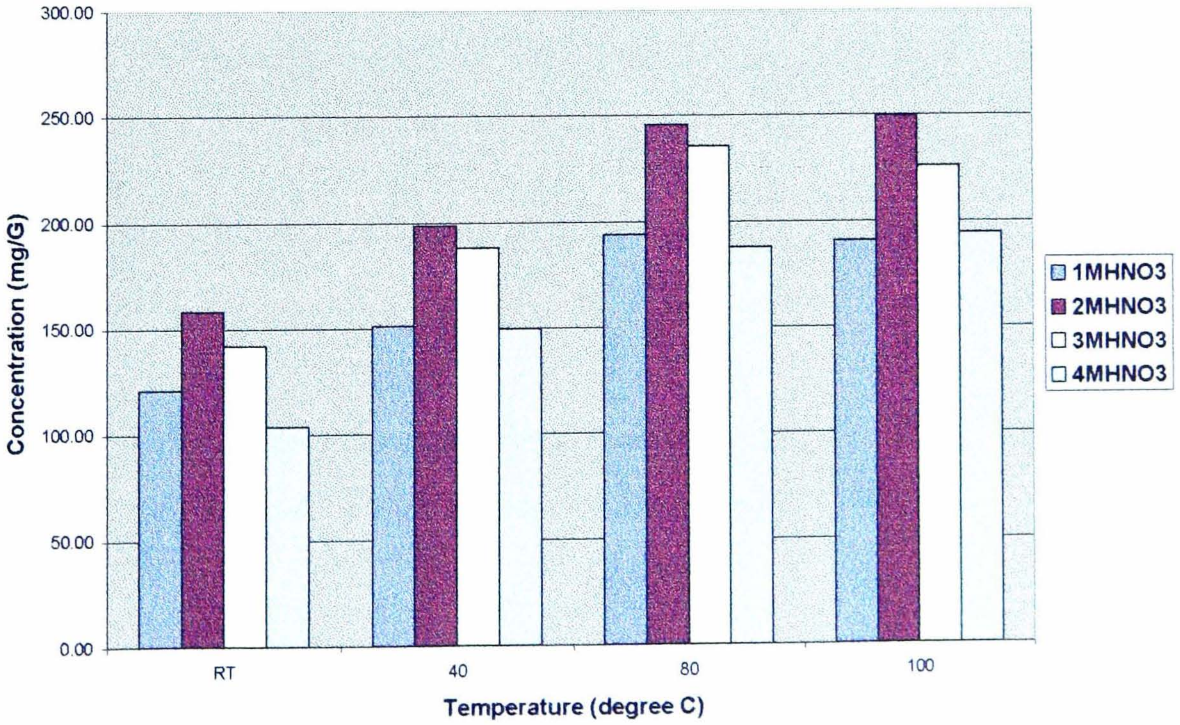


**Figure-2.22. Figure-2.18. Concentration of aluminium in washed black dross leached with $HNO_3$**

### *2.4.3.4 Sulphuric acid*

Leaching experiments were carried out under same conditions as described above, using $H_2SO_4$ in place of $HNO_3$. Figure-2.23 shows that 70% of black dross can be dissolved in 1M sulphuric acid at $80^0$C. A higher acid concentration does not render a more effective leaching of the black dross. The XRF (Figure-2.24) analysis shows that the 30% washed and oven-dried residue contains aluminium, silica, titanium, chromium, manganese and iron elements. The XRD analysis (Figure-2.25) confirms the presence of alumina ($\alpha$-$Al_2O_3$ or corundum), silica ($SiO_2$), and iron oxide ($FeFe_2O_4$) compounds. Data given in Table-2.10 are the different concentrations of metals recovered from black dross using different strengths of sulphuric acid and temperature. It can be seen that sulphuric acid is a less effective leaching medium than HCl and $HNO_3$ acids to recover maximum amount of metals from black dross. Figure-2.26 summarises the concentrations of aluminium recovered from black dross using different concentration of sulphuric acid at different temperatures. Maximum concentration of aluminium extracted in 3M $H_2SO_4$ acid at $100^0$C .

### *2.4.3.5. Aqua regia*

Data presented in Table-2.11 show that up to 80% of black dross is soluble in *aqua regia* at $80^0$C temperature. The XRF (Figure-2.27) analysis shows that the remaining 20% is mostly silica and very little aluminium. The XRD analysis (Figure-2.28) confirms the presence of alumina ($\alpha$-$Al_2O_3$ or corundum) and silica ($SiO_2$).

**Table-2.11. Solubility of black dross in *aqua regia* at different temperature**

| Temp ($^0$C) | Room temp | 40 | 80 | 100 |
|---|---|---|---|---|
| Weight (g) | 2.02 | 2.05 | 2.03 | 2.04 |
| dry residue (g) | 0.87 | 0.59 | 0.40 | 0.44 |
| %Solubility | 56.84 | 71.20 | 80.13 | 78.51 |

Table-2.12 shows the concentration of all the metals in the black dross leached by aqua regia. The maximum amount of aluminium was recovered at $80^0$C.

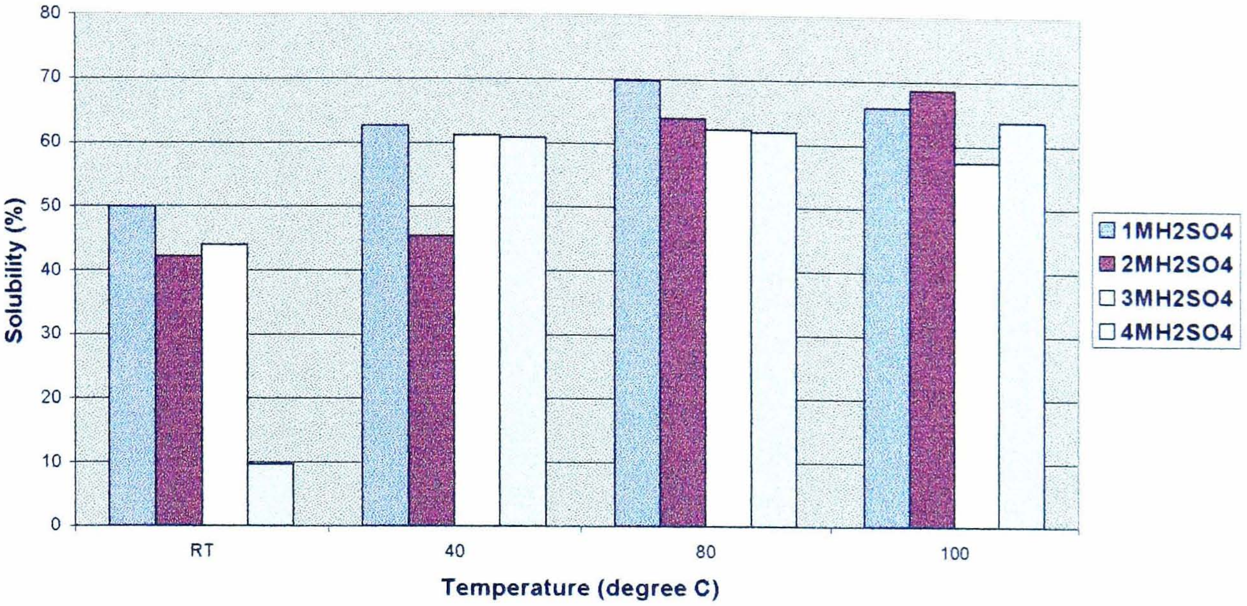


**Figure-2.23. %Solubility of washed black dross using different concentrations of $H_2SO_4$ and temperatures.**

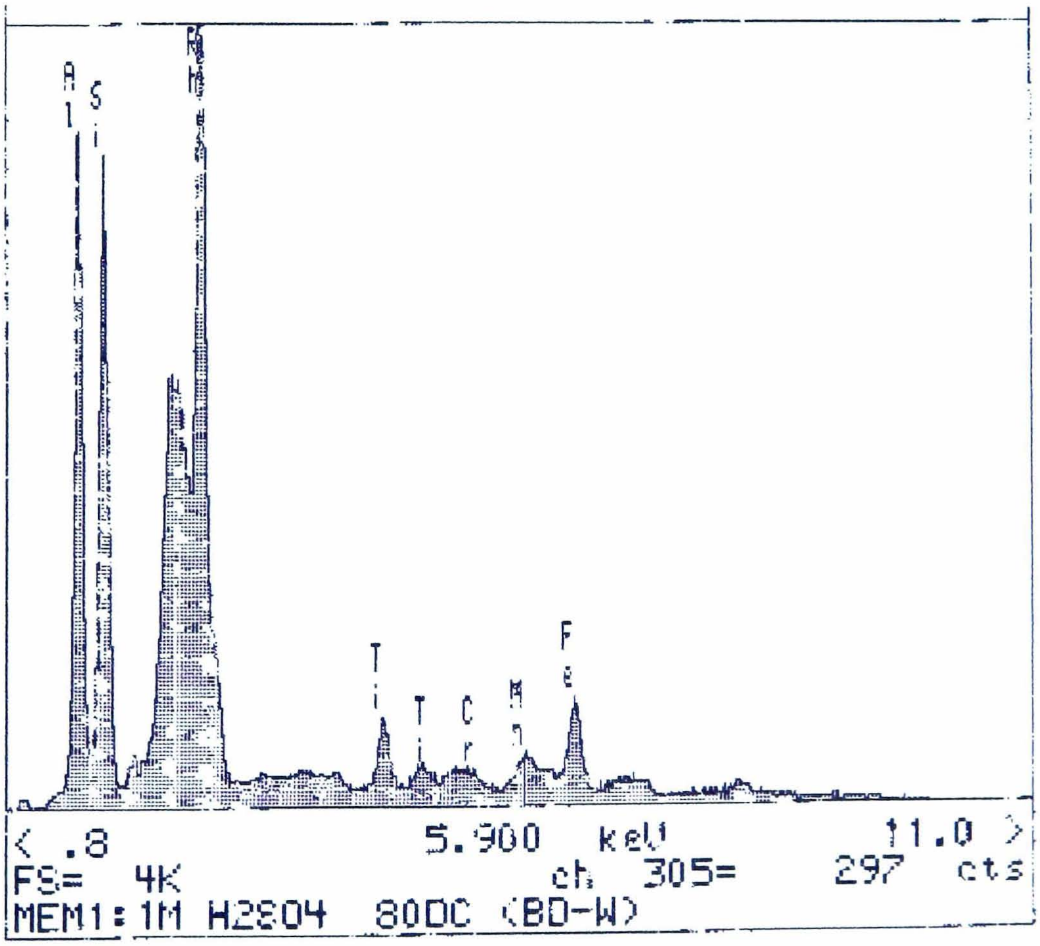


**Figure-2.24. XRF spectrum of black dross residue leached by 3M $H_2SO_4$ at 100$^0$C.**

**X-ray diffraction data of black dross residue leached by 1M $H_2SO_4$ at $80^0C$ temperature.**

| No | Angle($^0$) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 17.84 | 4.968 | 10 | | |
| 2 | 18.96 | 4.677 | 15 | $FeFe_2O_4$ | 4.67 |
| 3 | 20.8 | 4.267 | 12 | $SiO_2$ | 4.26 |
| 4 | 25.5 | 3.49 | 66 | $\alpha$-$Al_2O_3$ | 3.479 |
| 5 | 26.62 | 3.346 | 68 | $SiO_2$ | 3.342 |
| 6 | 28.4 | 3.14 | 56 | | |
| 7 | 29.02 | 3.074 | 8 | | |
| 8 | 30.18 | 2.959 | 11 | | |
| 9 | 31.22 | 2.863 | 14 | | |
| 10 | 33.12 | 2.703 | 10 | $Fe_2O_3$ | 2.7 |
| 11 | 35.06 | 2.557 | 100 | $\alpha$-$Al_2O_3$ | 2.552 |
| 12 | 35.98 | 2.494 | 10 | | |
| 13 | 36.84 | 2.438 | 30 | $FeFe_2O_4$ | 2.439 |
| 14 | 37.7 | 2.384 | 48 | $\alpha$-$Al_2O_3$ | 2.379 |
| 15 | 38.24 | 2.352 | 8 | | |
| 16 | 39.38 | 2.286 | 7 | $SiO_2$ | 2.29 |
| 17 | 40.18 | 2.242 | 6 | | |
| 18 | 43.26 | 2.09 | 97 | $\alpha$-$Al_2O_3$ | 2.08 |
| 19 | 47.26 | 1.922 | 28 | | |
| 20 | 50.12 | 1.819 | 9 | | |
| 21 | 50.4 | 1.809 | 6 | $SiO_2$ | 1.8 |
| 22 | 52.46 | 1.743 | 42 | $\alpha$-$Al_2O_3$ | 1.74 |
| 23 | 53.44 | 1.713 | 5 | | |
| 24 | 54.82 | 1.673 | 6 | $SiO_2$ | 1.672 |
| 25 | 56.06 | 1.639 | 20 | | |
| 26 | 57.4 | 1.604 | 83 | $\alpha$-$Al_2O_3$ | 1.601 |
| 27 | 59.32 | 1.557 | 14 | $SiO_2$ | 1.555 |
| 28 | 61.2 | 1.513 | 12 | $\alpha$-$Al_2O_3$ | 1.514 |
| 29 | 66.42 | 1.406 | 32 | $\alpha$-$Al_2O_3$ | 1.404 |
| 30 | 68.1 | 1.376 | 47 | $\alpha$-$Al_2O_3$ | 1.374 |
| 31 | 68.92 | 1.361 | 10 | $SiO_2$ | 1.369 |
| 32 | 75.6 | 1.257 | 5 | | |
| 33 | 76.76 | 1.241 | 17 | $\alpha$-$Al_2O_3$ | 1.239 |

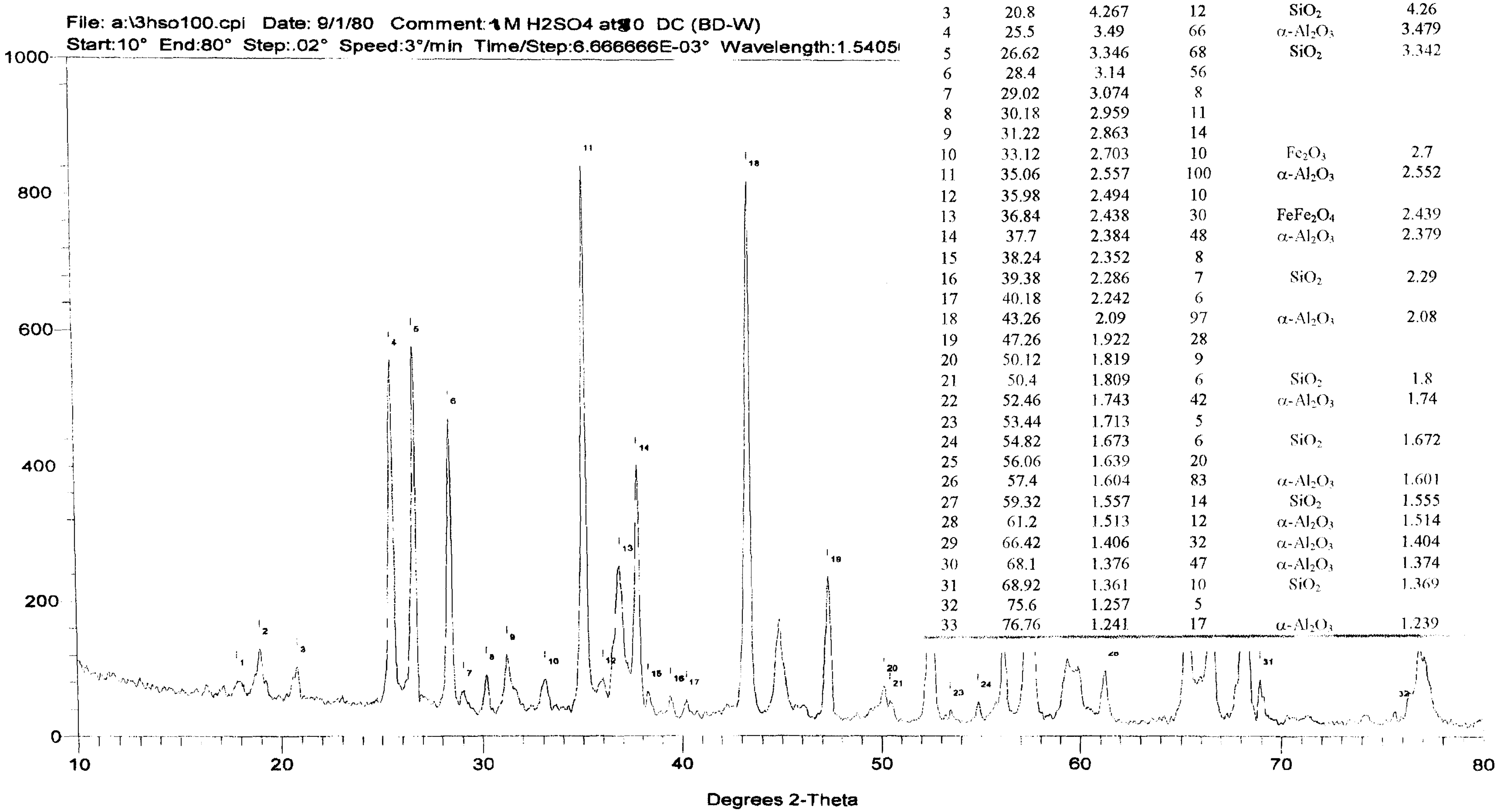


Figure-2.25. X-ray diffraction spectrum of black dross residue leached by 1M $H_2SO_4$ at $80^0C$.

**Table-2.10. Leachability studies of black dross using different concentrations of sulphuric acid and temperatures**

**1M $H_2SO_4$**

| Metals | Rt | $40^0$C | $80^0$C | $100^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 102.68<br>*sd 5.2* | 129.46<br>*sd 4.9* | 158.20<br>*sd 4 .0* | 167.61<br>*sd 2.0* |
| Ca | 0.14 | 0.25 | 0.21 | 0.20 |
| Cr | 1.00 | 0.98 | 1.01 | 1.05 |
| Cu | 2.97<br>*sd 5.1* | 3.70<br>*sd 4.5* | 3.76<br>*sd 4.3* | 3.10<br>*sd 1.9* |
| Fe | 8.91<br>*sd 5.0* | 9.59<br>*sd 5.0* | 8.65<br>*sd 4.2* | 9.67<br>*sd 2.3* |
| Mn | 0.68 | 0.75 | 0.74 | 0.75 |
| Ni | 0.00 | 0.00 | 0.00 | 0.00 |
| Ti | 1.29 | 1.57 | 1.66 | 1.63 |
| Zn | 0.83 | 0.90 | 0.91 | 1.06 |

**2M $H_2SO_4$**

| Metals | Rt | $40^0$C | $80^0$C | $100^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 117.71<br>*sd 3.3* | 168.20<br>*sd2.2* | 206.73<br>*sd3.3* | 206.99<br>*sd6.9* |
| Ca | 0.14 | 0.15 | 0.15 | 0.17 |
| Cr | 0.95 | 1.06 | 1.13 | 1.48 |
| Cu | 1.58<br>*sd 3.2* | 0.41<br>*sd 2.2* | 3.84<br>*sd3.5* | 3.61<br>*sd6.3* |
| Fe | 7.77<br>*sd 3.6* | 8.77<br>*sd 2.6* | 9.41<br>*sd 3.8* | 16.51<br>*sd 6.4* |
| Mn | 0.69 | 0.89 | 0.85 | 0.83 |
| Ni | 0.00 | 0.00 | 0.00 | 0.00 |
| Ti | 1.52 | 1.73 | 2.66 | 1.80 |
| Zn | 1.33 | 1.44 | 1.49 | 1.60 |

**3M $H_2SO_4$**

| Metals | Rt | $40^0$C | $80^0$C | $100^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 136.99<br>*sd 4.5* | 164.93<br>*sd 2.9* | 215.41<br>*sd 3.5* | 221.29<br>*sd 2.2* |
| Ca | 0.12 | 0.22 | 0.16 | 0.19 |
| Cr | 1.20<br>*sd 4.3* | 1.36<br>*sd 2.3* | 1.25<br>*sd 3.2* | 1.34<br>*sd 2.1* |
| Cu | 2.16<br>*sd 4.0* | 3.64<br>*sd 3.0* | 5.17<br>*sd 3.1* | 3.60<br>*sd 2.6* |
| Fe | 11.03 | 11.32 | 9.78 | 10.38 |
| Mn | 0.86 | 0.82 | 0.89 | 0.88 |
| Ni | 0.00 | 0.00 | 0.00 | 0.00 |
| Ti | 1.60 | 1.85 | 1.96 | 2.00 |
| Zn | 1.58 | 1.32 | 1.86 | 1.73 |

**4M $H_2SO_4$**

| Metals | Rt | $40^0$C | $80^0$C | $100^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 106.39<br>*sd3.1* | 144.17<br>*sd 3.3* | 181.44<br>*sd 6.3* | 181.74<br>*sd 2.2* |
| Ca | 0.16 | 0.24 | 0.23 | 0.25 |
| Cr | 1.24 | 1.08 | 1.16 | 1.29 |
| Cu | 2.55<br>*sd 3.0* | 3.82<br>*sd 3.4* | 3.29<br>*sd 6.1* | 2.90<br>*sd 2.8* |
| Fe | 12.74<br>*sd 3.0* | 10.97<br>*sd 3.2* | 10.04<br>*sd 6.0* | 10.44<br>*sd 2.0* |
| Mn | 1.51 | 0.81 | 0.99 | 0.91 |
| Ni | 0.00 | 0.00 | 0.00 | 0.00 |
| Ti | 1.50 | 1.90 | 1.92 | 1.84 |
| Zn | 0.77 | 1.04 | 0.87 | 0.90 |

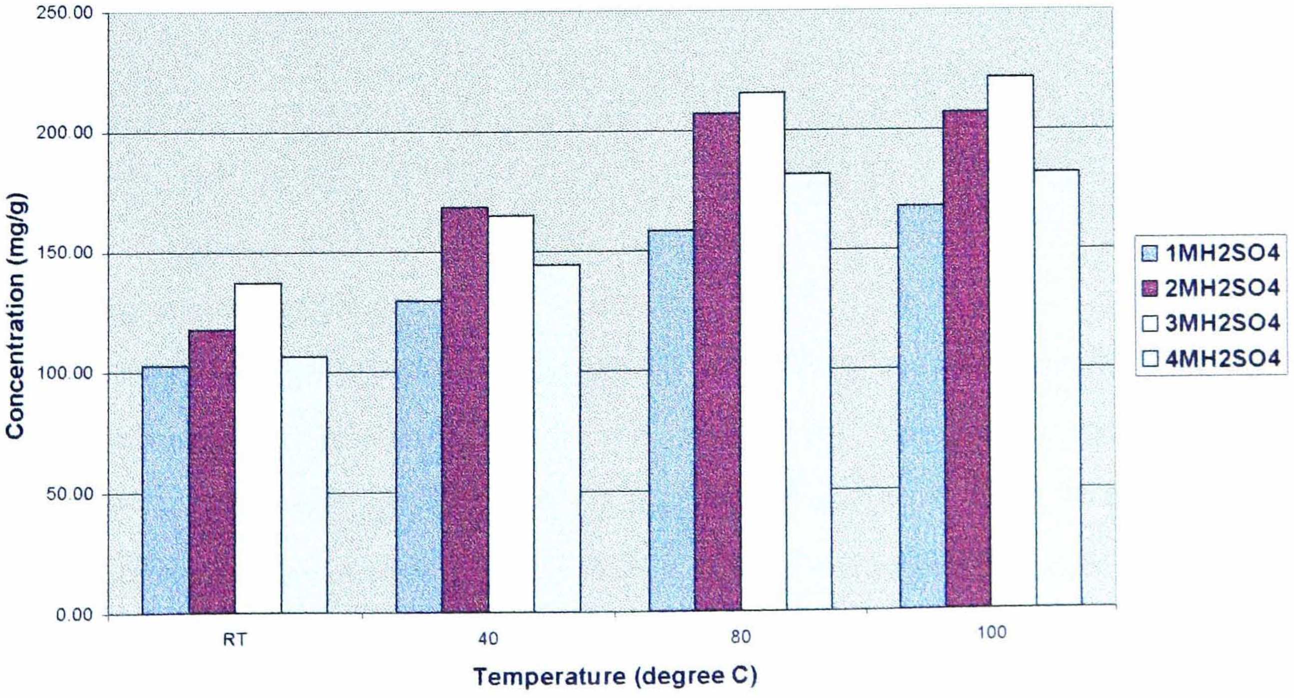


**Figure-2.26. Figure-2.18. Concentration of aluminium in washed black dross leached with $H_2SO_4$**

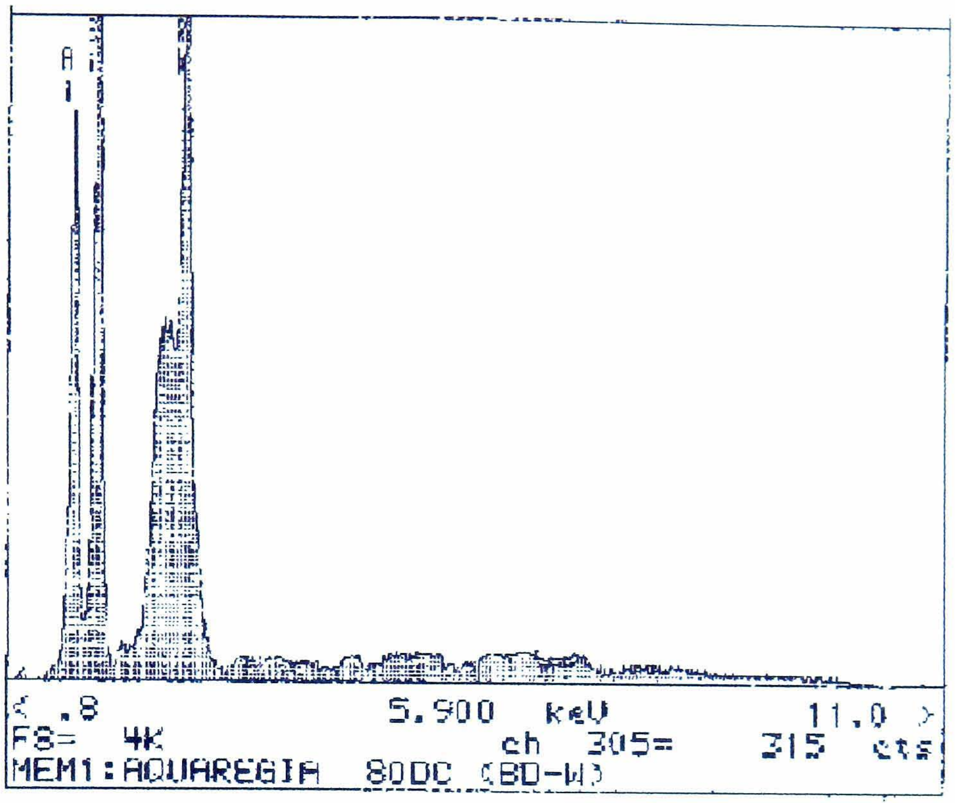


**Figure-2.27. XRF spectrum of black dross residue leached by *aqua regia* at 80$^0$C.**

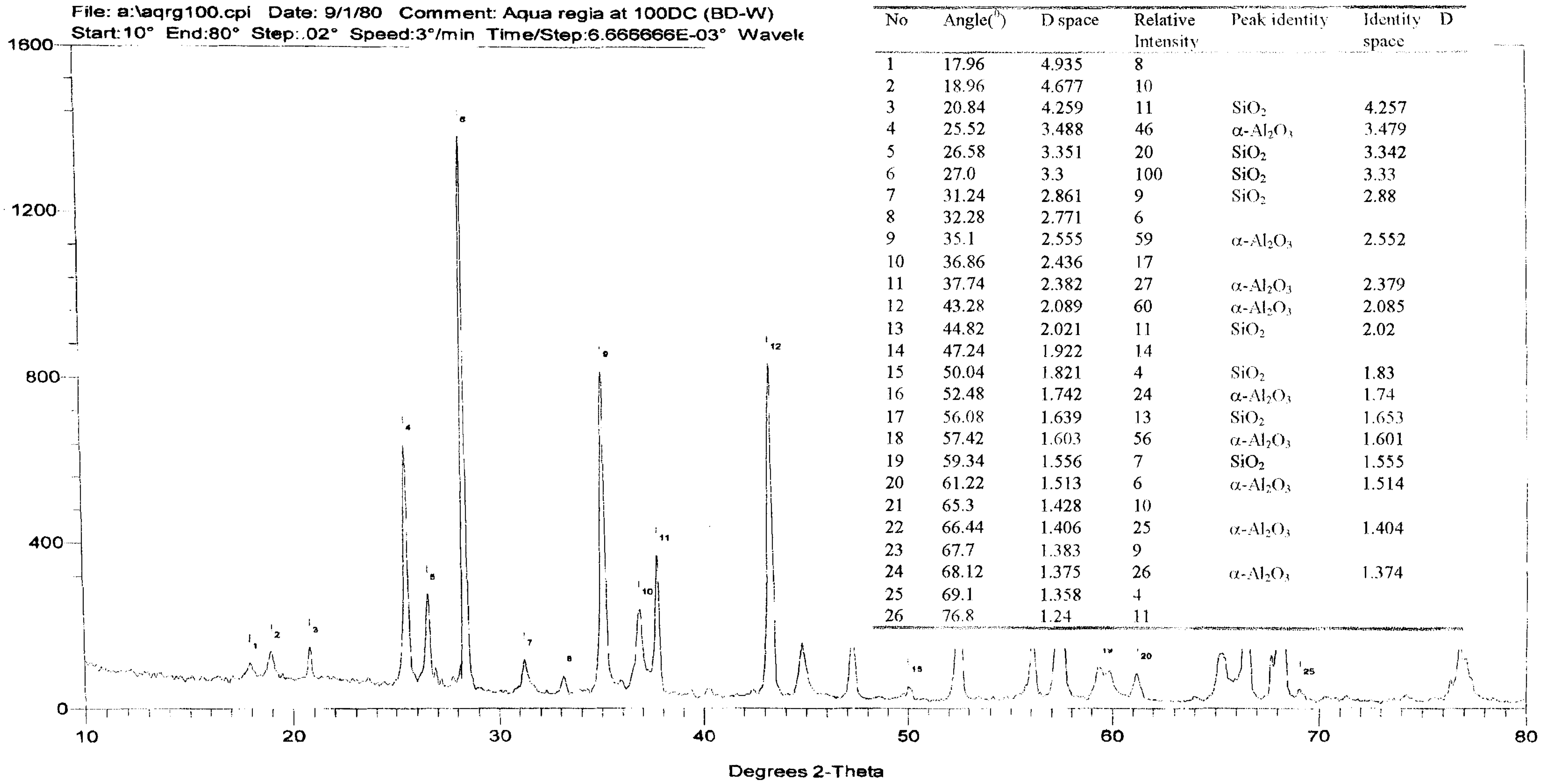
**Table-2.12. Concentrations of metals extracted from black dross using *aqua regia* at different temperatures.**

| Temp ($^0$C) | Room temp | 40 | 80 | 100 |
|---|---|---|---|---|
| Metals | Concentration (mg/g) | | | |
| Al | 155.711<br>*sd 5.72* | 185.3133<br>*sd 4.2* | 265.0656<br>*sd 5.25* | 247.9601<br>*sd 3.1* |
| Ca | 0.267 | 0.41 | 0.31 | 0.33 |
| Cr | 0.97 | 1.08 | 1.29 | 1.17 |
| Cu | 3.57<br>*sd 5.32* | 4.03<br>*sd 4.12* | 3.62<br>*sd 5.3* | 4.26<br>*sd 3.6* |
| Fe | 9.58<br>*sd 5.23* | 9.26<br>*sd 4.51* | 14.67<br>*sd 5.22* | 11.11<br>*sd 3.8* |
| Mn | 0.87 | 0.84 | 0.81 | 0.80 |
| Ni | 0 | 0 | 0 | 0 |
| Ti | 1.60 | 1.73 | 1.87 | 1.90 |
| Zn | 1.32 | 1.36 | 1.47 | 1.46 |

#### *2.4.3.6 Sodium hydroxide*

Figure-2.29 shows the percentage solubility of black dross in different concentrations of sodium hydroxide at different temperatures. Around 48% black dross was dissolved in 1M NaOH at 40$^0$C, 2M NaOH at 100$^0$C and in 3M NaOH at 40$^0$C temperature. 4M NaOH solution did not dissolve much black dross at any temperature compared to other concentrations of NaOH.

**X-ray diffraction spectrum of black dross residue leached by aqua regia at 80$^0$C temperature.**



| No | Angle($^0$) | D space | Relative Intensity | Peak identity | Identity D space |
|---|---|---|---|---|---|
| 1 | 17.96 | 4.935 | 8 | | |
| 2 | 18.96 | 4.677 | 10 | | |
| 3 | 20.84 | 4.259 | 11 | $SiO_2$ | 4.257 |
| 4 | 25.52 | 3.488 | 46 | $\alpha$-$Al_2O_3$ | 3.479 |
| 5 | 26.58 | 3.351 | 20 | $SiO_2$ | 3.342 |
| 6 | 27.0 | 3.3 | 100 | $SiO_2$ | 3.33 |
| 7 | 31.24 | 2.861 | 9 | $SiO_2$ | 2.88 |
| 8 | 32.28 | 2.771 | 6 | | |
| 9 | 35.1 | 2.555 | 59 | $\alpha$-$Al_2O_3$ | 2.552 |
| 10 | 36.86 | 2.436 | 17 | | |
| 11 | 37.74 | 2.382 | 27 | $\alpha$-$Al_2O_3$ | 2.379 |
| 12 | 43.28 | 2.089 | 60 | $\alpha$-$Al_2O_3$ | 2.085 |
| 13 | 44.82 | 2.021 | 11 | $SiO_2$ | 2.02 |
| 14 | 47.24 | 1.922 | 14 | | |
| 15 | 50.04 | 1.821 | 4 | $SiO_2$ | 1.83 |
| 16 | 52.48 | 1.742 | 24 | $\alpha$-$Al_2O_3$ | 1.74 |
| 17 | 56.08 | 1.639 | 13 | $SiO_2$ | 1.653 |
| 18 | 57.42 | 1.603 | 56 | $\alpha$-$Al_2O_3$ | 1.601 |
| 19 | 59.34 | 1.556 | 7 | $SiO_2$ | 1.555 |
| 20 | 61.22 | 1.513 | 6 | $\alpha$-$Al_2O_3$ | 1.514 |
| 21 | 65.3 | 1.428 | 10 | | |
| 22 | 66.44 | 1.406 | 25 | $\alpha$-$Al_2O_3$ | 1.404 |
| 23 | 67.7 | 1.383 | 9 | | |
| 24 | 68.12 | 1.375 | 26 | $\alpha$-$Al_2O_3$ | 1.374 |
| 25 | 69.1 | 1.358 | 4 | | |
| 26 | 76.8 | 1.24 | 11 | | |

Figure-2.28. X-ray diffraction spectrum of black dross residue leached by aqua regia at 80$^0$C.

Figure-2.30 shows the XRF analysis of the 52% black dross residue after leaching with 3M NaOH at $40^0$C. The spectrum shows the presence of aluminium, silica, chromium, manganese, iron and copper. The XRD analysis (Figure-2.31) confirms the presence of iron hydroxide ($Fe(OH)_3$), aluminium hydroxide ($Al(OH)_3$), alumina ($\alpha$-$Al_2O_3$), iron oxide ($Fe_3O_4$) and silica ($SiO_2$)

Table-2.13 lists the different concentration of metals recovered from black dross using the various concentrations of sodium hydroxide at different temperatures. It can be seen that only aluminium has been recovered significantly. Most of the other metals are recovered in trace amounts or if at all. Figure-2.32 summarises the concentration of aluminium leached from black dross using different concentrations of sodium hydroxide and different temperatures. The highest recovery of aluminium was with 2M NaOH at $100^0$C. Aluminium recovery under these conditions is higher than in the acidic conditions.

### *2.4.3.7. Summary of the leaching media and temperatures*

Black dross is an aluminium waste which contains many other metallic and non-metallic compounds. The aim of this project is to find the best conditions to dissolve black dross and to determine the total metal content. Because of the presence of various types of compounds, both acid and alkaline conditions were chosen for study of the dissolution of black dross. The Figure-2.33 summarises the results of the best leaching conditions (within the given conditions) to optimise the dissolution of the maximum amount of black dross. Total dissolution of black dross could not be achieved under either acidic or basic conditions at any temperature. 80% of black dross was dissolved using 3M HCl at $100^0$C and *aqua regia* at $80^0$C. The XRD analysis of the remaining residue after treated with *aqua regia* at $80^0$C confirmed that the remaining dried residue consist of mainly alumina and silicon oxide. It is well known that silicon oxide is very difficult to dissolve and alumina is not soluble under acidic conditions. Therefore, these compounds remain as residue under these leaching conditions.

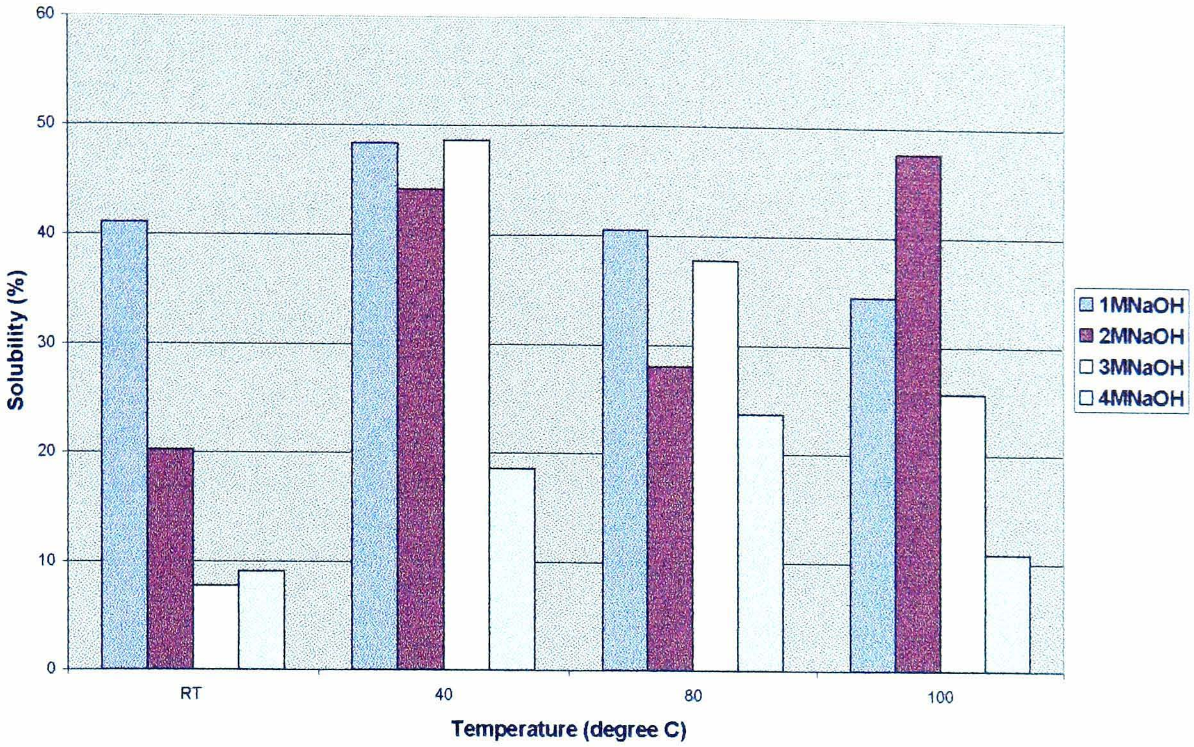


Figure-2.29. %Solubility of washed black dross using different concentrations of NaOH and Temperatures.

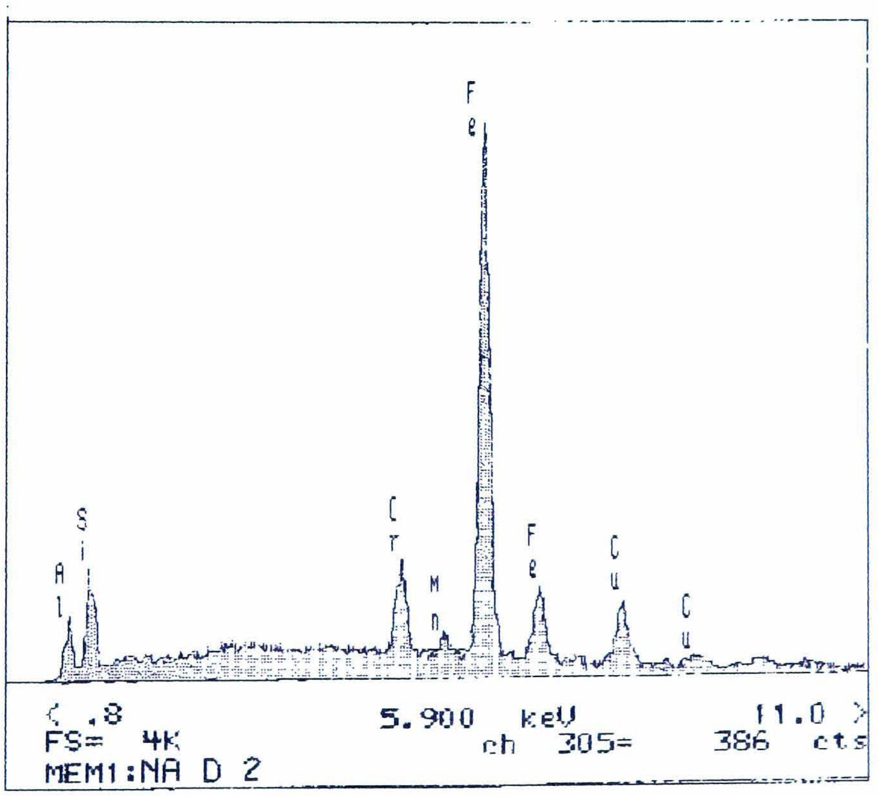


Figure-2.30. XRF spectrum of black dross residue leached by 3M NaOH at $40^0$C.

**X-ray diffraction data of black dross residue leached by 2M NaOH at 100$^0$C temperature.**

| No | Angle($^0$) | D space | Rel Int | Peak identity |
|---|---|---|---|---|
| 1 | 13.56 | 6.235 | | $Fe(OH)_3$ |
| 2 | 18.44 | 4.807 | 100 | $Fe(OH)_3$ |
| 3 | 20.28 | 4.375 | 34 | $SiO_2$ |
| 4 | 20.48 | 4.333 | 34 | $Al(OH)_3$ |
| 5 | 21.02 | 4.223 | 27 | $Al(OH)_3$ |
| 6 | 21.28 | 4.182 | 25 | $Fe(OH)_3$ |
| 7 | 22.64 | 3.924 | 19 | |
| 8 | 24.4 | 3.645 | 24 | $Fe_2O_3$ |
| 10 | 24.62 | 3.613 | 19 | $Al(OH)_3$ |
| 11 | 25.5 | 3.49 | 20 | $Al(OH)_3$ |
| 12 | 31.26 | 2.859 | 26 | $Fe_3O_4$ |
| 13 | 35.08 | 2.56 | 21 | $Fe(OH)_3$ |
| 14 | 37. | 2.428 | 45 | $Fe_3O_4$ |
| 15 | 37.48 | 2.398 | 49 | $Al(OH)_3$ |
| 16 | 39.64 | 2.272 | 32 | $Al(OH)_3$ |
| 17 | 40.58 | 2.21 | 23 | $Fe(OH)_3$ |
| 18 | 41.72 | 2.163 | 17 | $\alpha$-$Al_2O_3$ |
| 19 | 43.28 | 2.089 | 25 | $\alpha$-$Al_2O_3$ |
| 20 | 44.84 | 2.02 | 39 | $SiO_2$ |
| 21 | 47.76 | 1.93 | 27 | $Fe(OH)_3$ |
| 22 | 49.1 | 1.854 | 30 | |
| 23 | 51.18 | 1.783 | 18 | $Al(OH)_3$ |
| 24 | 52.48 | 1.74 | 14 | $Fe(OH)_3$ |
| 25 | 53. | 1.726 | 15 | $Fe(OH)_3$ |
| 26 | 57.4 | 1.604 | 18 | $Fe(OH)_3$ |
| 27 | 59.44 | 1.557 | 21 | $Fe_3O_4$ |
| 28 | 64.78 | 1.438 | 24 | $Fe_3O_4$ |

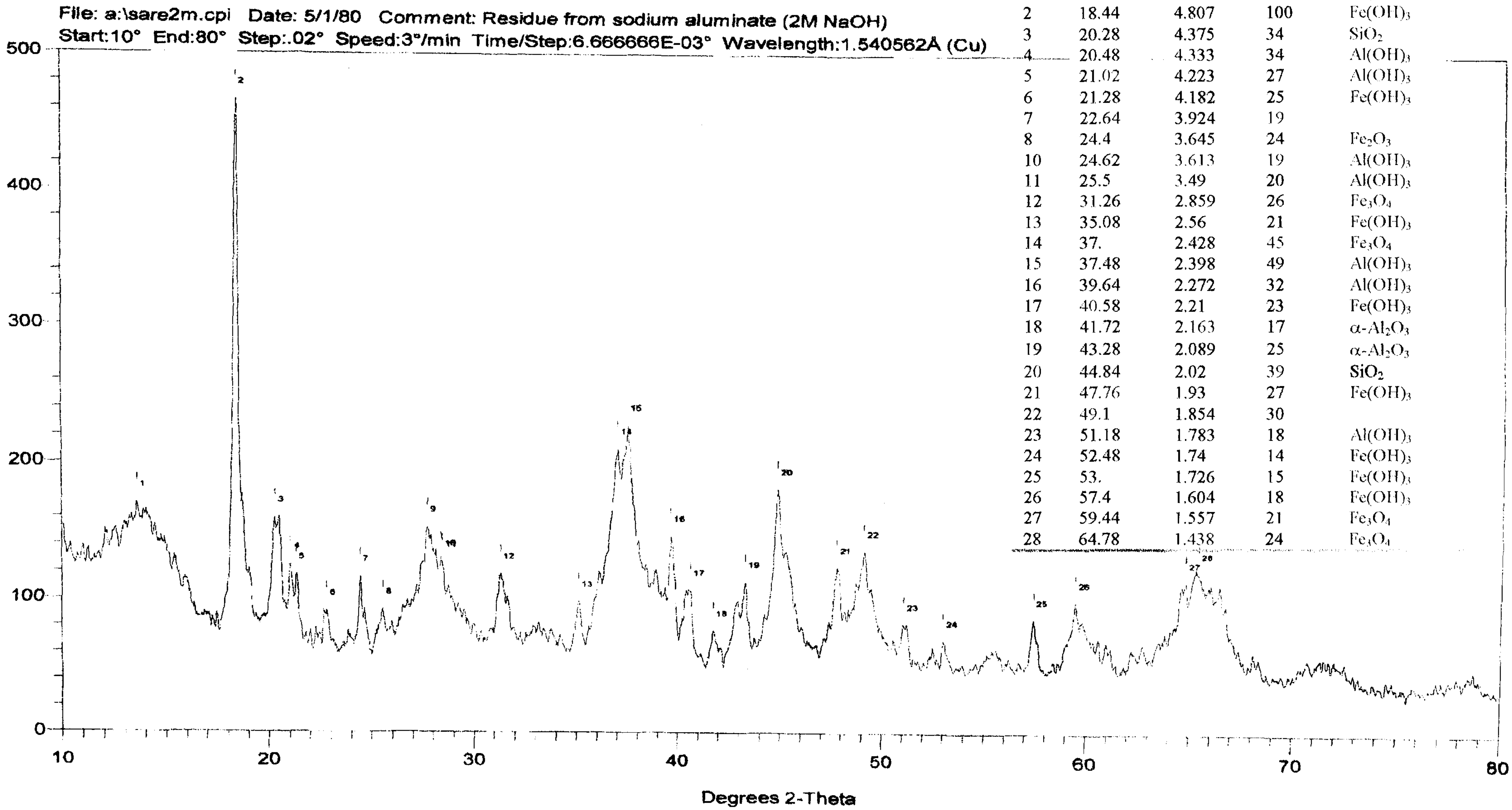


**Figure-2.31. X-ray diffraction spectrum of black dross residue leached by 2M NaOH at 100$^0$C.**

## Table-2.13. Leaching of black dross using different concentrations of sodium hydroxide and temperatures

**1M NaOH**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 118.55<br>*sd 1.7* | 172.37<br>*sd 3.1* | 134.92<br>*sd 2.4* | 131.15<br>*sd 3.0* |
| Ca | <0.09 | <0.09 | <0.09 | <0.09 |
| Cr | <0.07 | <0.07 | <0.07 | <0.078 |
| Cu | 0.079 | 0.29 | 0.18 | 0.07 |
| Fe | <0.1 | 0.15 | <0.1 | <0.1 |
| Mn | <0.05 | <0.05 | <0.05 | <0.05 |
| Ni | <0.14 | <0.14 | <0.14 | <0.14 |
| Ti | <1.8 | <1.8 | <1.8 | <1.8 |
| Zn | 0.3244 | 0.4371 | 0.4456 | 0.4736 |

**2M NaOH**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 124.95<br>*sd4.0* | 285.45<br>*sd 4.0* | 209.97<br>*sd7.4* | 363.31<br>*sd4.5* |
| Ca | <0.09 | <0.09 | <0.09 | <0.09 |
| Cr | <0.07 | <0.07 | <0.07 | <0.07 |
| Cu | 0.1574 | 0.6950 | 0.3511 | 0.1460 |
| Fe | <0.1 | 0.2544 | <0.1 | 0.13 |
| Mn | <0.05 | <0.05 | <0.05 | <0.05 |
| Ni | <0.14 | <0.14 | <0.14 | <0.14 |
| Ti | <1.8 | <1.8 | <1.8 | <1.8 |
| Zn | 0.5122 | 0.8563 | 0.8718 | 0.6117 |

**3M NaOH**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 124.50<br>*sd 7.8* | 222.00<br>*sd 6.2* | 146.14<br>*sd3.8* | 115.72<br>*sd4.5* |
| Ca | <0.09 | <0.09 | <0.09 | <0.09 |
| Cr | <0.07 | <0.07 | <0.07 | <0.076 |
| Cu | 0.1307 | 0.3939 | 0.2282 | 0.0763 |
| Fe | <0.1 | 0.2915 | 0.1062 | 0.1 |
| Mn | <0.05 | <0.05 | <0.05 | <0.05 |
| Ni | <0.14 | <0.14 | <0.14 | <0.14 |
| Ti | <1.8 | <1.8 | <1.8 | <1.8 |
| Zn | 0.5229 | 0.6830 | 0.7850 | 0.6032 |

**4M NaOH**

| Metals | Rt | 40$^0$C | 80$^0$C | 100$^0$C |
|---|---|---|---|---|
| Concentration (mg/g) | | | | |
| Al | 160.97<br>*sd 3.0* | 158.72<br>*sd5.4* | 340.63<br>*sd 4.2* | 128.73<br>*sd 3.0* |
| Ca | <0.09 | <0.09 | <0.09 | <0.09 |
| Cr | <0.07 | <0.07 | <0.07 | <0.07 |
| Cu | 0.2211 | 0.2847 | 0.3418 | <0.07 |
| Fe | 0.1044 | 0.2314 | 0.1678 | 0.1324 |
| Mn | <0.05 | <0.05 | <0.05 | <0.05 |
| Ni | <0.14 | <0.14 | <0.14 | <0.14 |
| Ti | <1.8 | <1.8 | <1.8 | <1.8 |
| Zn | 0.7372 | 0.8118 | 0.0742 | 0.0747 |

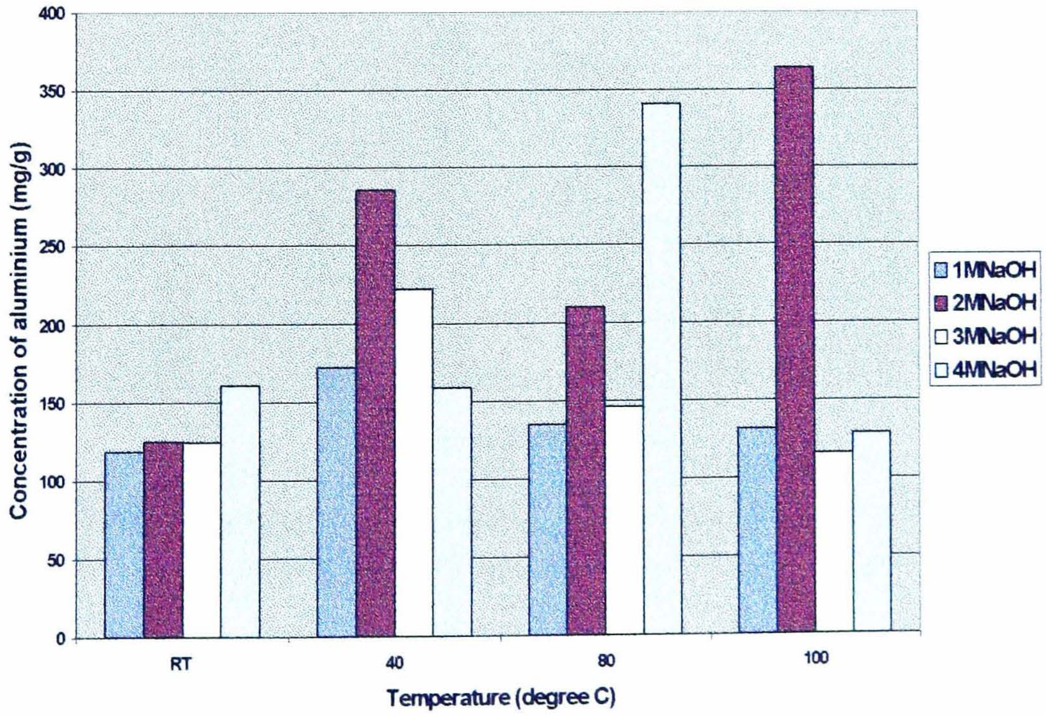


Figure-2.32. Concentration of aluminium in washed black dross leached with NaOH.

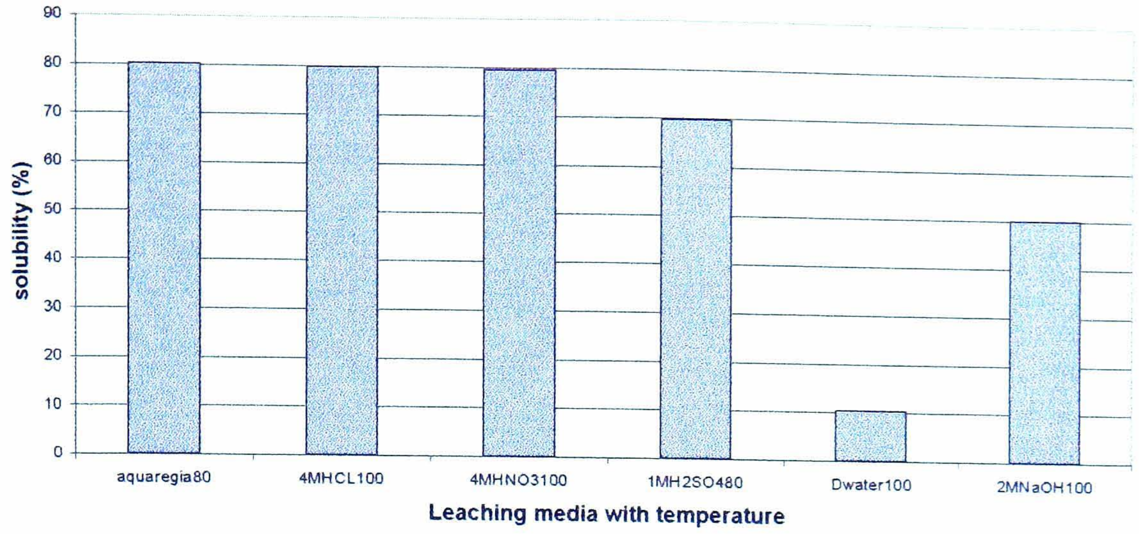


**Figure-2.33. % Solubility of washed black dross using different leaching media and temperatures.**

Figure-2.34 summarises the results of the best leaching conditions for recovery of the maximum amount of aluminium from black dross. The solubility results show that, although, acid is the best leaching medium to dissolve the maximum amount of black dross, sodium hydroxide is the best leaching medium to recover maximum amount of aluminium. 2M sodium hydroxide at 100$^0$C are the best leach conditions for aluminium dissolution. It has been shown (Figure-2.32), that increasing sodium hydroxide concentration above 2M does not improve aluminium dissolution.

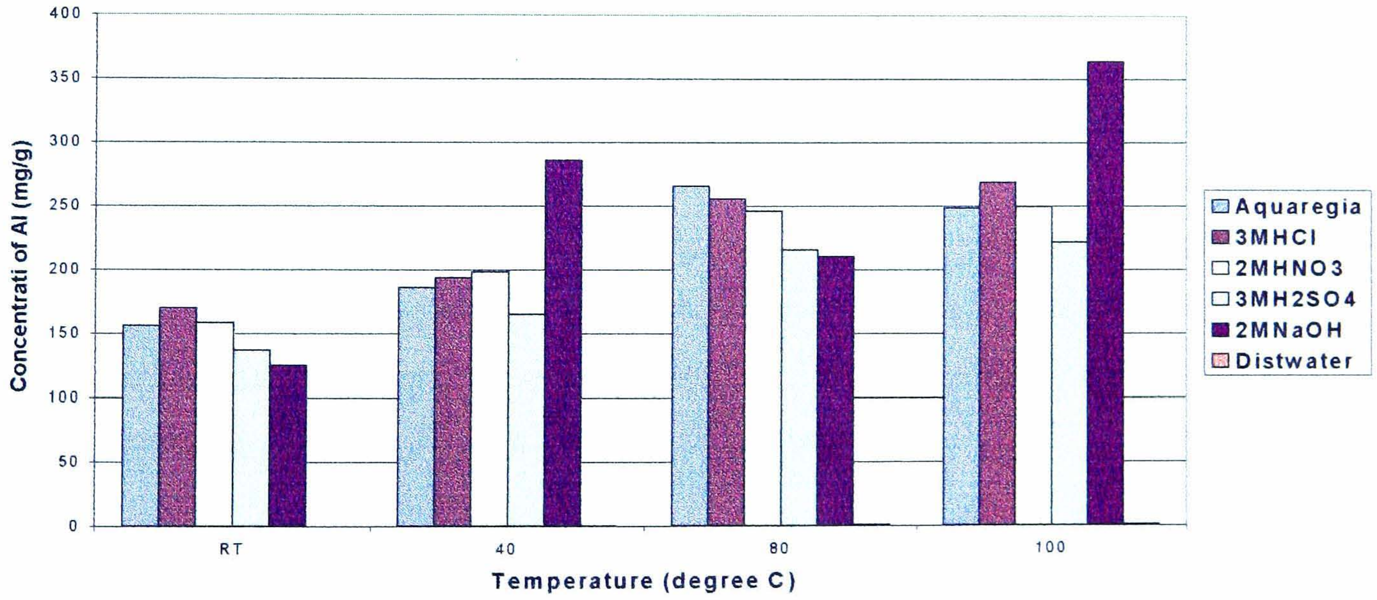


**Figure-2.34. Leaching of aluminium from washed black dross using different leaching media at different temperatures**

The solubility of aluminium generally follows the pattern given in Figure-2.35 which shows three distinct areas. In the first one at pH<4 dissolved $Al^{3+}$ and positively charged hydroxo complexes are dominant. At pH>4 the phase changes and precipitation of solid

$Al(OH)_3$ occurs, whereas at pH>8 dissolution and formation of dissolved negatively charged hydroxo complexes prevail.

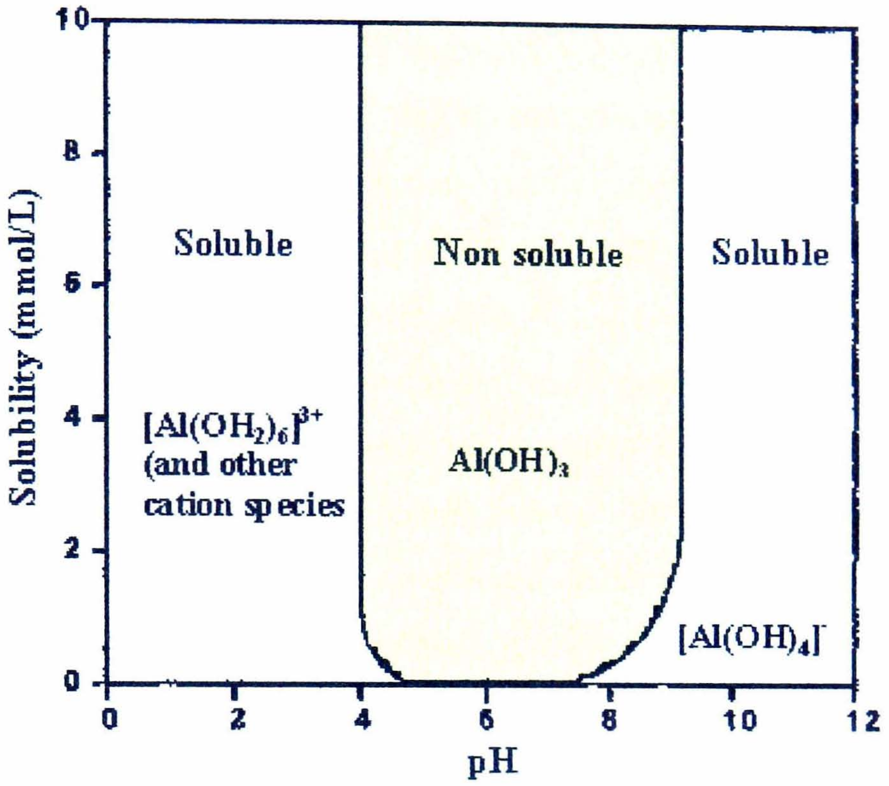


**Figure-2.35. Leaching of aluminium as a function of pH[5]**

In acidic media only aluminium metal is soluble and alumina remains in the residue. The following reaction takes place in acid leaching media.

$$2Al + 6H^+ \longrightarrow 2Al^{3+} + 3H_2$$

In aqueous solution, the aluminium ion is present as the hexaaquaalumnium ion, $[Al(OH_2)_6]^{3+}$, but it undergoes a hydrolysis reaction to give a solution of the hydroxopentaaquaaluminium ion, $[Al(OH_2)_5(OH)]^{2+}$, and the hydronium ion, and then to the dihydroxotetraaquaaluminium ion $[Al(OH_2)_4(OH)_2]^+$.

The higher concentration of aluminium in the case of basic leaching arises because not only is the aluminium being dissolved but also alumina is being leached out in basic solution. The following chemical reactions take place in basic media.

$$2Al + 2OH^- + 6H_2O \longrightarrow 2[Al(OH)_4]^- + H_2$$

$$Al2O_3 + 2OH^- + 3H_2O \longrightarrow 2[Al(OH)_4]^-$$

This soluble aluminate ion, upon cooling, precipitates as white aluminium oxide trihydrate.

$$2[Al(OH)]- \longrightarrow Al_2O_3.3H_2O + 2OH^-$$

Despite what is shown in Figure-2.35, in Section 2.4.3.6, the results showed that higher concentration of sodium hydroxide (i.e., higher pH) did not extract a higher amount of aluminium from black dross. Not 4M but 2M sodium hydroxide extracted the highest amount of aluminium (Figure-2.32). This is due to the fact that higher concentration of sodium hydroxide not only extracted aluminium into the solution, but also precipitated the other metallic impurities as their hydroxides, such as iron, zinc, copper hydroxides. These hydroxides remain in the residue and act as an adsorbent. As the concentration of sodium hydroxide is increased, the precipitation of metallic hydroxides is increased and as they act like adsorbents, the anionic or cationic aluminium species become adsorbed in the precipitate and therefore, less aluminium remains in the solution[6].

The acidic media dissolved aluminium along with other impurities to a significant extent, but sodium hydroxide dissolved only aluminium and its compounds. To achieve the total metal composition of black dross, acid leaching would be the best. The acid leaching results show that hydrochloric acid is marginally better than nitric or sulphuric acid for the leaching of aluminium and other metal impurities like iron, copper and zinc. This is due to the formation of soluble anionic chloride complexes. Examples of well known anionic chloride complexes include $FeCl_6^{3-}$, $CuCl_4^{2-}$, $ZnCl_4^{2-}$. Although most metals are able to form these complexes in hydrochloric acid, there are exceptions, such as aluminium, nickel, alkaline earth metals, which exist as simple cationic species[5]. If the interest is only to dissolve aluminium but not the impurities, sodium hydroxide would be the best solution to use at 80-100$^0$C. From this leaching study the percentage composition of each element in black dross is confirmed and presented in Table-2.14.

**Table-2.14. Percentage composition of washed black dross sample.**

| Metal | $Al_2O_3$ | CaO | CrO | CuO | $Fe_2O_3$ | MnO | NiO | $P_2O$ | $SiO_2$ | $TiO_2$ | ZnO |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition (%) | 70 | 0.4 | 0.2 | 1 | 2.4 | 0.13 | 0.1 | 0.05 | 20 | 0.33 | 0.32 |

### 2.4.4. Screening Test

#### *2.4.4.1 Determination of particle size distribution*

The distribution of particle size in unwashed black dross is given in Table-2.15. The dross sample used in this experiment was unwashed. The dross particles are very coarse size with only a small quantity of fines.

**Table-2.15. Percentage distribution of particle size.**

| Percentage distribution of particle size | | | | | | | |
|---|---|---|---|---|---|---|---|
| Aperture (mm) | +4 | -4+2.36 | -2.36+1.18 | -1.18+0.85 | -0.85+0.6 | -0.6+0.5 | 0.5 |
| Black dross(g) | 30.1 | 17.4 | 45.7 | 4.4 | 1.3 | 0.4 | 0.7 |

#### *2.4.4.2 Determination of aluminium and salt in each particle size*

Figure-2.36 shows the distribution of aluminium, potassium and sodium elements in each dross particle size. It can be seen that the aluminium content is higher in the larger particle sizes. As the particle size decreases the concentration of aluminium decreases as well.

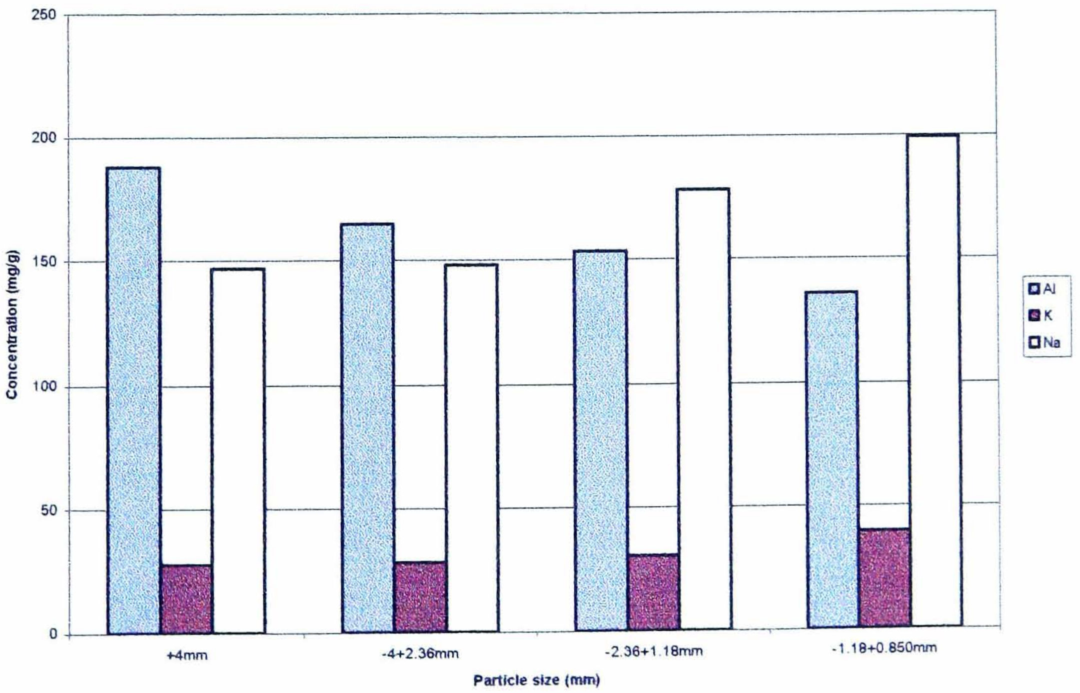


**Figure-2.36. Distribution of Al, K and Na in different particle sizes of black dross**

24% of aluminium was found in the +4mm fraction. On the contrary, sodium concentration is lower in the large particle size and increases considerably with decreasing particle size. 25% sodium was found in the –1.8+0.85mm fraction. The concentration of potassium remains the same in each fraction. 4% was the highest amount found in the –1.8+0.85mm fraction.

The coarse particles consist of pure aluminium metal covered with aluminium oxide layer. The fine particles are mainly salts and other impurities. Therefore, significant aluminium can be recovered (concentrated) by crushing black dross into reasonable particle size using crushers. Although by this method the presence of the salt cannot be avoided as it will be in every particle size distribution, its presence will be much less in the coarse fractions.

## 2.5. SUMMARY

Black dross tailings, which is aluminium waste product, have been produced by the aluminium smelters. Every year all of this dross is landfilled due to lack of an economically viable method to reclaim the metals, causing enormous economic loss to the industries.

In this chapter the black dross tailings have been physically and chemically characterised in order to achieve the characteristic properties of the dross. The dross sample has been found to consist of 47% salt mixture ( as sodium chloride and potassium chloride). A countercurrent washing process has been developed to successfully recycle the salt from the dross. The process has been found to be both environmentally and economically viable. After the salt is removed, the remaining dross consists of mainly aluminium, alumina, aluminium nitride, iron oxide and silica. A maximum of 80% of the dross can be dissolved in acidic media at high temperature. Sodium hydroxide however, has been found to be the best leaching medium to selectively dissolve the maximum amount of aluminium, without other metal impurities. A particle size analysis experiment has confirmed that salt in black dross is concentrated in the smaller fine size particles. Coarse size particles are enriched with alumina.

## 2.6. REFERENCES

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# CHAPTER THREE

# ENVIRONMENTAL IMPACT OF LANDFILLING BLACK DROSS

## 3.1 INTRODUCTION

It has been mentioned that almost all black dross is being landfilled every year without any treatment. This dross contains 5-15 wt% of aluminium, 50 wt% salts and the rest is other metallic impurities, which can be extremely hazardous for our environment. Therefore, it is very important to understand the fate of the metals in black dross in contact with soil and water and find a solution to minimise the pollution. No previous research work has been published on the environmental impact of landfilling black dross. In this chapter, the environmetal impact of landfilling black dross is investigated by studying its behaviour under simulated landfill conditions. Aluminium is the third most abundant element within the earth's crust[1]. Thus, a question arises regarding how the aluminium from black dross can cause problems to the environment. In the first section in this chapter, attention has been focused on the existence of aluminium in the natural environment and its toxicity to living organisms. The next two sections are focused on the constituents of natural soils and different leaching media that are associated with black dross. Finally, the environmental implication of landfilling black dross will be investigated by studying the behaviour of black dross under simulated landfill conditions.

**Table-3.1. Earth's crust elements[1]**

| Element | %(by weight) |
|---|---|
| Oxygen | 50 |
| Silicon | 23 |
| Aluminium | 8 |
| Iron | 5 |
| Calcium | 3.5 |
| Sodium | 2.7 |
| Magnesium | 2 |
| Phosphorus | 1.2 |
| Other elements | 4.6 |

### 3.1.1 Aluminium in the Environment[2]

Aluminium is the one of the most abundant elements in soils, making up approximately 8wt% of the solid matter in an average soil (Table-3.1). Particulate matter associated with soil/sediment represents the largest pool of aluminium on the surface of the Earth.

Within the earth's crust, aluminium is largely associated with aluminosilicate minerals, most commonly as feldspars in metamorphic and igneous rocks, and as clay minerals in well-weathered soils. In this form, aluminium is generally unavailable (unreactive) for chemical and biological reactions, because it is relatively insoluble in most surface waters. Through soil development, highly crystalline aluminosilicate minerals are decomposed and a small fraction of the total aluminium becomes available to participate in biogeochemical processes. Available soil/sediment pools of aluminium are generally characterised by operationally defined extraction techniques and are frequently termed "free" (nonsilicate-bound) aluminium. Several processes contribute to form free soil/sediment pools of aluminium. These processes include biological assimilation and release, as well as the weathering of aluminosilicate minerals by carbonic acid dissolution, organic acid dissolution, strong acid, i.e., acid rain dissolution, or neutral hydrolysis, followed by the secondary precipitation of aluminium. Aluminium is also retained on the surfaces of charged soil/sediments associated with organic matter and/or clay minerals. Finally, free soil/sediment aluminium may be associated with organic matter through microbial/plant transformations or formed by precipitation with organic solutes.

All forms of soil/sediment aluminium may potentially control solution concentrations. However, the release of aluminium from highly crystalline minerals is very slow and the concentration of dissolved aluminium in the natural waters is also very low because of very low solubility. Aluminium in solution is the most chemically and biologically available form, although this pool represents a small fraction of the total aluminium in the environment. Aluminium is a strongly hydrolysing metal and is relatively insoluble in the neutral pH range (6.0 to 8.0). Under acidic (pH <6.0) or alkaline (pH >8.0) conditions, and/or in the presence of complexing ligands, the solubility of aluminium is enhanced, making it more available for biogeochemical transformations. Within the aqueous phase, aluminium may be associated with a variety of inorganic and organic complexes. The extent of complexation depends on the availability for soil/sediment aluminium, solution pH, concentrations of complexing ligands, ionic strength and temperature. Aqueous aluminium may be redeposited to free soil/sediment pools, assimilated by living biomass, or transported from the system.

### 3.1.2. Aluminium speciation in soil solution

All of black dross is landfilled every year, and this dross contains 5-10 wt% aluminium as metal and 35 wt% as oxides, metallic aluminium trapped in to it. It is very important to study the behaviour of aluminium in soil solution because the chemical nature of aluminium is very different at different pHs and its toxicity to living organisms depends on the different aluminium species.

At low pH (<5.0), aqueous aluminium is almost entirely present as an aquo complex. The $Al^{3+}$ aquo-ion hydrolyses in aqueous media giving various hydrolysis species. Hydrolysis of aluminium forming monomeric (contains one metal ion or in this case, one $Al^{3+}$) species is shown below[3]:

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons \mathit{[Al(OH)(H_2O)_5]^{2+}} + H_3O^+$$
$$[Al(OH)(H_2O)_5]^{2+} + H_2O \rightleftharpoons \mathit{[Al(OH)_2(H_2O)_4]^{1+}} + H_3O^+$$
$$[Al(OH)_2(H_2O)_4]^{1+} + H_2O \rightleftharpoons \mathit{[Al(OH)_3(H_2O)_3]^{0+}} + H_3O^+$$
$$[Al(OH)_3(H_2O)_3]^{0+} + H_2O \rightleftharpoons \mathit{[Al(OH)_4(H_2O)_2]^{1-}} + H_3O^+$$

The monomeric hydrolysis products shown above (in italics), are produced as co-ordinated water is deprotonated. One of the important aspects of the reactions is that $H_3O^+$ or $H^+$ is produced, resulting in a decrease in pH or increased acidity. The magnitude of the pH decrease depends on the concentration of Al in the solution.

The formation of monomeric Al in the soil solution depends on the pH. Figure-3.1 shows the effect of pH on the solubilities of Al in water solutions.

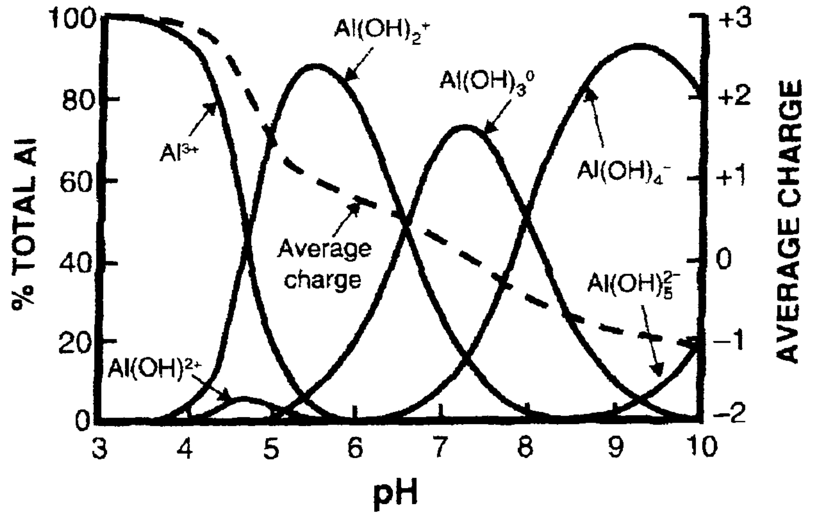

**Figure-3.1. Relationship between pH and the distribution and average charge of soluble aluminium species[4]**

At pH values below 4.7, $Al^{3+}$ predominates. Between pHs of 4.7 and 6.5 the positively charged hydroxo complexes: $Al(OH)^{2+}$ and $Al(OH)_2^+$ predominate and from pH 6.5 to pH 8.0 $Al(OH)_3$ is the primary species. At pH above 8.0, the negatively charged aluminate species $Al(OH)_4^-$ predominates. From pH 4.7 to 7.5 the solubility of aluminium is low. This is the pH range where aluminium is precipitated and remains as $Al(OH)_3$. Below pH 4.7 and above 7.5 the concentration of aluminium in solution increases rapidly. Free $Al^{3+}$ may comprise a small fraction of the total soil solution aluminium. Much of the aluminium may be complexed with inorganic species such as $F^-$ and $SO_4^{2-}$ or with organic species such as humic substances and organic acids. About 6-25% of the total aluminium in soil solutions occurs as free $Al^{3+}$. Most of the soil solution aluminium complexes[5] with organic species and with $F^-$.

### 3.1.3. Toxicity of aluminium

It has been assumed for many years that aluminium is completely harmless and non-toxic to humans. However, it is now considered that aluminium is toxic in its ionic form ($Al^{3+}$) but exhibits reduced toxicity when complexed by organic ligands (section 3.3.2) or bound to soil silicates. In acidic environments ionic aluminium has toxic effects on some aquatic and terrestrial organisms. Aluminium is not a plant or animal nutrient and therefore does not generally accumulate in living tissue[6,7]. At low pH, aluminium, iron and manganese become more soluble and can be toxic to plants. As pH increases, their solubility decreases and precipitation occurs.

One of the major problems for plants growing in acid soils is aluminium toxicity. Aluminium in soil solution causes stunted roots and tops in susceptible plants, but their degree of toxicity depends upon the species of aluminium and the variety of plants[8].

Aluminium concentration in solution >3.6mg/l reduced corn growth, and at >1.8mg/l soybean growth was depressed[9]. The effects of inorganic aluminium on the survival and growth of brook trout and white suckers was found to be complex[10]. At low pH levels (4.2 to 4.8), the presence of aluminium (up to 0.2mg/l for white suckers and 0.5mg/l for brook trout) was beneficial to egg survival through the eyed stage. In contrast, aluminium concentration of 0.1mg/l for white suckers and 0.2mg/l for brook trout were found to reduce in survival and growth of larvae and post larvae at all pH levels (4.2 to 5.6).

Monomeric aluminium [$Al(H_2O)_6^{3+}$] is found to be particularly toxic to plants and also, recently it has been shown that polymeric aluminium species in aqueous solution can be very toxic to plants such as soybean and wheat[11].

Total concentrations of aluminium as low as 100-200µg/l have been associated with specific biological effects[12]. It is clearly instrumental in mobilising the soil aluminium, which causes root damage in forests, and in leaching plant nutrients from foliage[13].

Aluminium toxicity to humans is also clearly recognised. Increased aluminium levels were found in the brains of Alzheimer's disease patients[14].

Experiments[15] carried out without aluminium in the pH range 4.9-7.1, show very little effect on the algal (*Chlorella pyrenoidosa*) growth. These experiments proved the presence of labile aluminium (toxic aluminium) caused the death of algae. Maximum aluminium toxicity occurs at pH 5.8 to 6.2, where as little as 5µg/l of labile aluminium significantly inhibits algal (*Chlorella pyrenoidosa*) growth. Dissolved aluminium would be highly toxic to algae, and perhaps to other aquatic organisms. Algal assay and computer modelling results implicate either $Al(OH)_2^+$ or the sum of $Al(OH)_2^+$, $Al(OH)^{2+}$ and $Al(OH)_3$ are the most toxic aluminium species to algae, in natural fresh waters which are slightly acidic and low in organic matter and nutrients such as phosphate and silicate. Toxic aluminium species $Al(OH)_2^+$ ion diffuses through the membrane of the organisms, whereas polymerised aluminium species i.e. $Al_{13}(OH)_{32}^{7+}$ bound with the organic ligands are unlikely to cross the membrane into the blood stream.

Experiments were carried out under simulated landfill conditions to investigate the leaching behaviour of aluminium along with other substances that can wash out from black dross. Potential interactions between the dross and organic and inorganic parts of the soil components under landfill conditions were investigated.

Leachability studies were carried out using de-ionised water, humic acid, acid rain and acetic acid to determine the amount of aluminium and other metal impurities that may be leached out from the dross under simulated landfill conditions. Clays used to investigate the interactions between soil and dross were kaolinite, bentonite and sand.

## 3.2. SOIL COMPONENTS

The most important part of the earth's crust is soil. Soil is a variable mixture of minerals (inorganic compounds), organic matters and water, capable of supporting plant life on the earth's surface. The solid fraction of typical productive soil is approximately 5% organic matter and 95% inorganic matter[16]. The minerals or inorganic components of soils include both primary and secondary minerals. A primary mineral is one that has not been altered chemically since its deposition and crystallisation from molten lava. Common examples of primary minerals are quartz and feldspar. A secondary mineral is the final product of the weathering action of physical, chemical and biological processes on primary minerals, which are also known as clay minerals. The common clay minerals in soils are kaolinite and montmorillonite.

All clay minerals consist of inorganic lattices composed of tetrahedral silica and octahedral alumina layers. They are distinguished from each other by general chemical formula, structure and chemical and physical properties. Normally clay minerals are predominantly negatively charged[17]. They are balanced by positive charged exchangeable cations. The ability of soil components to exchange cations is expressed as the cation exchange capacity (CEC). The CEC of clay minerals is very important in affecting the retention of inorganic species.

Soil minerals that exhibit negative charge, occur due to two reasons[3]:-

1) Isomorphic substitution: the negative charge on the clay minerals that results from isomorphous substitution. For an example, substitution of a divalent magnesium cation ($Mg^{2+}$) for a trivalent aluminium cation ($Al^{3+}$) can result in the loss of one positive charge. This type of negative charge on the clay surface is permanent or constant.

2) Ionisation: the negative charge on the clay minerals that results from deprotonation of functional groups. For example, hydroxyl groups at the edge of the lattice can ionise, resulting in the formulation of negative charge:

$$\text{Al-OH} \rightleftharpoons \text{Al-O}^- + \text{H}^+$$

Ionisations such as these usually increase as the pH increases, and therefore this type of negative charge is a pH dependent charge.

However, although the overall particle charge is always negative, both negatively and positively charged parts on the surface and broken edge of the clay particles simultaneously exist under acidic and alkaline conditions. The amphoteric sites, mainly Al-OH groups, situated at the broken edge and on the octahedral sheets of clay plates, develop charges depending on the pH. The ionisation of aluminol groups result in $\text{Al-OH}^+$ and $\text{Al-O}^-$ in acidic and alkaline conditions respectively[18].

The environmental impact of landfilling black dross was investigated in the laboratory, under simulated landfill conditions using the soil components described below.

### 3.2.1. Kaolin[3,19]

Kaolin, $Al_2(OH)_4.Si_2O_5$ is a secondary clay mineral more correctly known as kaolinite. It is also called china clay. Kaolin is a soft material, white in colour when it is fairly pure and is formed by the decomposition of granite.

Kaolinite has a structure of sheet silicate (Figure-3.2). Looking at the structure of kaolinite, it can be seen that the basic structure consists of a silicate tetrahedral sheet bonded to an aluminium octahedral sheet. Layers of kaolinite stack by hydrogen bonding (an electrostatic bond between a positively charged $H^+$ ion and a negatively charged ion such as $O^-$) and therefore there are no interlayer spaces present. The negative charge that occurs on the kaolinite surface is due to ionisation and, therefore, it is pH dependent.

Kaolinite is particularly valuable because it is essentially free from iron impurities and therefore colourless. Kaolin's whiteness, opaqueness, and non-abrasiveness make it an ideal filler material for paper production. As a coating agent in paper, kaolin provides a smooth, opaque surface with good printability and ink retention. Although about 80% of all kaolin production is used in paper, other uses include fillers for rubber, plastic, paint and adhesives, as well as in ceramics such as porcelain and refractory products.

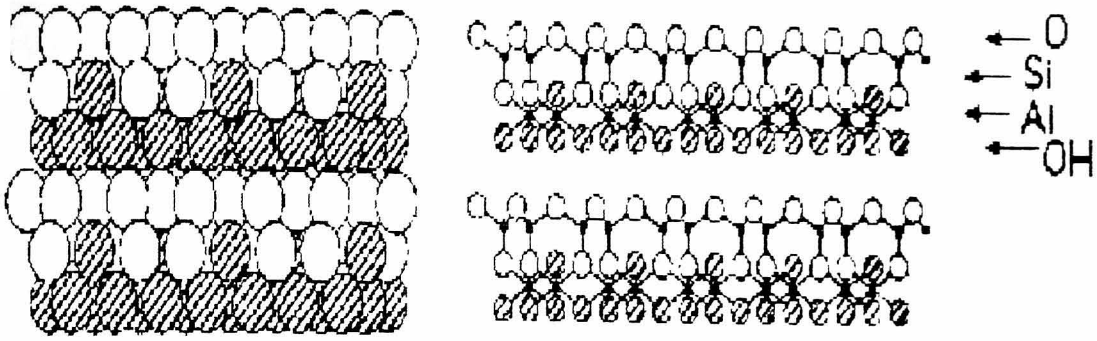

Figure-3.2. Schematic diagram of a kaolinite clay molecule[3]

### 3.2.2. Bentonite[3,19]

Bentonite is also a sheet silicate secondary clay mineral like kaolinite, and belongs to the group of montmorillonites, $Al_2(OH)_2.Si_4O_{10}.H_2O$. Bentonite is a sodium montmorillonite. Unlike kaolinite, the bentonite structure (Figure-3.3) consists of two tetrahedral silicate sheets co-ordinated to one octahedral aluminium sheet. Between the space (i.e., interlayer space) cations are co-ordinated with tetrahedral silicate sheets. Thus, bentonite has both interlayer and external layer spaces. The negative charge that occurs on the clay surface is due to isomorphic substitution, and therefore, the charge is constant. Bentonite has higher CEC due to being predominantly composed of constant charge sites and to the presence of fully expanded interlayers and outer layers, as opposed to kaolinite, which only has an external layer and therefore, low CEC. Bentonite is a fine textured colloidal clay that absorbs several times its volume. It is used as drilling mud and in water based emulsions.

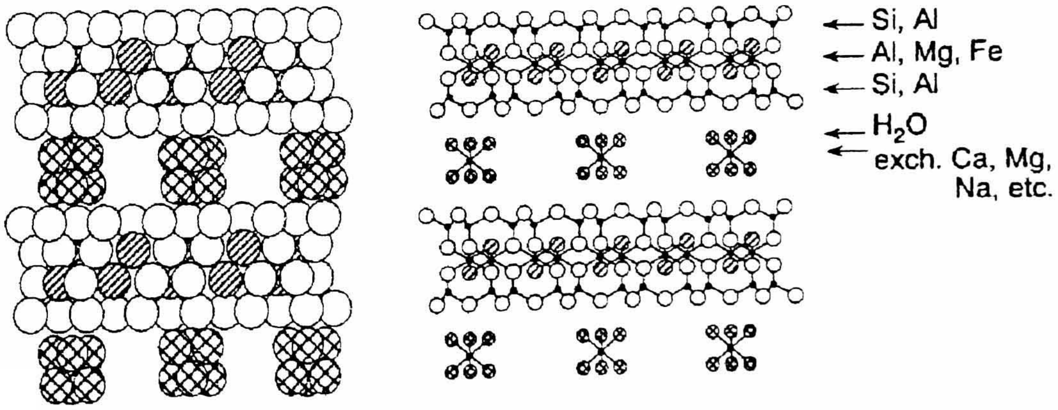

Figure-3.3. Schematic diagram of a bentonite clay molecule[3]

### 3.2.3. Sand[3,19]

Sand is a primary mineral. Most sand consists of silica, also known as silicon dioxide ($SiO_2$), that usually contain impurities such as iron oxides. Silicon dioxide contains a network of silicon-oxygen covalent bonds in a giant molecular lattice. Each silicon atom is bonded to four oxygen atoms, and each oxygen atom is bonded to two silicon atoms (Fig-3.4). Silicon dioxide is very unreactive and does not has many active sites like kaolinite and bentonite.

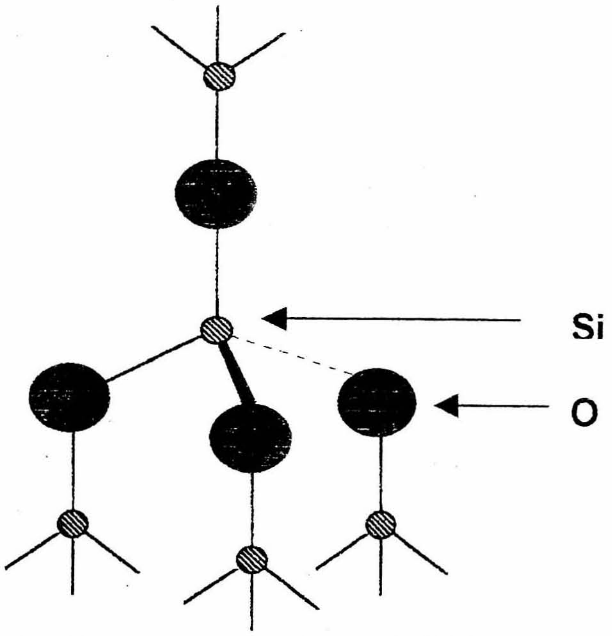

**Figure-3.4. The structure of sand (Silicon dioxide)[20]**

## 3.3. LEACHING AGENTS

The natural aquatic environment consists of water. Water has a number of unique properties that are essential to life. It is an excellent leaching medium for many materials; most ionic materials are dissociated in water. Thus, it is the basic transport medium for nutrients and water products in the life process. The chemistry of water is different from place to place. This is strongly influenced by the availability of chemical and biological species in that area. Human activities are also responsible for changing the chemistry of water. The leaching behaviour changes as the chemistry of water changes. These changes have a great number of effects on soil components and the other surrounding matter.

As black dross is landfilled, the metals leach out in contact with different leaching media. In this section, different types of leaching agents which are found in the environment either naturally or by human activities will be discussed.

### 3.3.1. Acid Rain

Rain water is naturally acidic. The dissolution of carbon dioxide from the atmosphere creates a solution of carbonic acid with an equilibrium pH of 5.6. The pH of rain, even in remote areas, is typically around 5.0 and the pH of natural waters ranges between 5.0 and 6.5 because of contributions from such sources as chloride in sea spray, volcanic emissions of acidic gases, and natural emissions of nitrogen and sulphur compounds. In addition, some acidity in natural waters is of benefit because it helps in the weathering process to release important nutrients from mineral soils[21].

Thus a general working definition for acid precipitation is that of having a pH of less than 5.0. There is little doubt that acidity in the environment has generally been increasing[21]. The actual phrase "acid rain" was first used by Robert Angus Smith in 1872 to describe the polluted air of Manchester which he noted damaged vegetation, bleached the colours of fabrics and corroded metal surfaces[21].

Acid rain has been regarded as a major threat to the environment in Europe and North America during the last three decades, as reflected in several existing environmental policy plans[22,23]. Both in Europe and in North America the Convention on Long-range Transboundary Air Pollution was signed in 1979. Since then, negotiations resulted in several protocols implementing this agreement. In the most recent Second Sulphur Protocol signed in 1994, European countries and Canada agreed to implement country-specific emission reduction targets, aiming for a cost effective abatement of acid rain in Europe[22,23].

Much concern has been expressed about the effects of acid rain on plants, bodies of water and soils. It is well documented that acid rain can deleteriously affect aquatic life by significantly lowering the pH of lakes and streams and can also cause damage to buildings and monuments, particularly those constructed of limestone and marble and it can cause corrosion of certain metals[22].

Acid rain results from various natural and human activities: the burning of fossil fuels such as coal, which generates sulphur dioxide and nitrogen oxides; from exhausts of motor vehicles, a main source of nitrogen oxides, and various other energy related industrial and agricultural sources. These gases combine in the atmosphere with water and other materials to produce nitric and sulphuric acids which may be carried for long distances by wind and then fall to the earth via precipitation such as rain, snow, sleet, mist or fog. On poorly buffered soils, such as many sandy soils, acid rain could increase their acidity over time.

The problem of acidification is, strictly speaking, more than merely an increase in the acidity of rain water (wet deposition). It encompasses the full range of effects of emissions of sulphur dioxide, nitrogen oxides and ammonia. In forest and grasslands, acid rain can have a significant effect not only on the trees but also on the chemistry of soils. Acid rain can cause leaching of nutrient cations such as $Ca^{2+}$, $Mg^{2+}$ and $K^+$ from the soil, resulting in low pHs and the solubilization of toxic metals such as aluminium and manganese. This can cause reduced soil biological activity such as nitrification (conversion of $NH_4^+$ to $NO_3^-$) and reduce fixation of atmospheric nitrogen by leguminous plants such as soybeans and can also reduce nutrient cycling. Over time, the productivity of forests and grasslands is decreased due to fewer nutrients and higher levels of toxic metals.

### ***Acid rain and soil interaction***

An extensive literature search was carried out on the study of the interaction of soil components with acid rain and humic acid before investigating the interaction of soil components with black dross in the presence of acid rain and humic acid leaching media.

The acid rain infiltrates the soil and can initiate three main reactions viz.: a) change in soil pH b) leaching of cations and c) removal of organic matters. The effect of these processes depends on the degree of rainfall acidification, on its duration and on soil quality.

### ***a) Change in soil pH***

The results obtained by Dowgiallo[24] showed that during six years of systematic exposure of soils to simulated acid rain, the change in the soil pH is not proportional to the number of hydrogen ions introduced into the soil. In the case of strong acid rain treatment, in which every three months the soil was treated with simulated acid rain of pH 1.4, only a small pH decrease had been noted, which suggests that the buffer system of the soil did not completely break down. In the case of the most intensive treatment (simultaneous treatment with systematically applied acid rain of pH 2.5 and with acid rain of pH 1.4, four times yearly), the soil pH was 5.07 after four years and 4.34 after six years. In comparison with the respective control values (6.52 and 6.44), the values obtained show a clear decrease in the pH. The decrease in pH does not mean an irreversible disturbance of the physicochemical equilibrium of the soil, because the contact with acid does not destroy the exchange capacity of cations and the properties of the soil are usually regenerated through base diffusion from deeper soil layers.

***b) Leaching of cations***

The acid rain infiltrates the soil and meets many chemical barriers resulting in neutralisation processes. The effectiveness of this neutralisation depends on the degree of rainfall acidification, on its duration and on soil quality.

The accepted admissible sulphur fall level is 5kg $ha^{-1}$ per year, which is the maximum amount tolerable by an average ecosystem without any acidification risk[25]. At present, a sulphur fall of more than 20 kg $ha^{-1}$ per year is noted in the Scandinavian countries, while in other European countries, including Poland, the value of 100kg $ha^{-1}$ per year can often be exceeded. It has been calculated[26] that assuming sulphur dioxide concentration in the air of 80μg/$m^3$ and that of nitrogen oxides of 50μg/$m^3$ (sanitary-epidemiological standards in some countries), the pH of rain actually failing onto the soil surface should theoretically reach a value of 2.7[27].

Tests were carried out[28] to determine the effects of pH on cation leaching of lime and cement stabilised soils. Simulated acid rain of composition 1: 1 sulphuric acid nitric acid was used. The results pointed out that the stronger acid rain accelerated the release of the cations from the chemically stabilised soils and changed the chemical composition of the leachate. The crystalline deposits found in the outflow water leached from the specimen was found to be an unknown compound formed between the cations leached from the specimens and the $CO_3^{2-}$ and $SO_4^{2-}$ ions. It was considered possible that the unknown compound might have consisted of a non-crystalline aluminium compound and others. Wang[29] reported elsewhere that the leaching of cations from soils promotes the sorption of incoming cations.

### *c) Removal of organic matters*

In general, the removal of organic matter reduces the sorption capacity of the soil and this change is dependent on the soil composition. The total removal of organic matter from soil can reduce the sorption of both cations and/or anions[29]. The interaction between aluminium and the soil is due to a positive correlation of aluminium with the organic content of the soil.

## 3.3.2. Soil organic matter

Soil organic matter (SOM), which consists of nonhumic and humic substances, plays a significant role in affecting the chemistry of soils[3]. SOM improves soil structure, water-holding capacity, aeration and aggregation. SOM has a high specific surface (as great as 800-900 $m^2 g^{-1}$) and a cation exchange capacity (CEC) that ranges from 150 to 300cmol $kg^{-1}$. Thus, the majority of a surface soil's CEC is in fact attributable to SOM. Due to high specific surface and CEC of SOM, it is an important sorbent of plant macronutrients and micronutrients, heavy metal cations and organic materials[3].

Soils formed under grass usually have the highest SOM content, while desert, semidesert and tropical soils have the lowest content of SOM. However, tropical soils often contain high quantities of humic substances. This is due to the formation of complexes between the humic substances (HS) and inorganic constituents such as quartz, oxides and amorphous materials (organo-inorgano complexes) that are quite stable. In a complexed form the HS are less susceptible to microbial attack.

The main effect of parent material on SOM content is the manner in which it affects soil texture. Clay soils have higher SOM contents than sandy soils. For example, montmorillonite, which has a high adsorption affinity for organic molecules, is very effective in protecting nitrogenous materials from microbial attack. Moist and poorly drained water soils are high in SOM since organic matter degradation is lessened due to the anaerobic conditions of soil. The number of main constituents of SOM are C(52-58%), O(34-39%), H(3.3-4.8%) and N(3.7-4.1%).

### *3.3.2.1. Humic Substances*

Humic substances can be defined as "a general category of naturally occuring, biogenic, heterogenous organic substances that can generally be characterized as being yellow to black in colour, of high molecular weight, and refractory"[3]. HS are hydrophilic and consist of globular particles which in aqueous solution contain hydration water. HS can be subdivided into humic acid (HA), fulvic acid (FA) and humin. Definitions of HS are classically based on their solubility in acid or base.

Humic substances are modified lignins that remain after microbial attack. Phenolic aldehydes and acids are released from lignin during microbial attack are enzymatically altered to quinones, which polymerize in the absence or presence of amino compounds to form HA and FA (Figure-3.5).

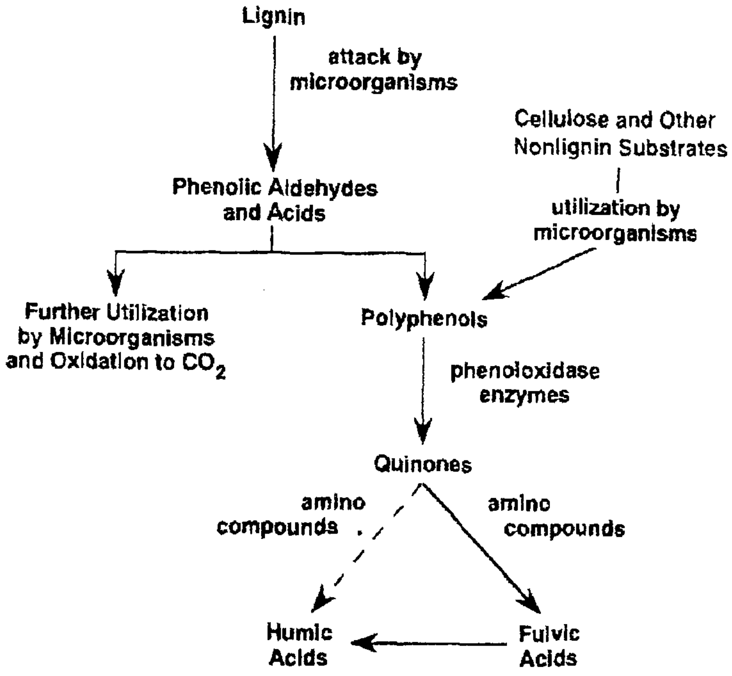

**Figure-3.5. Schematic representation of the polyphenol theory of humas formation[3]**

### *(i) Humic Acid*

Humic acids are extremely common. HA are found in soils, waters, sewage, compost heaps, marine and lake sediments, peat bogs, carbonaceous shales, lignites and brown coals. While they are not harmful, they are not desirable in potable water. HA are the fraction of humic substances that are insoluble in water under acidic conditions ($pH<2$) but soluble at higher pH values. They can be extracted from soil by various reagents and which is insoluble in dilute acid. HA are the major extractable components of soil humic substances. They are dark brown to black in colour.

### *Structure*

Humic acid has a negative charge which is primarily derived from ionization of acidic functional groups, e.g., carboxyls, phenols and quinols. The main acidic groups in HA are carboxyls and phenolic OH groups[3]. Electron microscopic observations revealed that the HA of different soils have polymeric structures, appearing in the form of rings, chains and clusters. While the elemental functional group compositions of humic acid is known, definitive knowledge of the basic "backbone structure" is still an enigma. Based on a variety of techniques and analyses Schulten and Schnitzer[30] have proposed a structure of HA (Figure-3.6). Oxygen is present as carboxyls, phenolic and alcoholic hydroxyls, and carboxylic esters and ethers, while nitrogen is present as heterocyclic structures and nitriles.The elemental composition of the HA structure in Figure-3.6 is $C_{308}H_{328}O_{90}N_5$; it has a molecular weight of 5540 Da and an elemental analysis of 66.8% C, 6% H, 26% O, 1.3% N (% by number). The predominant functional groups in HA are carboxyls, phenolic hydroxyls and alcoholic hydroxyls[31]. Many of these groups are acidic and are deprotonated at the pH of most natural waters (pH 6-8). The resulting anionic charge on the molecules accounts for many HA characteristics, including aqueous solubility, binding capacity for metals and buffer capacity[32].

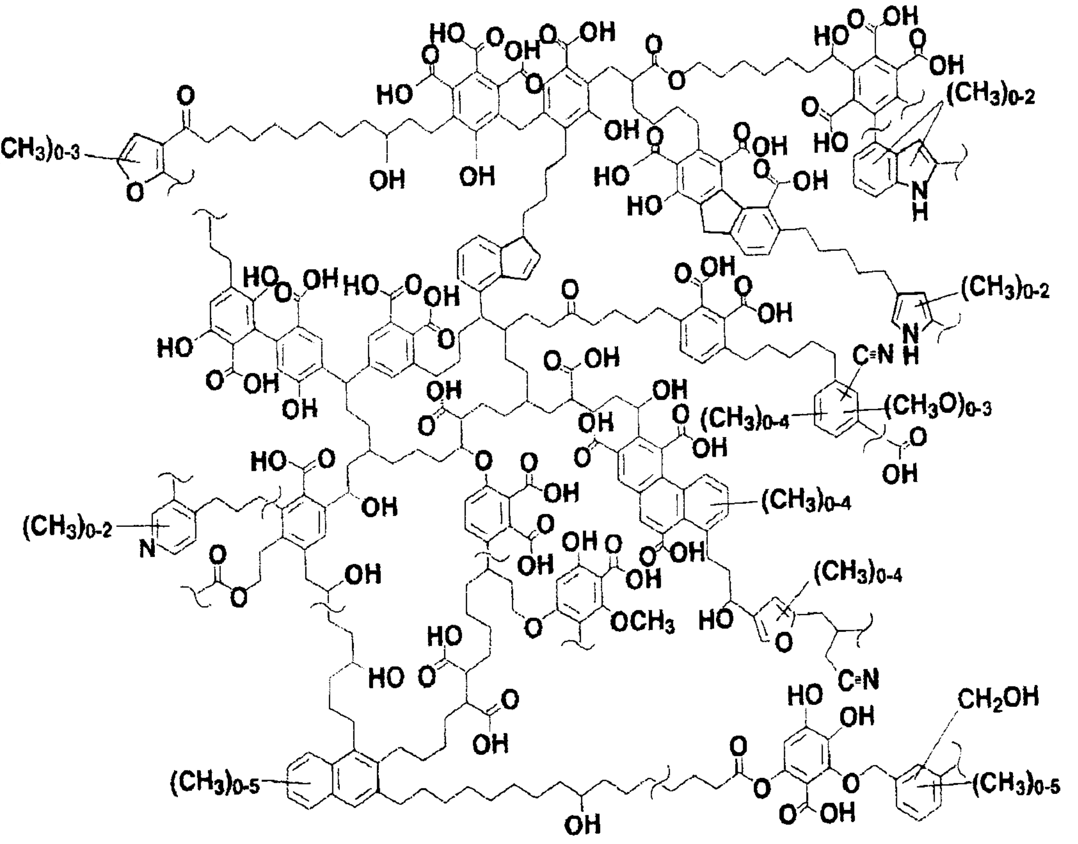

**Figure-3.6. Schematic diagram of humic acid structure[3]**

The main reason that the basic structure of HS is not fully understood is largely due to the heterogeneity and complexity of HS.

### *(ii) Fulvic Acid*[3]

Fulvic acids (FA) are the fraction of humic substances that are soluble in water under all pH conditions. They remain in solution after removal of HA by acidification. FA are light yellow to yellow-brown in colour.

Many investigators now believe that all dark coloured humic substances are part of a system of closely related, but not completely identical, high molecular weight polymers. According to this concept, differences between HA and FA, can be explained by variations in molecular weight, number of functional groups (carboxyl, phenolic OH) and extent of polymerisation.

The postulated relationships are depicted as the lower molecular weight FA have higher oxygen but lower carbon contents than the higher molecular weight HA. FA contain more functional groups of an acidic nature, particularly COOH. The total acidities of FA (900-1400 meq/100g) are considerably higher than for HA (400-870 meq/100g).

### *(iii)Humin*

Humin is the fraction of humic substances, similar to humic acid, but it is not soluble in water either in alkali or acidic condition. It is slightly less aromatic than HA. Humins are black in colour.

Naturally occurring high molecular weight organic compounds can serve as a sink for numerous organic and inorganic compounds[33,34,35] These compounds can have their bioavailability and toxicity as well as geochemical transport and fate affected by binding with these naturally occurring species[36,37].

### *3.3.2.2. Humic Acid and Soil Interactions*

The presence of HA in subsurface water is believed to enhance the transport of associated contaminants in the subsurface environment[38]. The sorption of HA on soil during transport decreases the mobility of the associated contaminants. In addition, the adsorbed HA can change the physicochemical properties of the soil surface whose behaviour (e.g. electrophoretic mobility, colloidal stability and transport) may be dominated by the adsorbed HA. The adsorbed HA coatings may also increase soil organic matter content and make the soil more capable of adsorbing further organic contaminants[32,39,40].

Soil organic matter plays a fundamental role in the formation and stabilisation of soil aggregates. It seems to have two opposing effects on aggregation. On the one hand it repels water[41] thereby decreasing the tendency of macroaggregates to disintegrate in water[42]; on the other it coats the soil clay, thereby increasing the negative charge of the fine particles and favouring dispersion. For example, Tarchitzky et al[43] added HA to Na-montmorillonite (bentonite) suspensions and found that it increased stability. They attributed the effect to an interaction between the negatively charged HA and the positively charged edges of soil clay particles. Giliman[44] attributed changes in the proportion of water-dispersible clay in basaltic soils to variations in its point of zero charge (PZC) caused by the addition of organic ions; and Visser and Caillier[45] observed that small concentrations (25 to 100mg $dm^{-3}$) of HA dispersed clay particles from a humic gleysol, whereas larger concentrations caused flocculation[46].

In many theoretical models of soil aggregation[47] caused by soil organic matter, there seems to be favourable conditions in the presence of metal ions, which can act as bridges between the anionic groups of polymeric organic matter and the negatively charged surfaces of clay particles. However, there are few experimental studies examining how soil components interact with associations of organic matter and polyvalent metal ions, or the effects of such associations on soil aggregation[46].

### *3.3.2.3. Humic Acid and Metal Interactions*

The complexation of metal ions by humic substances is extremely important in affecting the retention and mobility of metal contaminants in soil and waters. The metal binding capabilities in HA were represented by Alberts et. al[36]. In this study, they investigated the complexation of metals with natural organic matter, as represented by estuarine FA and HA. They concentrated on copper binding using copper binding capacity (CuBC), which is relatively easy to measure using selective ion electrodes, not as an intrinsically important value of the organics, but rather as a probe by which differences could be followed in humic substance-metal binding with various elements (Ca(II), Mg(II), Al(III), Fe(III)). Thus, they could examine the effect of competing elements on the CuBC of estuarine FA and HA acids. Finally, they employed Fourier transform infrared (FTIR) spectral analysis to characterise the isolated humic acid-metal complexes and attempt to deduce types of binding sites in these substances for specific metals[36].

The CuBC of estuarine FA and HA ranged from 0.159 ± 0.023 to 0.255 ± 0.044 μg atm $Cu^{2+}$ $mg^{-1}$ FA and from 0.171 ± 0.047 to 0.239 ± 0.026 μg atm $Cu^{2+}$ $mg^{-1}$ HA, which are similar to values for many naturally occurring organic matter, although there was considerable overlap in values among these supposedly different types of organic matter mixtures. The divalent ions Ca and Mg had little effect on the estuarine humic substances, while the trivalent ions Al and Fe reduced the CuBC by as much as 43% in HA and 33% in FA. The oxygen-containing functional groups appeared to play a greater role in the binding of copper in FA than in HA. Also, the FTIR spectra indicated significant differences in the electronic structures of the complexes of these natural organic mixtures with some environmentally significant metals, suggesting that these metals bind to the organic matter through different functionalities. Further studies were required to assign FTIR bands definitely to binding sites for metals. The results presented indicate significant differences in Cu(II) binding in estuarine HA relative to other competing metals. The existence of sites suggested by the metal competition studies, which were either sterically hindered or energetically more favourable for Cu(II) binding with these compounds relative to other metals, were supported by the FTIR spectral evidence. Furthermore, the FTIR spectral analyses indicated that cations Al(III), Ag(I), Ca(II), Fe(III), Hg(II), Mg(II) and Mn(II) appear to be bound to humic acids primarily through carboxyl functional groups, while Au(l) and Pb(II) apparently were bound through carboxyl and alcoholic moieties[36].

In particular aluminium binding in HA was studied by M. Petrovic et al[48] where the various composition and charge of aluminium was discussed. The results show that, regardless of pH, more than 85% of HA precipitate from the solution containing 50.0mg of HA/l and 12.5mg of Al/l (mass ratio Al/HA=0.25). The precipitation maximum is observed at pH 5-6 where 98% of HA appear in insoluble form. Section 3.1.2 described the aluminium speciation at different pHs.

In an acidic medium, especially at pH<5, a considerable amount of ionic aluminium is fixed in solid associated with humic substances. At pH 4.0, in conditions of full saturation, one gram of HA bound with 2mmol of aluminium in an insoluble associate, while FA bound with 3.8mmol of Al/g. HA and FA apparently bind aluminium through salicylate-type functional groups having a relatively large conditional stability constant[49]. Other possible binding sites in humic molecules are phthalic or aliphatic carboxyl groups, as discussed by Alberts et. al[36] with a variety of molecular arrangements. The main difference between the spectrum of HA in $H^+$ form and that of aluminium-humate is the disappearance of the bands centered at 1720cm$^{-1}$ and 1220cm$^{-1}$ and the appearance of new bands in the 1400-1450 cm$^{-1}$ region. The sorption band at 1720cm$^{-1}$, due to the carbonyl of the un-ionised carboxyl group, disappears upon the reaction with aluminium, providing direct evidence for the participation of carboxyl groups in the complexation. The sorption band at 1220cm-$^{1}$ assigned to the C-O stretching vibrations and OH bending deformations, due mainly to carboxyl groups, also disappears on producing the aluminium-humate[48].

The interaction of humic substances and aluminium at pH>5.5 is said to be primarily a surface complexation and sorption on *in situ* formed $Al(OH)_3$ flocs. The interaction is based on a charge neutralisation-precipitation mechanism where specific chemical interaction between positively charged hydrolysed aluminium species and ionised carboxyl groups on the humic macromolecules occurs. Humic substances bear a net negative charge and the first step, caused by electrostatic effects, involves rapid neutralisation of the positive charge of $Al(OH)_3$ flocs. This neutralisation is said to be followed by the formation of aggregates of hydrophilic colloids consisting of negatively charged humic substance spanned by a bridge of positively charged aluminium species. As a consequence of chain structure growth the larger aggregates are formed[48].

Naturally occurring organic matter, and especially the most stable components HA and FA, play an important regulatory role in determining the speciality, toxicity and mobility of aluminium ions. During weathering the series of aluminium hydroxides of variable charge and composition from $Al(OH)^{2+}$ to $Al(OH)_6^{3-}$ are formed. In acidic environments (soil and water) ionic aluminium has toxic effects on some aquatic and terrestrial organisms. While inorganic complexes are toxic, complexes of aluminium and naturally occurring organic substances (mainly humic substances) are apparently nontoxic[50,51]. Studying the effects of organic acids on aluminium toxicity in sub-soils, Hue et al[52] found that aluminium detoxifying capacity of carboxylic acids was positively correlated with the relative position of OH/COOH groups on their main C chain, positions that favoured the formation of stable 5- or 6- bond ring structures with aluminium. Humic substances contain a large number of oxygen-bearing functional groups (carboxyl, hydroxyl, carbonyl, phenolic and methoxyl) having a great affinity to co-ordinate with aluminium ions[53,54,55].

One of the factors that influences aluminium mobility is solubility of aluminium-humic complexes. These complexes can be either water-soluble or water-insoluble depending on environmental conditions[56]. The formation of water-insoluble associates reduces aluminium mobility and its availability to plant roots[48].

#### *3.3.2.4. Metal, Humic Acid. and Soil Interactions*

The effects of metal ratios in kaolin and bentonite soils on the sorption of humic acid was represented in research documented by Yun-Hwei Shen[32]. The results obtained from this study indicated the existence of a correlation between the atomic ratio of (Al + Fe): Si of soil colloid surfaces and the HA sorption capacity, where those soil colloids with larger values of the (Al + Fe): Si ratio were able to adsorbs HA more efficiently. This allowed the prediction that the HA sorption capacity for soil colloids increases with progressively increasing states of soil maturity.

The major mechanisms by which HA adsorbs onto mineral surfaces have been proposed to involve: (a) anion exchange (electrostatic interaction), (b) ligand exchange surface complexing, (c) hydrophobic interaction, (d) entropic effects, (e) hydrogen bonding and (f) cation bridging. A detailed description of these mechanisms has been presented by Sposito[57]. A ligand exchange mechanism between surface co-ordinated OH from iron and aluminium oxides and the dissolved organic matter (DOM) such as HA has been proposed by several investigators. Davis[58] demonstrated that extracts of fulvic and humic acids from lake sediments are significantly adsorbed by gibbsite, with maximum sorption occurring near pH 5. Schulthess and Huang[59] found that the sorption of humic and fulvic acids by solid phases is affected by the type of surface (silicon or aluminium oxide) present. Moore et al[60] determined dissolved organic carbon sorption isotherms for 48 soil samples and concluded that dissolved organic carbon sorption capacities were strongly related to the soils organic carbon content and the oxalate-extractable Al and dithionite-extractable Fe content of the soil. Kaiser and Zech[61] pointed out that increasing contents of sesquioxides (amorphous $Al(OH)_3$, ferrihydrite, goethite) strongly promoted the sorption of DOM on their soil samples. The previous work regarding the DOM on soil strongly indicate the importance of the chemical composition of the mineral content of a soil for the sorption of DOM such as HA by soil. The chemical and structural heterogeneities associated with the complex nature of soil and with HA complicates current understanding of the sorption of HA on soil[32].

Arias et al. investigated the effects of HA, Al-HA and Fe-HA associations on the aggregative properties of two substrates having different specific surface areas, namely kaolin and quartz[46].

It was noted that (a) precipitation of increasing amounts of Fe or Al oxides in the presence of kaolin caused both the point of zero charge and the flocculation interval to shift towards higher pH suggesting that the oxide precipitates mask the negative charges of the basal faces of the kaolin by coating those faces[62] and that (b) these precipitated iron and aluminium oxides, especially the latter, favoured aggregation of kaolin[63]. If the basal faces of the kaolin become partly coated with inorganic oxides, a large proportion of the HA added may absorb on to that oxide layer or associate with exposed area of the basal faces via adsorbed, partially hydroxylated metal ions. In these circumstances flocculation and aggregation of the HA-metal samples would be governed mainly by interactions between the positively charged edges of the kaolin particles and the residual negative charges of the HA[32].

### *3.3.2.5. Non-humic Substances*

Soil solution contains a wide variety of organic solutes including organic acids. In addition to high molecular weight (HMW) acids often referred to as fulvic acid and humic acids, low molecular weight (LMW) organic acids exist. The non-humic substances have recognisable physical and chemical properties and consist of carbohydrates, proteins, peptides, amino acids, fats, waxes and low-molecular-weight acids. These compounds are attacked easily by soil microorganisms and persist in the soil only for a brief time. Organic acids are negatively charged in the pH range of most soils but they are pH-dependently charged[3].

A number of different organic acids (including aliphatic and aromatic) have been found in soil. The most common are oxalic, citric, formic, acetic, malic, vanillic, benzoic acid etc[64,65,66]. The level of these acids are found in greatest concentration in the top soil layers and decline in the deeper layers. Several of these LMW organic acids can form strong complexes with aluminium and iron. LMW organic acids are produced during decomposition of organic material in soils, for example, decomposition of litter and dead roots by fungi and bacteria[67]. In the research work reported in this thesis, acetic acid has been used as an example of low molecular weight organic matter in order to investigate the fate of black dross in the natural environment (after landfilling). Acetic acid occurs in soil in different ways. It can be produced due to decomposition of dead organisms by microbial attack. The proteins in the dead organisms are broken down by an enzyme called protease which is secreted by fermentative bacteria found in soil. The proteins break down into amino acids which are decomposed by some anaerobic bacteria to form acetic acid[68]:

$$2C_3H_7NO_3 + O_2 \longrightarrow 2CH_3COOH + 3H_2 + N_2 + 2CO_2$$

Eventually, acetic acid will be broken down by bacteria called methanogens into methane gas, water and carbon dioxide which is a part of the carbon cycle. Furthermore, root exudates and leaf washings may contain these kinds of acids[69]. Carboxylic acids are also produced during plants food metabolism, the so called Kreb cycle[70], and are found in soil after decomposition. The concentration of carboxylic acids in soil solutions has been reported[71] to be in the range 2-5$\mu$mol $l^{-1}$.

Due to their complexing ability, LMW organic acids play a major role in soil weathering process. Naturally occurring organic acids have been shown to enhance the weathering rate of natural soils about three times at pH 5.0[72]. Furthermore, the LMW organic acids can act as a means of transport in the soil profile and contribute to the translocation of aluminium and iron[72].

LMW organic acids make up about 3-5 times more of the acidity than their percentage of the DOC (dissolved organic carbon) would suggest. This can be considered reasonable with regard to the high content of carboxyl groups of the LMW acids. Most major acids such as citric, fumaric and acetic acids have one COOH group per two carbons. In the soil solutions there was on average one COOH group per 9.5 carbons[73].

Size exclusion chromatography (SEC) and ultrafiltration results imply that LMW organic acids are important complex formers for aluminium in soil solution. In the organic rich soil horizon this fraction was generally 25-45% of the total aluminium in solution[74].

LMW organic acids contribute a great deal to the podzolization process. Podzolization is the most common soil forming process in coniferous forests in northern Europe and America[75]. LMW acids not only bind to free monomeric inorganic aluminium but also extract aluminium from amorphous and interlayered aluminium hydroxides. Under prevailing conditions, with a pH less than 4.0 and the presence of large concentrations of organic ligands, neither aluminium hydroxide nor aluminium silicates are thermodynamically stable. Under these conditions aluminium silicates act as Brönsted bases (proton acceptors). The reaction occurs between an aluminium silicate (proton acceptor) and acidic groups of LMW organic acids (proton donors), producing organically adsorbed aluminium.

$$3\mathrm{HOOC\text{-}R} + \mathrm{KAlSiO_4} + \mathrm{H^+} \longrightarrow \mathrm{Al(OOC\text{-}R)_3} + \mathrm{H_4SiO_4}_{\,(aq)} + \mathrm{K^+}$$

The water soluble organic aluminium compounds are transported downwards to deeper soil horizons. During the transportation, the organic acids undergo a complete decomposition forming water and carbon dioxide and release the aluminium. The released aluminium can then precipitate with Si to form solid phase at the deeper soil horizons[70]. Therefore, the amount of LMW organic acids declines in the deeper soil horizons and the aluminium concentrates. The solubility of the resulting metal-rich soils decreases.

The LMW organic acids are also involved in the formation of secondary mineral soils in the upper layer soil horizons following the above mechanism[72].

Less of the iron in soil solution seems to be complexed with LMW compounds compared to aluminium. The LMW fraction of iron was normally about 10-20%[72]. It has been reported that iron forms more stable complexes with HMW compounds such as fulvic and humic acids than aluminium[76]. However, in general, the major part of the aluminium (and iron) are found bound to HMW acids, not LMW acids.

## 3.4. EXPERIMENTAL PROCEDURE

The experimental work reported in this chapter was carried out in four parts:

1. The extent of leaching of as supplied black dross was determined using a number of simulated external media such as acid rain, humic acid, acetic acid, and de-ionised water.
2. The extent of leaching of the black dross was investigated with these respective external media together with various soil types: kaolinite, bentonite and sand.
3. The interactions of aluminium from the black dross with the leaching media and the soils were investigated in an attempt to represent, as far as possible within a laboratory environment, the environmental impact of landfilling black dross.
4. The washed black dross (washed as described in sub-section 2.4.2.1) was leached using the leaching media to determine the extent of leaching and compare the results with the as supplied (unwashed) dross.

All materials (kaolinite, bentonite, sand, humic acid, acetic acid) used in this research work were purchased from BDH.

To test the reproducibility, all experiments were repeated three times, and the results are presented as an average.

### 3.4.1. Leaching of black dross with leaching media

***De-ionised Water***

5g black dross and 100ml de-ionised water were placed in into a 250ml glass bottle and bottle capped. Using an oscillator shaker (Scientific Stuart Flask Shaker; SF1), the bottle was shaken (400 osc/min) at room temperature (~23$^0$C) for 8 hours. After this time, the contents were gravity filtered (filter paper of known weight – Whatman 542, hardened ashless, 150mm diameter) and the solid residue washed with de-ionised water into the filtrate, which was made up finally to 100ml with de-ionised water. The solid residue was dried at room temperature then weighed and retained. The filtrate was analysed for metal concentration using atomic absorption spectrophotometry.

### *Simulated Acid Rain, pH 2.5*

The de-ionised water experiment was repeated using simulated acid rain at pH 2.5. This was made from 1:1 0.5M $H_2SO_4$ and $HNO_3$ diluted with de-ionised water to pH 2.5[77].

### *50 mg/l humic acid*

The de-ionised water experiment was repeated with 50 mg/L humic acid solution (the concentration was chosen as a standard acceptable level[78]).

### *Acetic acid*

The previous experiment was repeated with acetic acid solution. The method described by Hussain[79] has been used here. Black dross was shaken with 100ml de-ionised water for 15min. The pH was then adjusted to pH 5 with 0.5M acetic acid. The pH was monitored after 1, 3 and 6 hours and controlled (using 0.5M acetic acid) at pH 5 +0.2 throughout the experiment.

## 3.4.2. Leaching of black dross with leaching media and soils

### *De-ionised water and clays*

5g black dross and 100ml de-ionised water were placed in a 250ml glass bottle along with 10g kaolinite, bentonite or sand. The bottles were capped and shaken (400 osc/min) using an oscillating shaker (Scientific Stuart Flask Shaker; SF1) at room temperature (~$23^0$C) for 8 hours. The contents of the flask were then gravity filtered (filter paper of known weight – Whatman 542, hardened ashless, 150mm) and the solid residue washed with de-ionised water to make a total volume of 100ml. The solid residue was dried at room temperature. The completely dried residue was weighed and retained. The filtrate was analysed for metal concentration by atomic absorption spectrophotometry.

The above adsorption and desorption experiments were repeated using the same conditions as described in section-3.4.1:

*Simulated acid rain (pH 2.5) and clays*

*50 mg/l humic acid solution and clays*

*Acetic acid and clays.*

### 3.4.3. Interactions of aluminium/metals from the black dross with the soil components in the presence of different leaching media

***Aluminium in de-ionised water and clays***

**Adsorption**

Black dross was leached with de-ionised water (50g/500ml) to prepare a stock solution of aluminium (concentation 100 ppm in 500ml). 0.5g kaolinite and bentonite were soaked separately in de-ionised water overnight in order to swell. Sand was excluded from this experiment. Each clay sample was centrifuged in order to separate them from the water. The water was discarded. Each clay sample was placed in separate 250ml glass bottles. 200ml of the aluminium solution in de-ionised water was introduced into each bottle. The bottles were capped and shaken (at 400 osc/min) using an oscillating shaker (Scientific Stuart Flask Shaker; SF1) at room temperature. 2ml aliquots of solution was collected from each bottle after 1hour and then every 24 hours until no further adsorption occurred. The concentration of aluminium in the solution was determined by atomic absorption spectrophotometry. pH was measured at each sample collection. At the end of the adsorption experiment, the clay solutions were gravity filtered (Whatman 542, hardened ashless, 150mm) and dried at room temperature. The completely dried clays were analysed using an x-ray diffractometer to determine the presence of aluminium/metals in the clays. A blank experiment was carried out with only de-ionised water (no presence of aluminium) and clays.

**Desorption**

After analysis by XRD the clay samples were used to carry out a desorption experiment. 200ml de-ionised water was placed into separate 250 ml glass bottle together with the experimented kaolinite and bentonite separately. The bottles were capped and were shaken (at 400 OSC/min) using an oscillator shaker (Scientific Stuart Flask Shaker; SF1) for 3 hours at room temperature. At the end of the shaking, the solutions were gravity filtered (Whatman 542, hardened ashless, 150mm). The filtered solutions were analysed using atomic absorption spectrophotometry to determine aluminium concentration. The clays were dried at room temperature and analysed using XRD to determine the presence of aluminium.

The above adsorption and desorption experiments were repeated with:

*Aluminium in pH 2.5 simulated acid rain solution and clays*

*Aluminium in humic acid solution and clays*

*Aluminium in Acetic acid solution and clays*

### 3.4.4. Leaching of washed black dross with leaching media

Experiment 3.4.2 was repeated with washed black dross instead of as supplied (unwashed) black dross using:

*De-ionisedwater*

*pH2.5 simulated acid rain*

*Humic acid*

*Acetic acid solution*

## 3.5. RESULTS AND DISCUSSIONS

### 3.5.1. Leaching of black dross with different leaching media

Preliminary experiments were carried out under simulated landfill conditions to investigate the leaching behaviour of aluminium ions along with other substances that can leach out from black dross. Leachability studies were carried out using de-ionised water, humic acid (50ppm- chosen as a standard acceptable level) strong simulated acid rain (pH 2.5) and acetic acid condition (pH 5- chosen as a standard acceptable level). The percentage solubility of black dross in different leaching media is recorded in Table-3.2a. It can be seen that 50-55% of black dross is soluble in each medium. The concentrations of aluminium and other metal impurities leached by the leaching agents are summarised in Table-3.2.b. The results show that measurable amount of each element leaches out from black dross in each leaching medium. This means that dissolved elements will eventually reach the aquifer, and over a period of time the concentration may increase to a toxic level due to the practice of landfilling of black dross tailings in each year. Figure-3.7 shows comparable leaching behaviour of aluminium in different leaching media. It can be seen that de-ionised water is the weakest and acetic acid is the strongest leaching medium to release maximum amount of aluminium in solution. As mentioned in chapter 2 the content of aluminium in the black dross is a mixture of metallic aluminium, aluminium nitride and alumina. Under water, humic acid and acid rain conditions metallic aluminium and aluminium nitride are soluble, whilst alumina remains in the residue. However, in the case of acetic acid both aluminium and alumina are being leached out due to the chemical nature of acetic acid.

**Table-3.2.a. Percentage solubility of black dross in different leaching media**

| Media | Distilled water | Humic acid | Acid rain | Acetic acid |
|---|---|---|---|---|
| Weight(g) | 5.09 | 5.05 | 5.03 | 5.04 |
| Residue(g) | 2.44 | 2.26 | 2.31 | 2.37 |
| % Solubility | 51.94 | 55.32 | 54 | 53 |
| Total Vol(ml) | 100 | 100 | 100 | 100 |

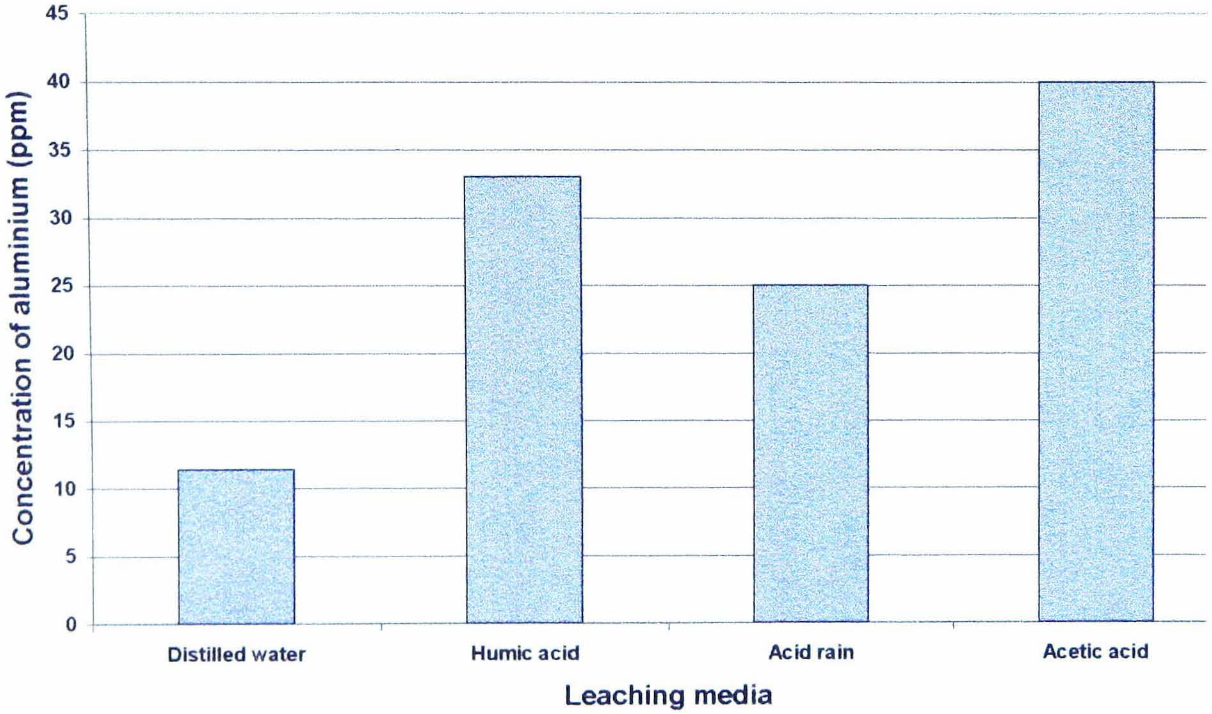

Figure-3.7. The leaching of aluminium in different leaching media under landfill conditions

**Table-3.2.b. Concentration of metals leached from black dross (Unwashed) using different leaching media**

| Metals | Distilled water | Humic acid | Acid rain | Acetic acid |
|---|---|---|---|---|
| | Concentration (ppm) | | | |
| Al | 11.4 | 33 | 25 | 40 |
| Ca | 3.47 | 4.45 | 5.03 | 15 |
| Cr | 0 | 0.11 | 0 | 0.17 |
| Cu | 4 | 4 | 7.63 | 7 |
| Fe | 31 | 28 | 26 | 22 |
| K | 4730 | 8510 | 8950 | 5830 |
| Mn | 0.63 | 0.85 | 0.86 | 1.22 |
| Na | 6000 | 6700 | 6500 | 6600 |
| Ni | 0.24 | 0.37 | 0.26 | 0.65 |
| Pb | 0.46 | 0.58 | 0.54 | 0.83 |
| Ti | 1.4 | 2.7 | 2.4 | 0.6 |
| Zn | 0.9 | 0.13 | 7 | 5 |

Acetic acid is much more acidic than any other class of organic compound[80]. In an aqueous solution acetic acid gives up a hydrogen ion resulting an aqueous acidic solution:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

The acetate anion ($CH_3COO^-$) is moderately basic, with an appreciable tendency to combine with protons. It reacts with water to increase the concentration of hydroxide ions, a reaction often referred to as hydrolysis. The resulting aqueous solution of acetate salt is slightly alkaline due to the acetate anions and the hydroxide ions.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Under this acidic and alkaline condition the following chemical reactions take place in the presence of aluminium ions:

$$2Al + 6H^+ \longrightarrow 2Al^{3+} + 3H_2$$

$$2Al + 2OH^- + 6H_2O \longrightarrow 2[Al(OH)_4]^- + H_2$$

$$Al_2O_3 + 2OH^- + 3OH_2O \longrightarrow 2[Al(OH)_4]^-$$

The interaction of aluminium with humic acid is primarily due to complex formation. Humic substances bear a net negative charge at pH greater than 3. As the pH increases, the degree of negative charge increases due to the deprotonation or dissociation of $H^+$ from functional groups[3]. The maximum adsorption of humic acid and aluminium ions occur at pH 5.0[81]. However, the pH of black dross in humic acid solution was >8.5. This was due to the presence of excessive amounts of NaCl and KCl. The first step in the leaching process, caused by electrostatic effects, involves rapid interaction of positively charged aluminium ion and humic acid to form Al-humic acid complex. Similar metal binding capabilities in humic acid were presented by Alberts et al[36] whose results indicated that $Al^{3+}$ appeared to be bound to humic acids primarily through carboxyl functional groups. They also noted that in acidic medium, specially at pH<5, a considerable amount of ionic aluminium was fixed in the solid associated with humic substances. Thus there is strong evidence supporting the aluminium to humic acid binding capabilities.

Water exists as an equilibrium mixture of undissociated water molecules, $H_2O$, hydrogen ions, $H^+$ and hydroxide ions, $OH^-$. Only metallic aluminium (and other elements) and aluminium nitrides are soluble and the oxides are insoluble in the de-ionised water. The dissolved aluminium is almost entirely present as $Al^{3+}$.

$$\begin{array}{rcl} H_2O & \rightleftharpoons & OH^- + H^+ \\ 2Al + 6H^+ & \longrightarrow & 2Al^{3+} + 3H_2 \end{array}$$

Acid rain is composed of a mixuture of sulphuric acid and nitric acid. The pH of the solution was 2.5. Under this acidic condition, $SO_4^{2-}$ and $NO_3^-$ complexes form a small percentage of total soluble aluminium because the elevated aluminium concentration readily complex available $SO_4^{82}$ and $NO_3$. The following reactions take place in acid rain solution:

$$\begin{array}{rcl} HNO_3 & & NO_3^- + H^+ \\ H_2SO_4 & \longrightarrow & SO_4^{2-} + 2H^+ \\ 2Al + 6H^+ & \longrightarrow & 2Al_3^+ + 3H_2 \\ Al^{3+} + NO_3^- & \longrightarrow & AlNO_3^{2+} \\ Al^{3+} + 2SO_4^{2-} & \longrightarrow & AlSO_4^+ \\ & \longrightarrow & \end{array}$$

## 3.5.2. Interactions between black dross and soil components in the presence of the different leaching media

Although there are a number of reports available on the interaction of aluminium and other metal ions with humic acid and acid rain[32,36,48,49], there are no reports in the literature on the interaction of aluminium, leached from black dross, and soil in the presence of different leaching media such as water, humic acid, acid rain and acetic acid. An investigation of the interaction between the dross and the leaching media in the presence of three soil components i.e., kaolinite, bentonite and sand carried out in this work is reported for the first time.

Table-3.3.a gives the percentage solubility of dross in the presence of different leaching media and clays. The results show that 15-20% of black dross is soluble in the presence of clays. Table-3.3.b shows that the presence of kaolinite and bentonite reduces the concentrations of aluminium and most other metals in water, humic acid and acid rain

## Table-3.3.a. Percentage solubility of BD in the presence of clays using different leaching media

| Media | De-ionised water | | | Humic acid | | |
|---|---|---|---|---|---|---|
| **Soils** | Kaol | **Bent** | Sand | Kaol | **Bent** | Sand |
| wt of soil(g) | 10.00 | 10.03 | 10.08 | 10.07 | 10.03 | 10.02 |
| Wt. of BD(g) | 5.02 | 5.06 | 5.05 | 5.013 | 5.06 | 5.01 |
| **Residue (g)** | 12.85 | 12.32 | 12.7 | 12.74 | 12.88 | 12.65 |
| %Solubility | 14 | 18 | 16 | 16 | 15 | 16 |
| **Total Vol(ml)** | 100 | 100 | 100 | 100 | 100 | 100 |

| **Media** | Acid rain | | | Acetic acid | | |
|---|---|---|---|---|---|---|
| **Soils** | Kaol | Bent | **Sand** | **Kaol** | Bent | Sand |
| wt of soil(g) | 10.09 | 10.08 | 10.04 | 10.09 | 10.06 | 10.03 |
| Wt. of BD(g) | 5.03 | 5.01 | 5.03 | 5.07 | 5.071 | 5.064 |
| **Residue (g)** | 12.941 | 12.27 | 12.49 | 12.47 | 11.73 | 12.47 |
| **%Solubility** | 14 | 19 | 17 | 18 | 22 | 17 |
| **Total Vol(ml)** | 100 | 100 | 100 | 100 | 100 | 100 |

## Table-3.3.b. Concentration of metals leached in the presence of clays using different leaching media

| Metals | Distilled water (100ml) ppm | | | Humic acid (100ml) ppm | | |
|---|---|---|---|---|---|---|
| | Kaol | **Bent** | Sand | Kaol | Bent | Sand |
| **Al** | 1.8 | 0.9 | 11.2 | 1.8 | 0.9 | 33.0 |
| **Ca** | 51 | 92 | 3.47 | 57 | 114 | 4.45 |
| **Cr** | 0.02 | 0.02 | 0.05 | 0.02 | 0.02 | 0.11 |
| **Cu** | 0.1 | 0.03 | 1.34 | 0.09 | 0.02 | 0.4 |
| **Fe** | 0.23 | 0.25 | 0.28 | 0.31 | 0.23 | 0.4 |
| **K** | 3030 | 5130 | 4050 | 3400 | 4860 | 3260 |
| **Mn** | 0.11 | 0.05 | 0.13 | 0 | 0 | 0.1 |
| **Na** | 1400 | 6400 | 2300 | 1000 | 5700 | 2100 |
| **Ni** | 0.2 | 0.13 | 0.24 | 0.16 | 0.07 | 0.2 |
| **Ti** | 0.3 | 0 | 1.4 | 2.0 | 0.2 | 2.3 |
| Zn | 0.1 | 0.04 | 0.11 | 0 | 0 | 0.03 |

| Metals | Acid rain (100ml) ppm | | | Acetic acid (100ml) ppm | | |
|---|---|---|---|---|---|---|
| | Kaol | Bent | Sand | **Kaol** | Bent | Sand |
| **Al** | 1.2 | 0.8 | 24 | 36 | 34 | 36 |
| **Ca** | 18 | 53 | 16 | 0.16 | 83 | 0.21 |
| **Cr** | 0 | 0 | 0 | 0 | 0 | 0 |
| **Cu** | 0.7 | 0 | 0 | 0 | 0.09 | 1.5 |
| **Fe** | 0.26 | 0.2 | 0.33 | 0.15 | 0.1 | 0.31 |
| **K** | 9050 | 9460 | 4060 | 5020 | 4710 | 6890 |
| **Mn** | 0.12 | 0.08 | 0.04 | 0.89 | 6 | 1.24 |
| **Na** | 7000 | 5600 | 5000 | 1000 | 3300 | 3000 |
| Ni | 0.24 | 0.26 | 0.25 | 0.39 | 0.3 | 0.41 |
| Ti | 0 | 0 | 2 | 0 | 0 | 0 |
| **Zn** | 0.03 | 0.06 | 0.07 | 0.12 | 0.66 | 0.49 |

leaching media. This reduction is due to the adsorption or ion exchange behaviour of the clay samples. Both kaolinite and bentonite are very good adsorbent materials because of the presence of negatively charged layers on their surfaces. In any leach medium very little interaction between aluminium and the sand sample was observed, whilst, in the case of acetic acid leach medium, no interaction between the aluminium and any of the clay samples (kaolinite, bentonite and sand) was observed. This is due to the zero interaction between the negatively charged aluminate ions, $[Al(OH)_4]^-$ (section 3.5.1) and the negatively charged clay surface. These results show that in the case of acetic acid leaching all of the aluminium will remain in soluble form due to the electrostatic force of repulsion between the similar charges. Figure-3.8 depicts the behaviour of aluminium in the presence and absence of soils with different leach media.

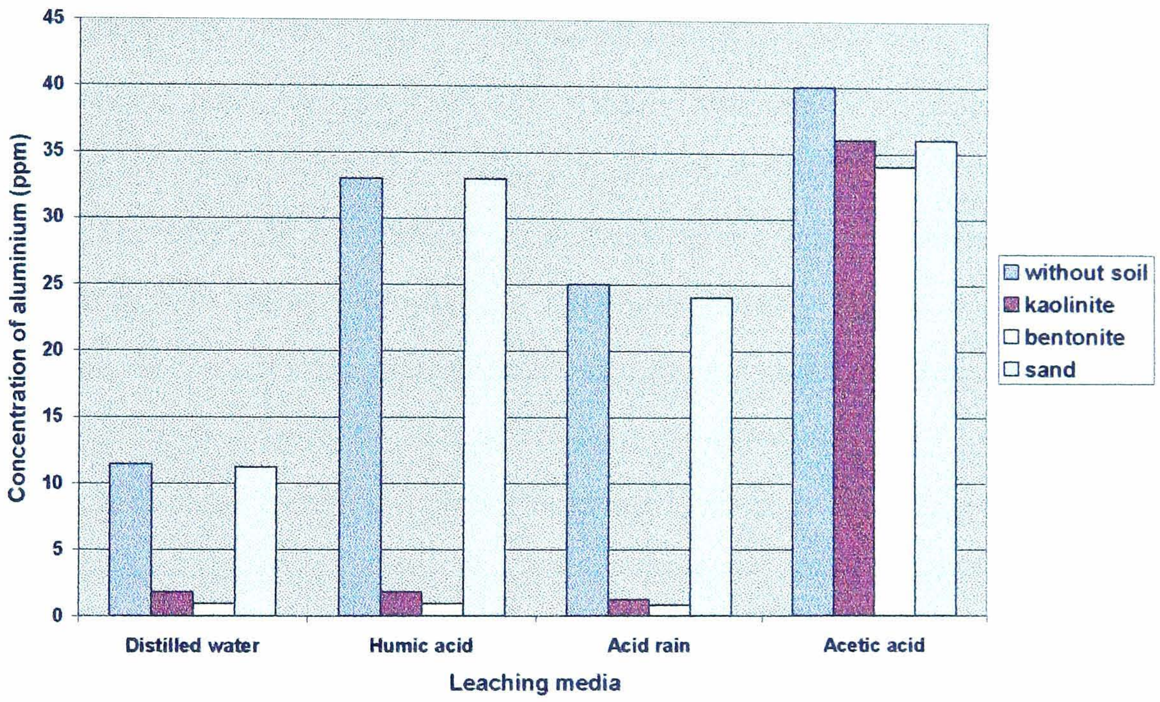

**Figure-3.8. The effect of different soil components on the leachability of aluminium in different leaching media under landfill conditions**

Kaolinite, $Al_2(OH)_4.Si_2O_5$ and bentonite $Al_2(OH)_2.Si_4O_{10}.H_2O$ are sheet silicate and both have negatively charged layers. Most metal cations, especially aluminium, can form a bridge bond between two negatively charged clay sheets. On the other hand, silicon dioxide, $SiO_2$ is not very reactive and does not has many active sites like kaolinite and bentonite. Therefore, similar concentrations of aluminium were found in the leaching solutions (leached without clays) and in the leaching solutions containing sand sample (Figure-3.8), because of zero adsorption or interaction between aluminium and sand. In the presence of bentonite the highest solubility of black dross (Table-3.3.a) is achieved, with the lowest concentration of metals in the leaching media (Table-3.3.b). This can be explained by this clay's higher cation exchange capacity. Bentonite is more capable of adsorbing cations than kaolinite. The reason for this is, in kaolinite's structure, only external ionic exchange sites are present; whereas, in bentonite both external and internal ion exchange sites are present[3], giving bentonite more potential ionic exchange sites.

To explain why the soil and humic acid sample leached less aluminium than humic acid sample alone, comparisons with various literature sources were made. Yun-Hwei Shen[32] researched the effects of metal ratios in kaolinite and bentonite soils on the sorption of humic acid. The results obtained indicated a correlation between the atomic ratio of (Al + Fe) : Si of soil colloid surfaces and the humic acid sorption capacity, where those soils with larger values of the (Al + Fe) : Si ratio were able to sorb humic acid more efficiently. Thus, aluminium is participating in interactions with humic acid and soil particles. Arias et al[62] noted that precipitation of increasing amounts of aluminium or iron oxides in the presence of kaolinite caused both the point of zero charge and the flocculation interval to shift towards higher pH, suggesting the oxide precipitates mask the negative charges of the basal faces of the kaolinite by coating those faces or by ion exchange, to suggest more evidence of aluminium and soil interaction. They went on to postulate that if the basal faces of the kaolinite become partly coated with inorganic oxides, a large proportion of the humic acid added may adsorb on that oxide layer or associate with exposed areas of the basal faces via adsorbed, partially hydroxylated metal ions. Sposito[57] theorised mechanisms by which humic acid would sorb onto mineral surfaces, of which one of them is the idea of cation bridging, one which supports the work of Arias et al[62]. Therefore, it can be suggested that the reason for the addition of soil samples to humic acid and dross mixtures decreasing the quantity of leachates formed may be due to the additional soil and aluminium interactions. The surface areas and cation exchange capacity (CEC) of humic acid is higher than the clay minerals[3]. In the previous section (3.5.1) it was mentioned that as humic acid is negatively charged at pH greater than 3, as pH increases, the degree of negative charge increases due to the deprotonation or dissociation of $H^+$ from functional groups. In section 3.3.2, it was discussed that the major functional groups in humic acid are carboxyls, phenols and quinols. Since these groups can deprotonate at pHs common in many soils, they are major contributors to the negative charge of soils.

### 3.5.3. Interaction mechanisms between metal ions and soil components in the leaching media

In the previous section the interaction between dross and soil components in the leaching media has been observed. The experiments showed that metals leached out from the dross under the different leaching media conditions and then interact with kaolinite and bentonite but not sand. The interaction between the metals from the dross with the clay components could be just physical attachment on the clay surface or the interaction could be chemical interaction. In this section the interaction mechanism has been investigated. A set of adsorption and desorption experiments was carried out in order to determine the types of interaction between the metals and the clays in the leaching media.

Table-3.4 presents the results of adsorption of aluminium on kaolinite and bentonite in the presence of four different leaching media. Aluminium in de-ionised water, humic acid and acid rain solutions were adsorbed on the clay surfaces, giving very similar results. No aluminium adsorption occurred in the acetic acid solution.

A set of "Blank" experiments (no aluminium in the leaching media, i.e., no black dross, labelled "Blank" in Table-3.4) were carried out in order to determine the leachability of the four leaching media on the clays. No aluminium leached out from the clays in the presence of de-ionised water and humic acid. The pH in these two solutions was approximately neutral. Only a trace amount of aluminium was released in the presence of acid rain and acetic acid. The pH of these two solutions was acidic which caused the aluminium to be released from the clay surface.

A set of "Test" experiments (with a starting solution of 100ppm at 0 hour, labelled "Test Solution" in Table-3.4) is used to describe the presence of aluminium (leached from black dross) in the four different leaching media. Aluminium ions in de-ionised water, humic acid and acid rain (Table-3.4a, b and c), showed almost complete adsorption on both kaolinite and bentonite within 6-8 days. It can be seen that the clays are extremely adsorptive as most of the adsorption occurred within an hour. The experiments were not continued after day-8 because no more adsorption occurred. The pH of all three solutions (de-ionised water, humic acid and acid rain) in both clays were very alkaline because the initial pH of the aluminium solution in each leach medium was very alkaline

## Table-3.4. Adsorption of aluminium in different leaching media and clays

**Table-3.4a. Adsorption of aluminium in de-ionised water with kaolinite and bentonite**

| Time (day) | Volume (ml) | Kaolinite |  |  |  | Bentonite |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Blank |  | Test solution |  | Blank |  | Test solution |  |
|  |  | Conc. of Al (ppm) | pH | Conc. of Al (ppm) | pH | Conc. Al (ppm) | pH | Conc. of Al(ppm) | pH |
| 0 | 200 | 0 | 6.0 | 100 | 10.6 | 0 | 9.2 | 100 | 10.7 |
| 1h | 198 | 0 |  | 10 |  | 0 | 8 | 14.2 |  |
| 1 | 196 | 0 |  | 7.2 |  | 0 |  | 8.7 |  |
| 2 | 194 | 0 |  | 6.2 |  | 0 |  | 7.2 |  |
| 3 | 192 | 0 |  | 5.7 |  | 0 |  | 6.7 |  |
| 4 | 190 | 0 | 6.8 | 4.2 | 11.4 | 0 |  | 5.3 | 10.8 |
| 5 | 188 | 0 |  | 3.9 |  | 0 |  | 5 |  |
| 6 | 186 | 0 |  | 3.9 |  | 0 |  | 5 |  |
| 7 | 184 | 0 |  | 3.7 |  | 0 |  | 4.7 | 10.8 |
| 8 | 182 | 0 | 7.16 | 3.7 | 10.86 | 0 | 10.4 | 4.7 | 10.8 |

**Table-3.4b. Adsorption of aluminium in humic acid with kaolinite and bentonite**

| Time (day) | Volume (ml) | Kaolinite |  |  |  | Bentonite |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Blank |  | Test solution |  | Blank |  | Test solution |  |
|  |  | Conc. of Al (ppm) | pH | Conc. of Al (ppm) | pH | Conc. of Al (ppm) | pH | Conc. of Al(ppm) | pH |
| 0 | 200 | 0 | 7.7 | 100 | 10.5 | 0 | 7.5 | 100 | 11.2 |
| 1h | 198 | 0 |  | 11 |  | 0 |  | 10.9 |  |
| 1 | 196 | 0 |  | 9.0 |  | 0 |  | 10.6 |  |
| 2 | 194 | 0 |  | 7.9 |  | 0 |  | 9.5 |  |
| 3 | 192 | 0 | 7.8 | 7.7 | 11.3 | 0 | 7.8 | 8.8 | 11.3 |
| 4 | 190 | 0 |  | 7.1 |  | 0 |  | 7.8 |  |
| 5 | 188 | 0 |  | 5.8 |  | 0 |  | 7.1 |  |
| 6 | 186 | 0 |  | 5.6 |  | 4 |  | 6.9 |  |
| 7 | 184 | 3.4 |  | 5.6 |  | 4 |  | 6.9 |  |
| 8 | 182 | 3.4 | 7.8 | 5.6 | 10.7 | 4 | 7.11 | 6.9 | 10.7 |

**Table-3.4c. Adsorption of aluminium in acid rain with kaolinite and bentonite**

| Time (day) | Volume (ml) | Kaolinite |  |  |  | Bentonite |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Blank |  | Test solution |  | Blank |  | Test solution |  |
|  |  | Conc. of Al (ppm) | pH | Conc. of Al (ppm) | pH | Conc. of Al (ppm) | pH | Conc. of Al(ppm) | pH |
| 0 | 200 | 0 | 2.82 | 100 | 10.16 | 0 | 2.91 | 100 | 10.2 |
| 1h | 198 | 0 |  | 6.8 |  | 0 |  | 7.5 |  |
| 1 | 196 | 0 |  | 4.9 |  | 0 |  | 5.7 |  |
| 2 | 194 | 0 |  | 4.9 |  | 0 |  | 5.2 |  |
| 3 | 192 | 0 |  | 3.5 |  | 0 |  | 5.0 |  |
| 4 | 190 | 0 |  | 2.4 |  | 0 |  | 3.6 |  |
| 5 | 188 | 0 |  | 1.8 |  | 0 |  | 2.9 |  |
| 6 | 186 | 0.01 |  | 1.7 |  | 0.04 |  | 2.6 |  |
| 7 | 184 | 0.01 |  | 1.6 |  | 0.04 |  | 2.4 |  |
| 8 | 182 | 0.08 | 2.3 | 1.8 | 10.38 | 0.04 | 2.75 | 2.4 | 10.5 |

**Table-3.4d. Adsorption of aluminium in acetic acid with kaolinite and bentonite**

| Time (day) | Volume (ml) | Kaolinite |  |  |  | Bentonite |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Blank |  | Test solution |  | Blank |  | Test solution |  |
|  |  | Conc. of Al (ppm) | pH | Conc. of Al (ppm) | pH | Conc. of Al(ppm) | pH | Conc. of Al(ppm) | pH |
| 0 | 200 | 0 | 3.88 | 100 | 5.8 | 8.3 | 4.13 | 100 | 5.14 |
| 1h | 198 | 0 |  | 100 |  | 9.0 |  | 94 |  |
| 1 | 196 | 0 |  | 80.5 |  | 9.5 |  | 92 |  |
| 2 | 194 | 0 |  | 96 |  | 9.5 |  | 91 |  |
| 3 | 192 | 0 |  | 93 |  | 11.1 |  | 92 |  |
| 4 | 190 | 1.5 |  | 93 |  | 12 |  | 92 |  |
| 5 | 188 |  |  | 94 |  | 11 |  | 94 |  |
| 6 | 186 |  |  | 43 |  | 11 |  | 93 |  |
| 7 | 184 |  |  | 93 |  | 9.1 |  | 93 |  |
| 8 | 182 | 0 | 4.0 | 92 | 5.5 | 9.9 | 4.2 | 93 | 5.6 |

to start with (pH 10.55). No adsorption of aluminium occurred on the clay surface treated with acetic acid solution (Table-3.4d).

After the adsorption experiments, desorption experiments were carried out in order to predict the fate and mobility of the aluminium ions in the soils. The desorption experiment discussed in section 3.4.2.3 showed no release of the adsorbed aluminium ions in de-ionised water and humic acid (Table-3.5a and b). Some aluminium ions were detected by AAS in the solution of kaolinite and bentonite samples treated with acid rain and acetic acid(Table-3.5c and 3.5d).

**Table-3.5. Aluminium desorption**

***Table-3.5a. De-ionised water***

| | Time (h) | Kaolinite | Bentonite |
|---|---|---|---|
| pH | 0 | 5.6 | 7.7 |
| | 3 | 6.27 | 8.59 |
| Conc. of Al (ppm) | 3 | 0 | 0 |

***Table-3.5b. Humic acid***

| | Time (h) | Kaolinite | Bentonite |
|---|---|---|---|
| pH | 0 | 5.45 | 7.94 |
| | 3 | 5.97 | 8.44 |
| Conc. of Al (ppm) | 3 | 0 | 0 |

***Table-3.5c. Acid rain***

| | Time (h) | Kaolinite | Bentonite |
|---|---|---|---|
| pH | 0 | 5.6 | 6.6 |
| | 3 | 6.57 | 6.7 |
| Conc. of Al (ppm) | 3 | 20 | 10 |

***Table-3.5d. Acetic acid***

| | Time (h) | Kaolinite | Bentonite |
|---|---|---|---|
| pH | 0 | 5.6 | 6.5 |
| | 3 | 6.27 | 6.6 |
| Conc. of Al (ppm) | 3 | 25 | 30 |

The absence of aluminium ions in solution following the desorption experiment, confirms that the adsorbed aluminium ions on the clay surface are bound very strongly. The positively charged aluminium ions interact with the negatively charged clays. The clay samples were analysed using XRD to investigate whether the structure of the clays was changed due to the adsorption and desorption. Table-3.6 and 3.7 present the XRD patterns of the adsorbed and desorbed clays treated with aluminium in de-ionised water and humic acid solution. The results show that this interaction changes the structure of the clays. Each table presents d spacing and angles ($^{0}2$-θ) of a pure (untreated) clay, the adsorbed clay from "Blank" and "Test" experiments, and desorbed clay from the "Test" experiment. The bold-italic-red colour numbers represent the changes in the d spacing. If there was no change in the clay structure, the d spacing of the experimented clays should be exactly the same as the pure clays. The XRD patterns (Table-3.6 and 3.7) of the adsorbed and desorbed clays are very similar which also suggests that adsorbed metal ions are not capable of being released from the clay surfaces due to being strongly

## Table-3.6. XRD patterns of kaolinite and bentonite treated with de-ionised water(DW)

***Table-3.6a. Adsorption and desorption of aluminium in de-ionised water and kaolinite***

| No | Kaolinite | | (Adsorption) | | | | Desorption | |
|---|---|---|---|---|---|---|---|---|
| | | | Blank(DW+ kaol) | | Test(Al in DW solution+kaol | | Test(Al in DW solution+kaol) | |
| | **D space** | **Angle** | **D space** | **Angle** | **D space** | **Angle** | **D space** | **Angle** |
| 1 | 9.972 | 8.86 | 9.95 | 8.88 | 9.902 | 8.94 | 9.905 | 8.92 |
| 2 | 7.155 | 12.36 | 7.144 | 12.38 | 7.144 | 12.38 | 7.144 | 12.38 |
| 3 | 4.996 | 17.74 | 4.99 | 17.76 | 4.99 | 17.76 | 4.99 | 17.76 |
| 4 | 4.462 | 19.88 | 4.454 | 19.92 | ***4.71*** | ***18.83*** | ***4.711*** | ***18.82*** |
| 5 | 4.358 | 20.36 | 4.358 | 20.36 | 4.452 | 19.94 | 4.454 | 19.92 |
| 6 | 4.176 | 21.26 | ***4.251*** | ***20.88*** | 4.358 | 20.36 | 4.358 | 20.36 |
| 7 | 3.847 | 23.1 | 4.172 | 21.28 | 4.17 | 21.3 | 4.172 | 21.28 |
| 8 | 3.736 | 23.8 | 3.85 | 23.08 | 3.847 | 23.1 | 3.849 | 23.08 |
| 9 | 3.576 | 24.88 | 3.726 | 23.86 | 3.739 | 23.78 | 3.739 | 23.78 |
| 10 | 3.334 | 26.72 | 3.57 | 24.92 | 3.572 | 24.1 | 3.573 | 24.9 |
| 11 | 2.562 | 35.0 | 3.329 | 26.76 | ***3.487*** | ***25.53*** | ***3.488*** | ***25.52*** |
| 12 | 2.495 | 35.96 | ***2.986*** | ***29.9*** | 3.331 | 26.74 | 3.331 | 26.74 |
| 13 | 2.383 | 37.72 | 2.559 | 35.04 | ***3.195*** | ***27.9*** | ***3.197*** | ***27.88*** |
| 14 | 2.341 | 38.42 | 2.494 | 35.98 | **3.046** | **29.19** | 2.56 | 35.02 |
| 15 | 2.294 | 39.24 | 2.38 | 37.76 | 2.56 | 35.02 | 2.493 | 36.0 |
| 16 | 1.996 | 45.4 | 2.34 | 38.44 | 2.493 | 36.0 | 2.382 | 37.74 |
| 17 | 1.94 | 46.8 | 2.291 | 39.3 | 2.381 | 37.75 | 2.339 | 38.46 |
| 18 | 1.838 | 49.56 | ***2.028*** | ***44.64*** | 2.339 | 38.46 | 2.292 | 39.28 |
| 19 | 1.787 | 51.06 | 1.994 | 45.44 | 2.292 | 39.28 | ***2.22*** | ***40.6*** |
| 20 | 1.664 | 55.14 | 1.937 | 46.86 | ***2.21*** | ***40.65*** | 1.997 | 45.38 |
| 21 | 1.619 | 56.82 | 1.786 | 51.1 | 1.995 | 45.42 | 1.94 | 46.8 |
| 22 | 1.586 | 58.1 | 1.663 | 55.2 | 1.94 | 46.8 | 1.841 | 49.48 |
| 23 | 1.541 | 59.98 | 1.62 | 56.8 | 1.841 | 49.48 | 1.789 | 51.02 |
| 24 | 1.489 | 62.3 | 1.54 | 60.04 | 1.788 | 54.04 | ***1.723*** | ***53.1*** |
| 25 | 1.34 | 70.1 | 1.489 | 62.32 | ***1.721*** | ***53.15*** | 1.662 | 55.24 |
| 26 | 1.307 | 72.24 | 1.341 | 70.14 | 1.662 | 55.24 | 1.618 | 56.84 |
| 27 | | | 1.301 | 72.4 | 1.618 | 56.84 | 1.487 | 62.38 |
| 28 | | | | | 1.488 | 62.36 | 1.341 | 70.1 |
| 29 | | | | | 1.341 | 70.1 | 1.307 | 72.22 |
| 30 | | | | | 1.307 | 72.22 | | |

***Table-3.6b. Adsorption and desorption of aluminium in de-ionised water and bentonite***

| No | Bentonite | | Adsorption | | | | Desorption | |
|---|---|---|---|---|---|---|---|---|
| | | | Blank(DW+ Bentonite) | | Test(Al in DW solution+Bent) | | Test(Al in DW solution+Bent) | |
| | D space | Angle | D space | Angle | D space | Angle | D space | Angle |
| 1 | 15.225 | 5.8 | 15.121 | 5.84 | ***12.9*** | ***6.85*** | ***12.95*** | ***6.82*** |
| 2 | 4.485 | 19.78 | 13.381 | 6.6 | ***12.46*** | ***7.12*** | ***12.51*** | ***7.06*** |
| 3 | 4.267 | 20.8 | 5.263 | 16.92 | ***7.211*** | ***12.24*** | ***7.213*** | ***12.26*** |
| 4 | 4.055 | 21.9 | 4.485 | 19.78 | ***4.724*** | ***18.78*** | ***4.726*** | ***18.76*** |
| 5 | 3.757 | 23.66 | 4.267 | 20.8 | 4.48 | 19.8 | 4.48 | 19.8 |
| 6 | 3.346 | 26.62 | 4.041 | 21.98 | ***4.374*** | ***20.3*** | ***4.375*** | ***20.28*** |
| 7 | 3.213 | 27.74 | 3.767 | 23.6 | 4.261 | 20.84 | 4.263 | 20.82 |
| 8 | 3.177 | 28.06 | 3.341 | 26.66 | 4.051 | 21.92 | 4.051 | 21.92 |
| 9 | 3.081 | 28.96 | 3.252 | 27.4 | ***3.89*** | ***22.8*** | ***3.9*** | ***22.78*** |
| 10 | 2.567 | 34.92 | 3.213 | 27.74 | 3.773 | 23.56 | 3.773 | 23.56 |
| 11 | 1.819 | 50.1 | 3.081 | 28.96 | 3.351 | 26.58 | 3.351 | 26.58 |
| 12 | 1.694 | 54.08 | 2.567 | 34.92 | 3.228 | 27.72 | 3.229 | 27.6 |
| 13 | 1.494 | 61.9 | 2.444 | 36.74 | 3.075 | 29.0 | ***2.843*** | ***31.44*** |
| 14 | | | 2.029 | 44.62 | ***2.843*** | ***31.44*** | 2.567 | 34.92 |
| 15 | | | 1.821 | 50.04 | 2.567 | 34.92 | 2.461 | 36.48 |
| 16 | | | 1.672 | 54.88 | 2.461 | 36.48 | ***2.284*** | ***39.42*** |
| 17 | | | 1.497 | 61.94 | ***2.282*** | ***39.44*** | ***2.224*** | ***40.52*** |
| 18 | | | 1.374 | 68.18 | ***2.222*** | ***40.54*** | ***2.171*** | ***41.56*** |
| 19 | | | | | ***2.171*** | ***41.56*** | 2.027 | 44.68 |
| 20 | | | | | 2.025 | 44.69 | 1.821 | 50.06 |
| 21 | | | | | 1.82 | 50.08 | ***1.798*** | ***50.74*** |
| 22 | | | | | ***1.798*** | ***50.74*** | 1.674 | 54.78 |
| 23 | | | | | 1.674 | 54.78 | ***1.544*** | ***59.84*** |
| 24 | | | | | ***1.543*** | ***59.86*** | 1.498 | 61.9 |
| 25 | | | | | 1.498 | 61.9 | | |

## Table-3.7. XRD patterns of kaolinite and bentonite treated with humic acid (HA)

***Table-3.7a. Adsorption and desorption of aluminium in humic acid and kaolinite***

| No | Kaolinite | | Adsorption | | | | Desorption | |
|---|---|---|---|---|---|---|---|---|
| | | | Blank (HA+Kaol) | | Test (Al in HA solution+kaol) | | Test (Al in HA solution+kaol) | |
| | D space | Angle | D space | Angle | D space | Angle | D space | Angle |
| 1 | 9.972 | 8.86 | 7.178 | 12.32 | 9.861 | 8.96 | 9.905 | 8.92 |
| 2 | 7.155 | 12.36 | 5.007 | 17.7 | 7.098 | 12.46 | 7.132 | 12.4 |
| 3 | 4.996 | 17.74 | 4.471 | 19.84 | 4.968 | 17.84 | 4.979 | 17.8 |
| 4 | 4.462 | 19.88 | 4.367 | 20.32 | *4.691* | *18.9* | *4.706* | *18.84* |
| 5 | 4.358 | 20.36 | 4.187 | 21.2 | 4.44 | 19.98 | 4.454 | 19.92 |
| 6 | 4.176 | 21.26 | 3.867 | 22.98 | 4.341 | 20.44 | 4.35 | 20.4 |
| 7 | 3.847 | 23.1 | 3.745 | 23.74 | 4.164 | 21.32 | 4.176 | 21.26 |
| 8 | 3.736 | 23.8 | 3.581 | 24.84 | 3.837 | 23.16 | 3.844 | 23.12 |
| 9 | 3.576 | 24.88 | 3.338 | 26.68 | 3.717 | 23.92 | 3.729 | 23.84 |
| 10 | 3.334 | 26.72 | 2.564 | 34.96 | 3.562 | 24.98 | 3.57 | 24.92 |
| 11 | 2.562 | 35.0 | 2.539 | 35.32 | 3.324 | 26.8 | 3.329 | 26.76 |
| 12 | 2.495 | 35.96 | 2.499 | 35.9 | *3.227* | *27.62* | *3.197* | *27.88* |
| 13 | 2.383 | 37.72 | 2.388 | 37.64 | *3.191* | *27.94* | *2.986* | *29.9* |
| 14 | 2.341 | 38.42 | 2.345 | 38.36 | *3.029* | *29.46* | 2.559 | 35.04 |
| 15 | 2.294 | 39.24 | 2.297 | 39.18 | *2.813* | *31.78* | *2.531* | *35.44* |
| 16 | 1.996 | 45.4 | 1.998 | 45.2 | 2.556 | 35.08 | 2.493 | 36.0 |
| 17 | 1.94 | 46.8 | 1.95 | 46.7 | 2.49 | 36.04 | 2.38 | 37.76 |
| 18 | 1.838 | 49.56 | 1.789 | 51.0 | 2.378 | 37.8 | 2.338 | 38.48 |
| 19 | 1.787 | 51.06 | 1.667 | 55.06 | 2.334 | 38.54 | 2.293 | 39.26 |
| 20 | 1.664 | 55.14 | 1.623 | 56.68 | 2.287 | 39.36 | *2.22* | *40.6* |
| 21 | 1.619 | 56.82 | 1.543 | 59.9 | *2.216* | *40.68* | *2.129* | *42.42* |
| 22 | 1.586 | 58.1 | 1.49 | 62.26 | 1.994 | 45.44 | 1.994 | 45.44 |
| 23 | 1.541 | 59.98 | 1.431 | 65.12 | 1.786 | 51.1 | 1.936 | 46.88 |
| 24 | 1.489 | 62.3 | 1.342 | 70.08 | *1.719* | *53.26* | 1.787 | 51.08 |
| 25 | 1.34 | 70.1 | 1.307 | 72.24 | 1.661 | 55.26 | *1.722* | *53.16* |
| 26 | 1.307 | 72.24 | 1.342 | 70.08 | 1.487 | 62.42 | 1.663 | 55.2 |
| 27 | | | 1.307 | 72.24 | 1.338 | 70.32 | 1.618 | 56.86 |
| 28 | | | | | 1.307 | 72.24 | 1.489 | 62.32 |

***Table-3.7b. Adsorption and desorption of aluminium in humic acid and bentonite***

| No | Bentonite | | Adsorption | | | | Desorption | |
|---|---|---|---|---|---|---|---|---|
| | | | Blank (HA+Bent) | | Test(Al in HA solution+Bent) | | Test(Al in HA solution+Bent) | |
| | D space | Angle | D space | Angle | D space | Angle | D space | Angle |
| 1 | 15.225 | 5.8 | 5.839 | 15.16 | *12.44* | *7.1* | *12.43* | *7.1* |
| 2 | 4.485 | 19.78 | 4.489 | 19.76 | *4.726* | *18.76* | *4.716* | *18.8* |
| 3 | 4.267 | 20.8 | 4.263 | 20.82 | 4.489 | 19.76 | 4.485 | 19.78 |
| 4 | 4.055 | 21.9 | 4.059 | 21.88 | 4.405 | 20.14 | *4.371* | *20.3* |
| 5 | 3.757 | 23.66 | 3.77 | 23.58 | 4.259 | 20.84 | 4.259 | 20.84 |
| 6 | 3.346 | 26.62 | 3.466 | 25.68 | *4.195* | *21.9* | *4.048* | *21.94* |
| 7 | 3.213 | 27.74 | 3.348 | 26.6 | 4.055 | 26.56 | 3.928 | 22.62 |
| 8 | 3.177 | 28.06 | 3.22 | 27.68 | 3.353 | 27.3 | *3.776* | *23.54* |
| 9 | 3.081 | 28.96 | 3.182 | 28.02 | *3.264* | *27.64* | *3.346* | *26.62* |
| 10 | 2.567 | 34.92 | 3.144 | 28.36 | 3.225 | 28.04 | *3.22* | *27.68* |
| 11 | 1.819 | 50.1 | 2.915 | 30.64 | 3.18 | 28.26 | *2.714* | *32.98* |
| 12 | 1.694 | 54.08 | 2.85 | 31.36 | *3.155* | *29.88* | 2.563 | 34.98 |
| 13 | 1.494 | 61.9 | 2.727 | 32.82 | *2.988* | *30.64* | *2.539* | *35.32* |
| 14 | | | 2.569 | 34.9 | 2.915 | 31.66 | *2.282* | *39.46* |
| 15 | | | 2.466 | 36.4 | *2.824* | *34.84* | *2.222* | *40.56* |
| 16 | | | 2.283 | 39.44 | 2.573 | 40.5 | 1.819 | 50.1 |
| 17 | | | 2.234 | 40.34 | *2.225* | *54.38* | *1.745* | *52.38* |
| 18 | | | 2.166 | 41.66 | *1.997* | *50.38* | *1.722* | *53.14* |
| 19 | | | 1.124 | 42.52 | 1.819 | 50.1 | 1.674 | 54.8 |
| 20 | | | 1.985 | 45.66 | *1.725* | *53.04* | *1.656* | *55.44* |
| 21 | | | 1.956 | 46.38 | *1.701* | *53.86* | *1.623* | *56.68* |
| 22 | | | 1.82 | 50.08 | 1.676 | 54.72 | *1.593* | *57.82* |
| 23 | | | 1.675 | 54.74 | *1.631* | *56.38* | *1.541* | *59.96* |
| 24 | | | 1.542 | 59.94 | 1.543 | 59.9 | 1.497 | 61.92 |
| 25 | | | 1.496 | 61.96 | 1.497 | 61.92 | *1.454* | *63.98* |
| 26 | | | 1.378 | 67.98 | *1.412* | *66.12* | *1.374* | *68.2* |
| 27 | | | 1.29 | 73.3 | 1.375 | 68.14 | *1.331* | *70.7* |
| 28 | | | 1.248 | 76.22 | *1.263* | *75.18* | | |

bound, or in other words ionic exchange on the clay surfaces. No compounds were identified in de-ionised water and humic acid conditions. Under both conditions, aluminium cations simply interacted on the clay surfaces without forming any kind of compound. The adsorption of the additional aluminium and other cations on the negatively charged clay surfaces in the absence of humic acids, is due to electrostatic interaction. In the presence of humic acid, the metal cations form bridges between the negatively charged organic humic acid molecules and inorganic clay mineral surfaces (HA-metal-clay mineral). Calcium is weakly held as a cation bridge and can be easily displaced, whereas $Al^{3+}$ and $Fe^{3+}$ are usually bound nonelectrostatically and are difficult to remove. Several reports also proposed on this kind of interaction[83,84]. Extraction of Al from these complexes is difficult[85]. In the case of the adsorbed clay samples treated with acid rain leaching media, some of the modified d spacing were identified as aluminium nitrate [$Al(NO_3)_3$] and aluminium sulphate [$Al_2(SO_4)_3$] (Table-3.8). After the desorption, some extra d spacing were detected, but there was no evidence of aluminium compounds on the structure of clays. The aluminium nitrate and sulphate were precipitated on the surface of the clays after drying the adsorbed clays. During the desorption, these compounds were washed off from the surfaces. The small changes of d spacing can be interpreted as resulting from some ionic exchange between the metal ions and clays (electrostatic interaction). It also can be noticed that there are more changes in the d spacing in bentonite than in kaolinite. This means that bentonite's structure changed more (due to the ion exchange) than kaolinite. This is because bentonite (and other montmorillonite type of soils) has a higher cation exchange capacity (CEC), which is predominantly composed of constant charge sites, as opposed to kaolinite, which has low CEC and is variably charged[3]. Furthermore, bentonite contains both external and internal ionic exchange sites where as kaolinite has only external ionic exchange sites (section-3.5.3), therefore, bentonite can interact with more cations than kaolinite.

No adsorption of aluminium occurred on the clay surfaces treated with acetic acid (Table-3.4.d). The desorption experiment showed some presence of aluminium in the solution (Table-3.5.d). The XRD patterns (Table-3.9) shows changes in d spacing in the adsorbed clays. The changes can be attributed to the presence of aluminium acetate [$Al(CH_3COO)_3$].

# Table-3.8. Absorption and desorption of aluminium in acid rain and clays

## *Table-8.a. Absorption and desorption of aluminium in acid rain and kaolinite*

| No | Kaolinite | | Adsorption | | | | | Desorption | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Blank (AR+kaolinite) | | Test(Al in AR solution+kaolinite) | | | Test(Al in AR solution+kaol) | |
| | D space | Angle | D space | Angle | D space | Angle | Identified compound | D space | Angle |
| 1 | 9.972 | 8.86 | 9.928 | 8.9 | 9.883 | 8.94 | | 9.995 | 8.84 |
| 2 | 7.155 | 12.36 | 7.144 | 12.38 | 7.121 | 12.42 | | 7.167 | 12.34 |
| 3 | 4.996 | 17.74 | 4.984 | 17.78 | 4.979 | 17.8 | | 5.001 | 17.72 |
| 4 | 4.462 | 19.88 | 4.458 | 19.9 | *4.706* | *18.84* | | *4.726* | *18.76* |
| 5 | 4.358 | 20.36 | 4.354 | 20.38 | 4.449 | 19.94 | | 4.467 | 19.86 |
| 6 | 4.176 | 21.26 | 3.854 | 23.06 | 4.346 | 20.42 | | 4.367 | 20.32 |
| 7 | 3.847 | 23.1 | 3.729 | 23.84 | *4.235* | *20.96* | | *4.233* | *20.98* |
| 8 | 3.736 | 23.8 | 3.57 | 24.92 | 4.164 | 21.32 | | 4.184 | 21.22 |
| 9 | 3.576 | 24.88 | 3.331 | 26.74 | 3.847 | 23.1 | | 3.854 | 23.06 |
| 10 | 3.334 | 26.72 | 2.56 | 35.02 | 3.732 | 23.82 | | 3.739 | 23.78 |
| 11 | 2.562 | 35.0 | 2.494 | 35.98 | 3.567 | 24.94 | | 3.579 | 24.86 |
| 12 | 2.495 | 35.96 | 2.382 | 37.74 | 3.324 | 26.8 | | 3.336 | 26.7 |
| 13 | 2.383 | 37.72 | 2.338 | 38.48 | *3.195* | *27.9* | $Al(NO_3)_3$ | 2.564 | 34.96 |
| 14 | 2.341 | 38.42 | 2.293 | 39.26 | *3.031* | *29.44* | $Al(NO_3)_3$ | 2.497 | 35.94 |
| 15 | 2.294 | 39.24 | 1.996 | 45.4 | *2.982* | *29.94* | $Al(NO_3)_3$ | 2.385 | 37.68 |
| 16 | 1.996 | 45.4 | 1.787 | 51.06 | *2.817* | *31.74* | NaCl | 2.341 | 38.42 |
| 17 | 1.94 | 46.8 | 1.664 | 55.14 | 2.557 | 35.06 | | 2.296 | 39.2 |
| 18 | 1.838 | 19.56 | 1.62 | 56.8 | 2.493 | 36.0 | | *2.21* | *40.7* |
| 19 | 1.787 | 51.06 | 1.586 | 58.12 | 2.38 | 37.76 | | 1.999 | 45.34 |
| 20 | 1.664 | 55.14 | *1.541* | *59.96* | 2.335 | 38.52 | | 1.789 | 51.02 |
| 21 | 1.619 | 56.82 | 1.488 | 62.36 | 2.291 | 39.3 | | 1.664 | 55.16 |
| 22 | 1.586 | 58.1 | *1.431* | *65.14* | *2.22* | *40.6* | $Al(NO_3)_3$ | 1.621 | 56.74 |
| 23 | 1.541 | 59.98 | 1.34 | 70.16 | 1.994 | 45.44 | | 1.586 | 58.1 |
| 24 | 1.489 | 62.3 | 1.306 | 72.28 | 1.936 | 46.9 | | 1.542 | 59.92 |
| 25 | 1.341 | 70.15 | | | 1.787 | 51.08 | | 1.489 | 62.3 |
| 26 | 1.304 | 72.35 | | | *1.72* | *53.22* | NaCl | 1.339 | 70.24 |
| 27 | | | | | 1.662 | 55.24 | | 1.306 | 72.28 |
| 28 | | | | | 1.617 | 56.88 | | | |
| 29 | | | | | 1.584 | 58.2 | | | |
| 30 | | | | | 1.54 | 60.02 | | | |
| 31 | | | | | 1.487 | 62.4 | | | |
| 32 | | | | | 1.43 | 65.2 | | | |
| 33 | | | | | 1.34 | 70.2 | | | |
| 34 | | | | | 1.303 | 72.48 | | | |

*Table-3.8b. Adsorption and desorption of aluminium in acid rain and bentonite*

| No | Bentonite | | Adsorption | | | | | Desorption | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Blank(AR+ Bentonite) | | Test(Al in AR solution+Bentonite) | | | Test(Al in AR | |
| | D space | Angle | D space | Angle | D space | Angle | Identified compound | D space | Angle |
| 1 | 15.22 | 5.8 | 4.471 | 19.84 | *12.54* | *7.04* | | *12.47* | *7.08* |
| 2 | 4.485 | 19.78 | 4.259 | 20.84 | *12.13* | *7.28* | | *7.866* | *11.24* |
| 3 | 4.267 | 20.8 | 4.033 | 22.02 | *4.726* | *18.76* | $Al_2(SO4)_3$ | *6.487* | *13.64* |
| 4 | 4.055 | 21.9 | 3.907 | 22.74 | 4.48 | 19.8 | | 4.494 | 19.74 |
| 5 | 3.757 | 23.66 | 3.824 | 23.24 | 4.263 | 20.82 | | 4.275 | 20.76 |
| 6 | 3.346 | 26.62 | 3.767 | 23.6 | 4.048 | 21.94 | | 4.048 | 21.94 |
| 7 | 3.213 | 27.74 | 3.604 | 24.68 | *3.884* | *22.88* | $Al_2(SO4)_3$ | 3.773 | 23.56 |
| 8 | 3.177 | 28.06 | 3.453 | 25.78 | 3.786 | 23.48 | | 3.351 | 26.58 |
| 9 | 3.081 | 28.96 | 3.341 | 26.66 | *3.672* | *24.22* | $Al_2(SO4)_3$ | 3.225 | 27.64 |
| 10 | 2.567 | 34.92 | 3.245 | 27.46 | 3.604 | 24.68 | | 3.153 | 28.28 |
| 11 | 1.819 | 50.1 | 3.211 | 27.76 | 3.346 | 26.62 | | 2.567 | 34.92 |
| 12 | 1.694 | 54.08 | 3.182 | 28.02 | 3.188 | 27.96 | | 2.026 | 44.7 |
| 13 | 1.494 | 61.9 | 3.127 | 28.52 | *3.044* | *29.32* | | 1.821 | 50.06 |
| 14 | | | 2.562 | 35. | *2.917* | *30.62* | $Al(NO_3)_3$ | 1.794 | 50.86 |
| 15 | | | 2.456 | 36.66 | 2.82 | 31.7 | | 1.658 | 55.38 |
| 16 | | | 2.282 | 39.46 | *2.715* | *32.96* | $Al_2(SO4)_3$ | 1.5 | 59.9 |
| 17 | | | 2.238 | 40.26 | 2.559 | 35.04 | | 1.498 | 61.9 |
| 18 | | | 2.163 | 41.72 | *2.461* | *36.48* | $Al(NO_3)_3$ | 1.376 | 68.06 |
| 19 | | | 2.126 | 42.48 | *2.42* | *37.12* | $Al_2(SO4)_3$ | | |
| 20 | | | 2.021 | 44.8 | *2.345* | *38.36* | $Al_2(SO4)_3$ | | |
| 21 | | | 1.98 | 45.8 | 2.283 | 39.44 | | | |
| 22 | | | 1.957 | 46.36 | 2.127 | 42.46 | | | |
| 23 | | | 1.818 | 50.14 | *2.094* | *43.16* | $Al(NO_3)_3$ | | |
| 24 | | | 1.792 | 50.92 | 2.026 | 44.7 | | | |
| 25 | | | 1.672 | 54.88 | *1.995* | *45.42* | NaCl | | |
| 26 | | | 1.542 | 59.94 | 1.821 | 50.06 | | | |
| 27 | | | 1.496 | 62. | 1.794 | 50.86 | | | |
| 28 | | | 1.382 | 67.72 | *1.63* | *56.42* | NaCl | | |
| 29 | | | 1.376 | 68.1 | 1.544 | 59.86 | | | |
| 30 | | | 1.36 | 69.02 | 1.495 | 61.9 | | | |
| 31 | | | 1.317 | 71.58 | *1.411* | *66.16* | NaCl | | |
| 32 | | | 1.288 | 73.44 | 1.372 | 68.3 | | | |
| 33 | | | 1.255 | 75.7 | 1.289 | 73.38 | | | |
| 34 | | | | | *1.262* | *75.24* | NaCl | | |

## Table-3.9. Adsorption and desorption of aluminium in Acetic acid and clays

### *Table-3.9a. Adsorption and desorption of aluminium in Acetic acid and kaolinite*

| No | Kaolinite | | (adsorption) | | | | | Desorption | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Blank(AA+ kaolinite) | | Test(Al in AA solution+Kaolinite) | | | Test(Al in AA solution+kaol) | |
| | D space | Angle | D space | Angle | D space | Angle | Identified compounds | D space | Angle |
| 1 | 9.972 | 8.86 | 9.928 | 8.9 | 9.95 | 8.8 | | 10.04 | 8.8 |
| 2 | 7.155 | 12.36 | 7.144 | 12.38 | 7.155 | 12.36 | | 7.202 | 12.28 |
| 3 | 4.996 | 17.74 | 4.99 | 17.76 | 4.996 | 17.74 | | 5.018 | 17.66 |
| 4 | 4.462 | 19.88 | 4.458 | 19.9 | 4.445 | 19.96 | | 4.471 | 19.84 |
| 5 | 4.358 | 20.36 | 4.35 | 20.4 | 4.346 | 20.42 | | 4.38 | 20.26 |
| 6 | 4.176 | 21.26 | 4.176 | 21.26 | 4.16 | 21.34 | | 4.191 | 21.18 |
| 7 | 3.847 | 23.1 | 3.847 | 23.1 | 3.841 | 23.14 | | 3.87 | 22.96 |
| 8 | 3.736 | 23.8 | 3.736 | 23.8 | 3.723 | 23.88 | | 3.748 | 23.72 |
| 9 | 3.576 | 24.88 | 3.573 | 24.9 | 3.57 | 24.92 | | 3.587 | 24.8 |
| 10 | 3.334 | 26.72 | 3.331 | 26.74 | 3.329 | 26.76 | | 3.346 | 26.62 |
| 11 | 2.562 | 35.0 | *2.996* | *29.8* | *3.255* | *27.38* | NaCl | 2.567 | 34.92 |
| 12 | 2.495 | 35.96 | 2.56 | 35.02 | *3.195* | *27.9* | $Al(CH_3COO)_3$ | *2.536* | *35.36* |
| 13 | 2.383 | 37.72 | 2.495 | 35.96 | *3.142* | *28.38* | $Al(CH_3COO)_3$ | 2.388 | 37.64 |
| 14 | 2.341 | 38.42 | 2.382 | 37.74 | *2.984* | *29.92* | $Al(CH_3COO)_3$ | 2.345 | 38.36 |
| 15 | 2.294 | 39.24 | 2.339 | 38.46 | *2.82* | *31.7* | NaCl | 2.299 | 39.16 |
| 16 | 1.996 | 45..4 | 2.292 | 39.28 | 2.557 | 35.06 | | 2.002 | 45.26 |
| 17 | 1.94 | 46.8 | 1.994 | 45.44 | 2.491 | 36.02 | | 1.791 | 50.96 |
| 18 | 1.838 | 49.56 | 1.788 | 51.04 | 2.38 | 37.76 | | 1.665 | 55.1 |
| 19 | 1.787 | 51.06 | 1.66 | 55.08 | 2.339 | 38.46 | | 1.622 | 56.72 |
| 20 | 1.664 | 55.14 | 1.62 | 56.8 | 2.291 | 39.3 | | 1.545 | 59.82 |
| 21 | 1.619 | 56.82 | 1.537 | 60.14 | *2.247* | *40.1* | | 1.49 | 62.28 |
| 22 | 1.586 | 58.1 | 1.489 | 62.32 | *2.22* | *40.6* | $Al(CH_3COO)_3$ | 1.341 | 70.14 |
| 23 | 1.541 | 59.98 | 1.34 | 70.18 | *2.028* | *44.64* | $Al(CH_3COO)_3$ | 1.307 | 72.24 |
| 24 | 1.489 | 62.3 | 1.306 | 72.3 | 1.994 | 45.44 | | | |
| 25 | 1.34 | 70.15 | | | 1.787 | 51.08 | | | |
| 26 | 1.305 | 72.35 | | | 1.663 | 55.18 | | | |
| 27 | | | | | 1.627 | 56.52 | | | |
| 28 | | | | | 1.542 | 59.92 | | | |
| 29 | | | | | 1.488 | 62.34 | | | |
| 30 | | | | | *1.429* | *65.22* | $Al(CH_3COO)_3$ | | |
| 31 | | | | | 1.339 | 70.36 | | | |
| 32 | | | | | 1.305 | 72.36 | | | |
| 33 | | | | | *1.262* | *75.2* | | | |

***Table-3.9b. Adsorption of aluminium in Acetic acid and bentonite***

| No | Bentonite | | Adsorption | | | | | Desorption | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Blank(AA+ Bentonite) | | Test(Al in AA solution+Bentonite) | | | Test(Al in AA solution+Bent) | |
| | D space | Angle | D space | Angle | D space | Angle | Identified compounds | D space | Angle |
| 1 | 15.22 | 5.8 | 17.65 | 5.0 | *12.33* | *7.16* | | 15.2 | 5.79 |
| 2 | 4.485 | 19.78 | 15.60 | 5.66 | *10.08* | *8.76* | | 4.494 | 19.74 |
| 3 | 4.267 | 20.8 | 5.248 | 16.88 | *7.237* | *12.22* | $Al(CH_3COO)_3$ | 4.292 | 20.68 |
| 4 | 4.055 | 21.9 | 4.498 | 19.72 | *6.534* | *13.54* | $Al(CH_3COO)_3$ | 4.055 | 21.9 |
| 5 | 3.757 | 23.66 | 4.283 | 20.72 | 4.476 | 19.82 | | *3.935* | *22.58* |
| 6 | 3.346 | 26.62 | 4.048 | 21.94 | 4.267 | 20.8 | | 3.783 | 23.5 |
| 7 | 3.213 | 27.74 | 3.757 | 24.66 | 4.041 | 21.98 | | 3.356 | 26.54 |
| 8 | 3.177 | 28.06 | 3.356 | 26.54 | *3.619* | *24.58* | $Al(CH_3COO)_3$ | 3.225 | 27.64 |
| 9 | 3.081 | 28.96 | 3.229 | 27.6 | 3.348 | 26.6 | | 3.021 | 29.54 |
| 10 | 2.567 | 34.92 | 3.114 | 28.64 | *3.262* | *27.32* | $Al(CH_3COO)_3$ | *2.855* | *31.3* |
| 11 | 1.819 | 50.1 | 2.957 | 30.2 | *3.209* | *27.78* | | 2.563 | 35.36 |
| 12 | 1.694 | 54.08 | 2.771 | 32.28 | *3.151* | *28.3* | | 1.822 | 50.02 |
| 13 | 1.494 | 61.9 | 2.582 | 34.72 | *2.822* | *31.68* | NaCl | 1.693 | 54.14 |
| 14 | | | 2.027 | 44.68 | *2.539* | *35.32* | | 1.497 | 61.94 |
| 15 | | | 1.989 | 45.56 | *2.465* | *36.42* | $Al(CH_3COO)_3$ | | |
| 16 | | | 1.969 | 54.02 | *2.285* | *39.4* | $Al(CH_3COO)_3$ | | |
| 17 | | | 1.5 | 61.82 | 2.03 | 44.6 | | | |
| 18 | | | | | *1.996* | *45.4* | $Al(CH_3COO)_3$ | | |
| 19 | | | | | 1.817 | 50.16 | | | |
| 20 | | | | | *1.63* | *56.4* | | | |
| 21 | | | | | *1.541* | *59.96* | $Al(CH_3COO)_3$ | | |
| 22 | | | | | 1.499 | 61.86 | | | |
| 23 | | | | | *1.41* | *66.86* | $Al(CH_3COO)_3$ | | |
| 24 | | | | | *1.262* | *75.22* | $Al(CH_3COO)_3$ | | |

Aluminium acetate was produced during the leaching of black dross in acetic acid solution and it (aluminium acetate) precipitated out on the clay surfaces after drying the samples. These compounds were not bound on the clay surfaces but just physically attached. They were washed off during the desorption experiment.

The XRD patterns of the clays from "Blank" experiments shows negligible change in d spacing. No aluminium was present to bind on the clay surface. The very small changes are due to the release of trace amounts of aluminium.

The results from this study suggest that, once black dross is landfilled, aluminium ions and the other impurities will leach out under different leaching environments. Different chemical activities of aluminium may take place under the environmental conditions: (a) aluminium ions bound (ionic exchange) on clay surfaces, (b) aluminium ions form humic acid-metal-clay mineral complexes (c) precipitation of the aluminium compounds occur on clay surfaces and (d) dissolution of the precipitate in soil solution and possibly reach rivers and lakes becoming available for aquatic life. Plants, algae etc. are capable of uptaking the metals which are ionically exchanged on the clay surfaces and therefore cause damage to these living organisms. Whereas metals such as aluminium and iron forming the complexes with humic acid are not available to the living systems, because extraction of these metals is extremely difficult[85]. Soluble aluminium ions under acidic environments are toxic for the living organisms.

### 3.5.4. Leaching of washed black dross with leaching media

In section 3.5.1, leaching of as supplied or unwashed black dross was discussed. In this section washed black dross, which contains no salts, was leached with de-ionised water, humic acid, acid rain and acetic acid. It can be seen in Table-3.10a, that the percentage solubility of washed black dross is not as much as unwashed black dross (Table-3.2a). This arises because, in the washed black dross, most of the soluble aluminium and other elements (including the heavy metals) were leached out during the washing step, in order to recover salt content. Very little soluble aluminium and other impurities remained in the residue. Table-3.10b shows that very low levels of aluminium are leached out from the washed black dross.

## Table-3.10.a. Concentration of metals leached from washed black dross using different leaching media

| Metals | Distilled water | Humic acid | Acid rain | Acetic acid |
|---|---|---|---|---|
| | Concentration (ppm) | | | |
| Al | 1.7 | 1.5 | 1.3 | 22 |
| Cr | 0 | 0 | 0 | 0 |
| Cu | 0 | 0 | 0 | 1.03 |
| Fe | 0.13 | 0.18 | 0.2 | 0.17 |
| Mn | 0.01 | 0.01 | 0.01 | 0.01 |
| Ni | 0.13 | 0.13 | 0.28 | 0.22 |
| Ti | 0 | 0 | 0 | 0 |
| Zn | 0.1 | 0.13 | 6.0 | 2.0 |

## Table-3.10.b. Percentage solubility of washed black dross in different leaching media

| Media | Distilled water | Humic acid | Acid rain | Acetic acid |
|---|---|---|---|---|
| Weight(g) | 5.08 | 5.08 | 5.01 | 5.03 |
| Residue(g) | 4.75 | 4.82 | 4.73 | 4.62 |
| % Solubility | 6.53 | 5.1 | 5.63 | 8.3 |
| Total Vol(ml) | 100 | 100 | 100 | 100 |

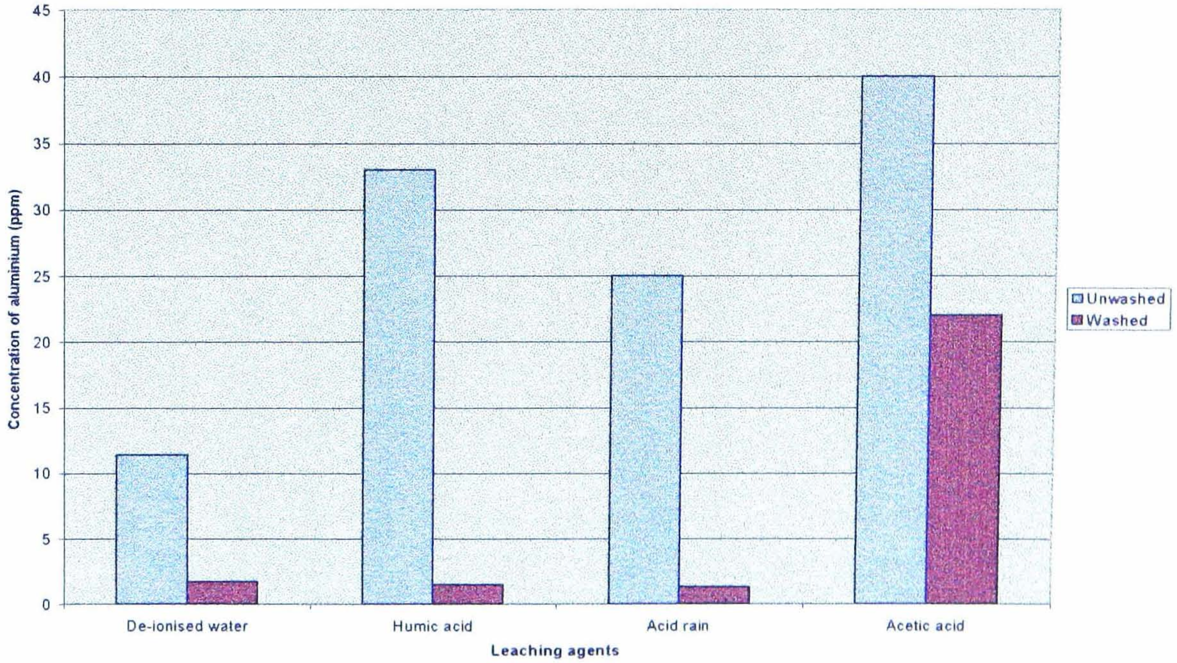

**Figure-3.9. The effect of washing on the leachability of aluminium in de-ionised water, humic acid, acid rain and acetic acid leaching agents under landfill conditions.**

The other impurities also have reduced by a large amount compared to unwashed black dross (Table-3.2.b). Figure-3.9 shows the effect of washing black dross on the leachability of aluminium under the leach media simulating landfill

conditions. The effect is extremely noticeable. In the previous sections, the problems of landfilling untreated black dross were discussed. This problem can be dramatically reduced by washing the black dross before landfilling.

Once the black dross is washed, only alumina and other insoluble metallic oxides remain in the dross, which are not going to leach out in the landfill and contaminate land and water.

There is another problem of landfilling untreated black dross. The unwashed black dross is extremely (50%) rich in sodium chloride and potassium chloride. Continous landfilling of the dross will cause accumulation of the salts (unless they are leached out), which will lead to soil salinity. High levels of soluble salts, can have a deleterious effect on animals and plant growth and yields[86]. Lands contaminated with high amounts of salts or any saline rich soils can be no longer productive[87]. However, if the salts leach out (during rainfall) from the soil, it will result in salinity of drainage water, that will cause pollution of waters, a major concern in saline environments. An example of sodium chloride rich soil found in Netherlands where land reclaimed from the sea has to be leached with fresh water to remove the sodium salt and then treated with gypsum (calcium sulphate). In this case the calcium replaces the sodium coat round the clay and allows the clay particles to stick together (clay particles are linked together specially by calcium are better for cultivation)[88].

Washing the black dross can solve two problems. It offers:

1) Economical solution – the recovery and recycling of salts and
2) Environmental solution – the removing of soluble aluminium and other impurities.

## 3.6. SUMMARY

Every year thousand of tonnes of aluminium black dross tailings are landfilled by aluminium industries. It is very important to monitor the fate of the dross in the natural environment. The research work described in this chapter has shown that measurable amount of all the elements from black dross leach out under water, acid rain, humic acid and acetic acid conditions. Research work also has shown that depending on the leaching media, aluminium remains bound on the clay surface or form precipitation. The dissolved elements may eventually reach the aquifer, and/or remain bound on the surface of clays. Continuous landfilling of black dross will lead to excessive accumulation of the elements in both the aquifer and on land, which may be fatal to aquatic and terrestrial life. Further research work has been carried out with washed black dross which is free from salt and other water soluble impurities. The results showed that washed black dross is not soluble in different leaching media. This result suggests that prior to landfilling, black dross needs to be washed to remove the salt and other soluble elements. Therefore, no contamination may occur in the environment.

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# CHAPTER FOUR

# PREPARATION OF ADDED VALUE CHEMICALS USING ALUMINIUM BLACK DROSS, AND ECONOMICAL ANALYSIS

## 4.1. INTRODUCTION

The aluminium waste product black dross tailing, which is generated from the secondary aluminium smelters, is currently landfilled due to the lack of viable methods to process it. The cost of black dross landfilling has been analysed in the Chapter 1, showing losses of millions of pounds every year worldwide. In Chapter 2 it has been calculated that about 50 wt% of this dross tailing contains a mixture of sodium chloride (35 wt%) and potassium chloride (15 wt%). The remaining 50 wt% is composed of metallic aluminium, aluminium nitride and alumina (36 wt%), silica (8 wt%) and varied amounts of other impurities (6 wt%). By landfilling the black dross tailing, there is also loss of valuable aluminium. In Chapter 3 the environmental impact of landfilling black dross has been investigated; this showed that under landfilling conditions, measurable amounts of aluminium leaches out, contaminating the aquifer and/or interacting on the clay surface making it available for plant uptake. Within a longer period of time heavy accumulation of aluminium, including the salts and other impurities, both in aquifer and soil surface will lead to serious toxic effects to all living things.

In this chapter the research is directed to finding opportunities for reusing the black dross tailings. The research work has been carried out considering both environmental and economical aspects. A number of commercially viable aluminium compounds have been produced from the black dross tailings. An economical analysis has been undertaken to confirm the importance of using the black dross tailings rather than the traditional raw materials.

## 4.2. ALUMINIUM COMPOUNDS

Archaeologists gathered evidence that chemical and medicinal usage of aluminous materials (alum) goes back over 4000 years. Alum was found from the Egyptian hieroglyphic signs and also from pieces of leather of tombs, where it was used a as dye. Greeks and Romans also continued the uses of alum for dyeing and further purposes such as leather tanning and ceramic making[10].

Today aluminium compounds find their way into almost every sphere of human activity and several are manufactured on a vast industrial scale. The most important aluminium compounds apart from aluminium silicate-based ceramics and clay products are sodium aluminate, aluminium hydroxide, aluminium oxide which are raw materials in the manufacture of aluminium. Other industrial important aluminium compounds are aluminium sulphate, aluminium nitrate, aluminium chloride, and aluminium carboxylates. Below, the commercial manufacture and uses of some aluminium compounds have been described which will be produced from black dross in this project.

## 4.2.1. Sodium Aluminate

### *4.2.1.1. Production*

The commercial product of sodium aluminate is available as either a liquid containing about 40% by weight of sodium aluminate or as a solid product, which is essentially anhydrous[1].

Sodium aluminate $NaAlO_2$ (also common used formulae: $Na_2O.Al_2O_3$, $Na_2Al_2O_4$) is the circulating liquid medium of the Bayer process for the production of alumina from bauxite. In order to obtain commercially colourless sodium aluminate solution or white sodium aluminate powder, a low-iron aluminium trihydroxide (<0.01% $Fe_2O_3$) is used, which is dissolved in sodium hydroxide solution at atmospheric boiling point. Commercial grades of sodium aluminate generally contain some water of hydration and an excess of soda. Liquid sodium aluminate requires the higher $Na_2O:Al_2O_3$ ratio (up to 1.5:1) for good stability and storage properties[1].

### *4.2.1.2. Uses*

The use of sodium aluminate as a commercial product began in the 1920s. It has a large number of uses as a coagulating agent. It is also used in conjunction with other coagulating agents such as aluminium sulphate, ferric salts, clays and polyelectrolytes[11]. Its use has been growing in the treatment of water, in the paper industry for improving sizing and filler retention. When added to titania paint pigment, the non-chalking behaviour of outdoor paints is improved. In the process of acrylic and polyester synthetic fibres, the use of sodium aluminate enhances dyeing, antipiling, and antistatic properties of the fibres. Sodium aluminate is often used in the preparation of alumina based catalysts. The reaction of sodium aluminate with silica or silicates can produce porous crystalline alumino-silicates which are used as adsorbents and catalyst supports[1].

### 4.2.2. Aluminium hydroxide

Aluminium forms a wide range of hydroxides. Some of these hydroxides are in crystalline form and well understood, others are amorphous form, not so well understood. The crystalline form of the aluminium hydroxides are divided into the trihydroxides $Al(OH)_3$, and the oxide hydroxides AlO(OH). The trihydroxides exist in three forms[1]: gibbsite ($\gamma$-aluminium trihydroxide), bayerite ($\alpha$- aluminium trihydroxide) and nordstrandite. The oxide hydroxides[1] exist as boehmite ($\gamma$-aluminium oxide hydroxide) or diaspore ($\alpha$ -aluminium oxide hydroxide). All these are found in nature, apart from bayerite, which is prepared free from alkali. Gibbsite always contains some alkali[3] (0.2-0.3% $Na_2O$).

#### *4.2.2.1. Production[1,4]*

With the exception of small tonnages of boehmite and bayerite, the aluminium hydroxide normally produced is gibbsite, the $\gamma$-aluminium trihydroxide. The most important commercial route for the production of gibbsite is the Bayer process starting from bauxite. In the Bayer process sodium aluminate is produced by dissolution of bauxite in concentrated caustic soda solution at elevated temperature and under pressure. The solution is settled and filtered to separate the impurities and then cooled to between 50$^0$C and 70$^0$C. The clear solution is then mixed with large quantities of recycled seed particles of gibbsite (up to four times by weight of the amount dissolved), whereupon a large part of the dissolved hydroxide precipitates out as aluminium hydroxide ($Al(OH)_3$):

$$Al(OH)_4^- + H_2O \longrightarrow Al(OH)_3 + OH^-$$

Types of aluminium hydroxides produced depend on the concentration of sodium aluminate solution, the temperature and the quantity of seed added. The initial product is usually a gel, which however will transform to crystalline trihydroxide on ageing if the hydroxyl ion concentration is subsequently kept sufficiently high. Bayerite is made by rapid precipitation from alkaline solution in the cold[4]:

$$2[Al(OH)_4]^-aq + CO_2(g) \longrightarrow 2Al(OH)_3 + CO_3^{2-}(aq) + H_2O$$

Nordstrandite is obtained from gelatinous hydroxide by ageing it in the presence of a chelating agent such as EDTA[4].

Crystalline boehmite is matured from gibbsite at pH >12, 80°C. Diaspore can be obtained from any aluminium hydroxide or oxide by steaming at >140 atm, 275-425°C and seeding with diaspore[3].

#### *4.2.2.2. Uses*

Apart from its further processing to metallic aluminium, aluminium hydroxide is mainly used in the manufacture of aluminium compounds (alumina, aluminium fluoride, synthetic cryolite, sodium aluminate, aluminium sulphate) and active aluminas (used as an adsorption agent for water and gases, and as catalysts). In a finely divided form it is utilised as a flame retardant and/or filler in carpets, plastics, foam rubber, paper, paint, glass, wall elements, pharmaceuticals and toothpaste.

### 4.2.3. Aluminium Oxide (Alumina)[1,4]

There are many forms of aluminium oxide ($\alpha$, $\chi$, $\beta$, $\eta$, $\delta$, $\kappa$, $\theta$, $\gamma$, $\rho$, $\iota$) but $\alpha$-aluminium oxide, also known as corundum is the only thermodynamically stable form. $\beta$-alumina, derived from Bayer process during alumina preparation, was first thought to be another form of alumina, but subsequent investigation showed presence of sodium oxide and hence it was called $\beta$-alumina. The idealised chemical formula is $Na_2O.11Al_2O_3$. The presence of sodium is known to be essential for $\beta$-alumina molecules stability[4]. The other forms of aluminas are frequently termed transition aluminas and arise during the thermal decomposition of aluminium trihydroxides and oxide-hydroxides under varying conditions.

#### *4.2.3.1. Production*

Industrial grades of aluminium oxide are often divided into: smelter, acitivated, catalytic, calcined, low-soda, reactive, tabular, fused and high purity. These differ in their particle size, morphology, $\alpha$-alumina content, and impurities, specially the soda level. With the exception of very small quantities they are produced by calcination of Bayer derived gibsite. The aluminium hydroxide is calcined to aluminium oxide ($\alpha$-

$Al_2O_3$) in a rotary kiln or fluidised bed calciners[5] at 1200°C to 1300°C. Figure-4.1 shows the calcination process of transformation of α-alumina from gibbsite.

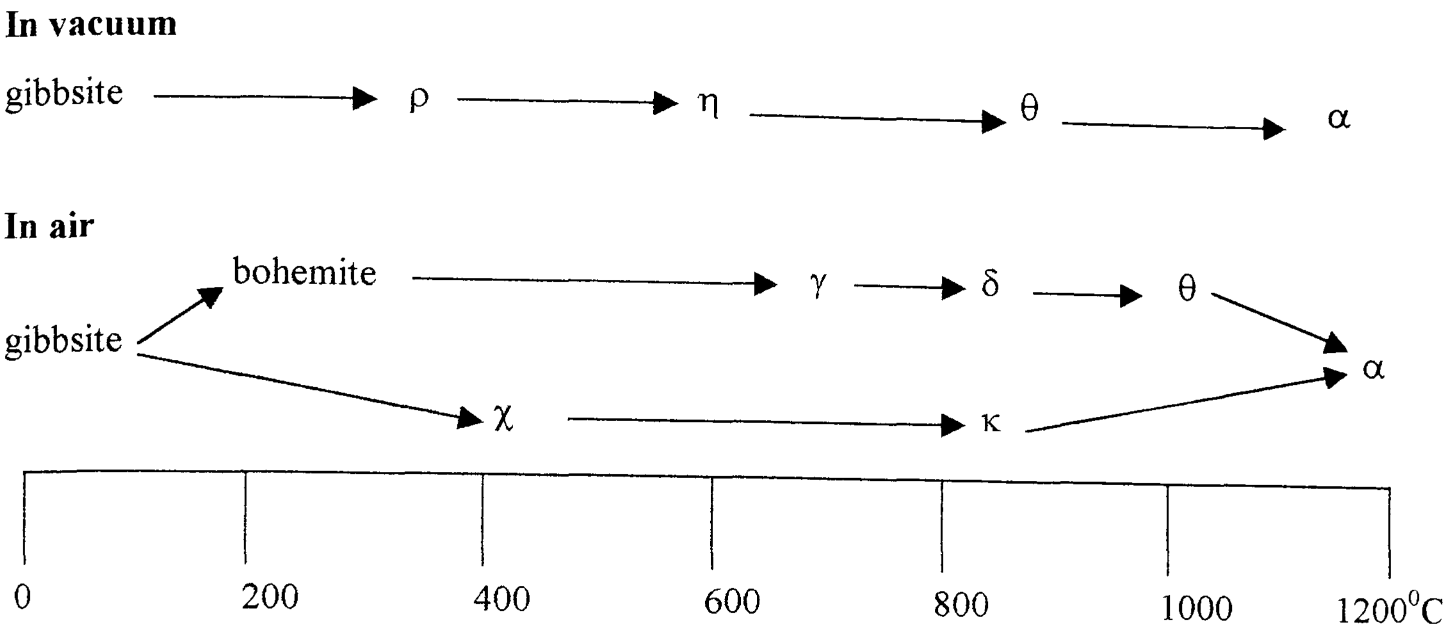


**Figure-4.1. Thermal transformation sequence for gibbsite to alumina[1].**

Activated aluminas are obtained by controlled thermal dehydration of aluminium hydroxides. The dehydration product is a porous, high-surface-area metal that has found extensive application[6]. Appropriate forming technology has been developed to yield products of the desired shape and mechanical strength suitable for industrial applications. β-alumina is produced[4] by heating $Na_2CO_3$ or $NaNO_3$ or NaOH with any modification of $Al_2O_3$ or its hydrates to ~1500°C in a Pt vessel to avoid loss of $Na_2O$.

### 4.2.3.2. Uses

The most α-aluminium oxide (corundum) is utilised for aluminium manufacture. The rest (<10%) is utilised for the manufacture of refractory, grinding, ceramic, glass and enamel products and electrocorundum. It is also used as a filler in polymers (polesters, epoxy resins). β-alumina has high ionic conductivity and is consequently used in electrochemical cells. The compound has been used in sodium/sulphur battery system in vehicles which provides higher energy than the lead-acid battery. Active aluminas (obtained when aluminium hydroxide is heated at temperatures below that necessary to form α-alumina) are used as adsorbent agents for water and gases, as catalyst or catalysts carriers and as filter materials[1].

### 4.2.4. Aluminium Sulphate

#### *4.2.4.1. Production*[1]

Aluminium sulphate, $Al_2(SO_4)_3$, is a white powder, which is currently manufactured by dissolution of pure valuable aluminium sources such as aluminium hydroxide, alumina or clay in hot (100-120$^0$C) concentrated sulphuric acid (30-60%):

$$2Al(OH)_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 6H_2O$$

$$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2SO_4 + 3H_2O$$

Traditionally the formula $Al_2(SO4)_3.18H_2O$ has been written for commercial dry aluminium sulphate but the material is generally amorphous. Aluminium sulphate is sold as either 'commercial' purity (with an iron level up to 0.5%) or 'iron free'. The world-wide market of 'commercial' grade aluminium sulphate is over 2 million tonnes per annum whilst the 'iron free' grade is about a quarter of this total.

#### *4.2.4.2. Uses*

Aluminium sulphate has, in recent years, been in increasing demand, principally for use as a flocculant in water clarification for industrial and sewage treatment plants. Because of its excellent coagulating characteristics, aluminium sulphate is used to remove suspended solids, reduce colour and reduce the presence of micro-organisms in water[1].

In paper making the principal use of aluminium sulphate is to promote the combination of resin and cellulose fibres to improve both the strength of the paper and its resistance to water and ink. In addition the aluminium sulphate is used to neutralise the acidity of the wood pulp, soften hard water, and to treat the resulting effluent.

Other uses of aluminium sulphate include water-proofing textiles, dyeing, tanning, photography, for the production of colloidal aluminium hydroxide for gastric disorders, as a fire retardant in cellulosic fibre loft insulation, slug killing products, and in fire extinguishers[7].

## 4.2.5. Aluminium Nitrate

### *4.2.5.1. Production*

Aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) is a stable white crystalline material, has a melting point of $73^0C$, and is soluble in cold water, alcohols and acetone. In general aluminium nitrate nonahydrate is prepared by dissolving aluminium trihydroxide in dilute nitric acid and crystallising from the resulting aqueous solution. Other methods which have been patented involve treating bauxite or calcined clay with nitric acid. Liquor purification generally requires removal of dissolved iron from the leach liquor before crystallisation takes place. This is generally achieved by solvent extraction[1].

### *4.2.5.2. Uses*

Aluminium nitrate nonahydrate is primarily used as a salting agent in the extraction of actinides. It is also used as source of alumina in the preparation of insulating papers, in transformer core laminates and in cathode-ray tube heating elements.

## 4.2.6. Aluminium Chloride

### *4.2.6.1. Production*

Aluminium chloride ($AlCl_3$) is almost exclusively in its anhydrous form. In the pure form, anhydrous aluminium chloride exists as a white solid but commercial grades vary in colour and are most often pale yellow. It reacts violently with water and most alcohols. The compound is currently manufactured predominantly by the chlorination of liquid aluminium in ceramic-lined reaction vessels at $600^0C$ to $750^0C$. Some recent plants prefer reductive chlorination (carbochlorination) of aluminium oxide or clay due to a much lower energy requirement.

Hydrated aluminium chloride ($AlCl_3.6H_2O$) is a deliquescent powder which is soluble in both alcohol and water. It is commercially available as a 28% by weight solution and as a crystalline solid. It is usually manufactured by dissolving aluminium hydroxide in concentrated hydrochloric acid at atmospheric boiling[1]. When the acid is used up, aluminium chloride hexahydrate is crystallized from the solution by first cooling at $0^0C$ and then sparging with HCl gas. Any impurities remain in the solution.

#### *4.2.6.2. Uses*

Anhydrous aluminium chloride is mainly used as a catalyst in organic chemistry, for an example, in Friedel-Craft reactions. It is also used to make hydrated aluminium chloride.

Aluminium chloride hexahydrate has a large number of applications in industry. It is used in pharmaceuticals, water treatment, cosmetics, as a flocculant and for impregnating textiles.

### 4.2.7. Aluminium Carboxylates

#### *4.2.7.1. Production*

The aluminium salts of carboxylic acids are known as aluminium carboxylates, such as, aluminium acetate, aluminium formate etc. They are produced by dissolving aluminium hydroxide in the appropriate carboxylic acids, where the hydroxyl groups are replaced by carboxylate anions. They are also produced by the direct reaction of the acid with aluminium chloride in an organic solvent[1].

#### *4.2.7.2. Uses*

About twenty of the aluminium carboxylates are of industrial importance and have commercial applications. They are used as:

- finishing agents for the water-proofing of cloth
- mordants in the dyeing of textiles
- pharmaceutical preparations
- in cosmetics.

## 4.3. EXPERIMENTAL PROCEDURE

Preparation of added value chemicals was carried out from washed black dross and unwashed black dross. The prepared compounds are compared with analytical grade compounds or identified from the "Powder Diffraction File"[8]. To test the reproducibility, all experiments were repeated three times, and the results are presented as an average.

### 4.3.1. Preparation of Sodium Aluminate

10g of washed black dross and 10g of unwashed black dross samples were introduced into separate 500ml cap. Pyrex flange reaction vessels containing 100ml of 2M sodium hydroxide solution respectively. The reactions were carried out by heating the reaction mixtures at 100$^0$C for 4 hours with continuous stirring on a hot plate and under reflux conditions. At the end of each experiment, the reaction mixture was allowed to cool and the solid – liquid fractions were separated by vacuum filtration using sinter glass funnel, porosity-2. The filtrate was heated on a hot plate to obtain crystals of sodium aluminate. The cooled products were weighed in order to determine the yields. Depending on the product's physical appearance (dry or wet), they were characterised by X-ray diffraction spectroscopy. XRD analysis of analytical grade sodium aluminate was also undertaken in order to compare the sodium aluminate obtained from the black dross.

### 4.3.2. Preparation of Aluminium hydroxide

Once good quality sodium aluminate was produced, preparation of aluminium hydroxide was undertaken. Following the above experimental procedure (Section-4.3.1) a large amount of sodium aluminate solution (not powder) was prepared as a stock solution and the amount of sodium aluminate content in the solution was measured and kept in cold room (-10$^0$C). In a glass beaker of 250ml capacity, 50ml portion of sodium aluminate solution was placed and the pH of the solution was measured using a pH meter. While the solution was stirred very slowly (using a magnetic stirrer, at 50 rpm) at ambient temperature, a total of 50ml portion of 30% $H_2O_2$ solution was added very slowly to the solution. During the addition of $H_2O_2$, a white precipitate was observed in the solution. The final pH of the solution was recorded. The resulting white precipitate was filtered by vacuum filtration using sinter glass filter porosity-4. The precipitated aluminium hydroxide was washed thoroughly with cold de-ionised water in order to remove the alkalinity (checked by litmus paper) and then dried in an oven at 120$^0$C for 12 hours. XRD analysis of the recovered aluminium hydroxide was made.

In order to determine the highest yield of the product, different volumes of 30% $H_2O_2$ (75, 100 and 150ml) was added to the same volume of sodium aluminate solution (50ml) separately. The pH was monitored at the beginning and at the end of each reaction.

### 4.3.3. Preparation of Aluminium Oxide (Alumina)

Aluminium hydroxide recovered from washed black dross sample was calcined in a static atmosphere of air at various temperatures using a muffle furnace. The chosen temperatures were: $600^0$C, $800^0$C, $900^0$C and $1200^0$C. At each temperature, samples were kept for 4 hours. The compounds obtained were cooled then crushed into fine powder, using a pestle and mortar, and analysed by XRD and XRF.

### 4.3.4. Preparation of Aluminium Sulphate

Aluminium sulphate was prepared from black dross using two different raw materials:

#### *4.3.4.1. Dissolution of dross in sulphuric acid*

10g of washed black dross and 10g unwashed black dross samples were introduced into separate 500ml Pyrex flange reaction vessels containing 100ml of 3M sulphuric acid solution. The reactions were carried out by heating the mixtures at $100^0$C for 4 hours with continuous stirring on a hot plate under reflux. At the end of each experiment, the reaction mixture was allowed to cool and the solid – liquid fractions were separated by vacuum filtration using sinter glass funnel, porosity-2. The filtrate was heated on a hot plate to obtain crystals of aluminium sulphate. The cooled products were weighed in order to determine the yields. Depending on the product's physical appearance (dry or wet), they were characterised by X-ray diffraction spectroscopy.

#### *4.3.4.2. Dissolution of aluminium hydroxide (prepared from washed black dross) in sulphuric acid.*

5g of aluminium hydroxide was placed in a 250ml glass beaker. 100ml of 2M sulphuric acid was introduced in the glass beaker. The dissolved clear solution was continuously stirred and heated (at $100^0$C) on a hot plate until white crystalline aluminium sulphate appeared. The crystals were dried completely and cooled and weighed. XRD and XRF analyses were carried out to determine the compound.

### 4.3.5. Preparation of Aluminium Nitrate

Aluminium nitrate was prepared from black dross using the two different raw materials as described in section 4.3.4. Nitric acid was used in this method instead of sulphuric acid.

### 4.3.6. Preparation of Aluminium Chloride

Aluminium chloride was prepared from black dross using the two different raw materials as described in section 4.3.4. Hydrochloric acid was used in this method instead of sulphuric acid.

### 4.3.7. Preparation of Aluminium Formate and Aluminium Acetate

In two separate 250ml capacity glass beakers, 5g of aluminium hydroxide was placed. 100ml of formic acid and 100ml of glacial acetic acid were introduced separately to each glass beaker. The solutions were continuously stirred and heated (at $100^0$C) on a hot plate until white crystalline aluminium compounds appeared. The filtered crystals were dried completely and cooled and weighed. XRD and XRF analyses were carried out to determine the compounds.

### 4.3.8. Preparation of Sodium Aluminate from Bulk Content of Washed Black Dross

In section 4.3.1, sodium aluminate was prepared successfully using a small amount of black dross (10g). In this section, a bulk amount of washed black dross was used and the appropriate conditions were developed to prepare a good quality of sodium aluminate. Economic calculations will be performed later, based on this result.

A Pyrex reaction vessel of 3 litre capacity was used in which aluminium was leached from washed black dross samples. The reaction vessel was charged with 250g of washed black dross and 500ml of 0.5M sodium hydroxide solution (prepared by dissolving standard grade sodium hydroxide pellets in de-ionised water). Aluminium leaching was carried out by heating the reaction mixture at ~$100^0$C for four hours with continuous stirring (magnetic stirrer) on a hot plate. At the end of the experiment, the reaction mixture was allowed to cool and the solid – liquid fractions were separated by filtration using a sinter glass filter (porosity-2). The residue were dried in an oven over night and weighed. The filtrates were heated on a hot plate to obtain crystals of sodium aluminate.

The above experiment was carried out with 1M, 2M, 3M, 4M and 5M sodium hydroxide solution.

### 4.3.9. Analysis of black dross residue after leaching with sodium hydroxide

After leaching washed black dross sample with sodium hydroxide, the residue was subjected to analysis for the content of remaining elements and therefore, its possible uses.

Black dross residue was analysed using X-ray fluorescence and X-ray diffractometry to identify the elements present. 2.5g dross residue was placed in three separate 500ml capacity Pyrex reaction vessels. Two vessels were filled with 100ml de-ionised water and the third vessel with 100ml of 2M hydrochloric acid. The leaching was carried out at room temperature for the first de-ionised water and at $100^0$C for the second de-ionised water; and 2M hydrochloric acid at $100^0$C for three hours. At the end of the leaching period, the solutions were filtered using filter paper (Whatman 542, hardened ashless, 150mm). The residues were dried in an oven overnight and weighed and analysed using X-ray fluorescence and X-ray diffractometry. The filtrates were analysed using atomic absorption spectrometry.

## 4.4. RESULTS AND DISCUSSIONS

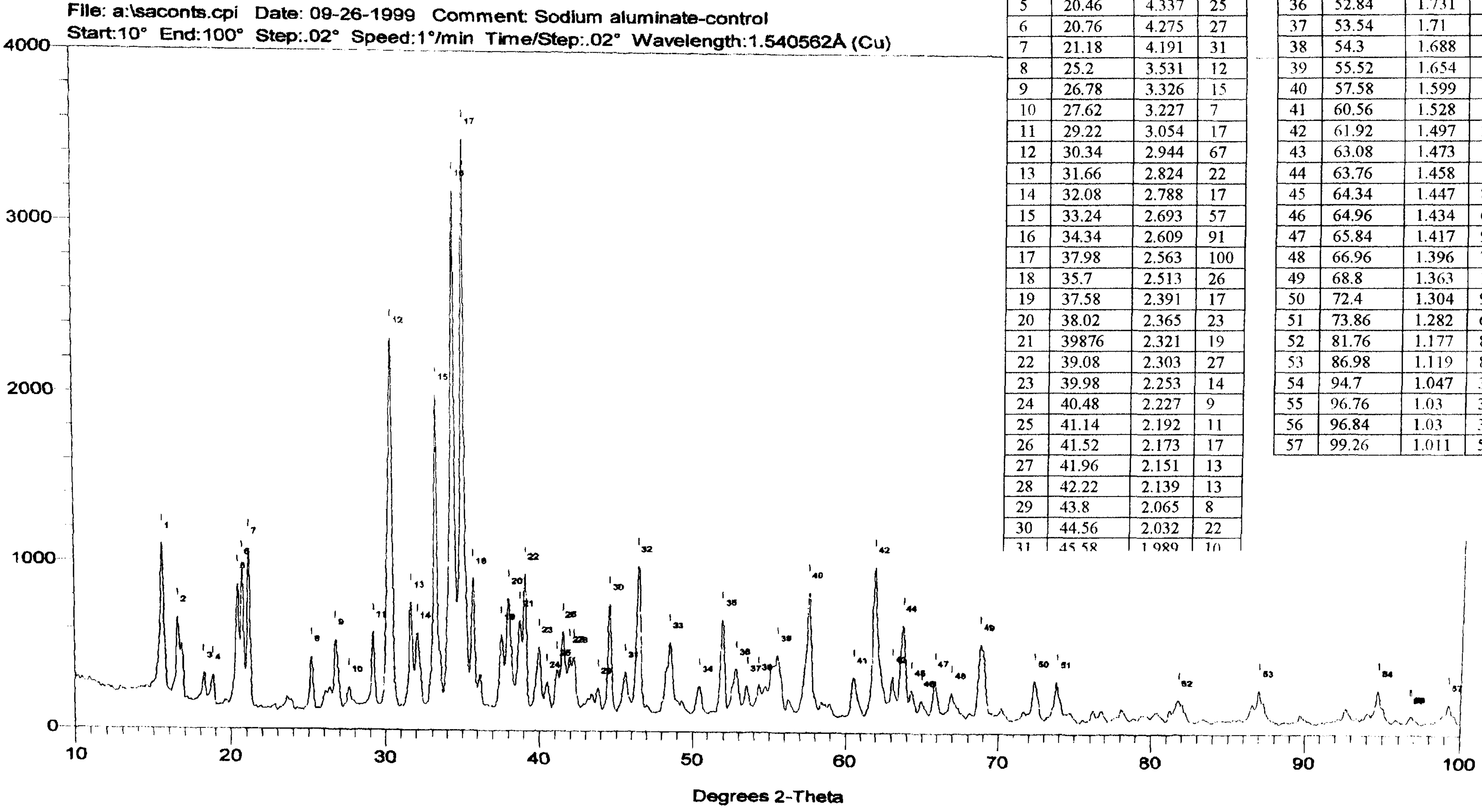
### 4.4.1. Preparation of Sodium aluminate

In this experiment washed black dross (BD-W) and unwashed black dross (BD-U) samples were leached with 2M sodium hydroxide at $100^0$C. Table-4.1 summarises the product characteristics of the sodium aluminate obtained from the different types of drosses.

**Table-4.1. Sodium aluminate (SA) produced from aluminium dross.**

| Dross | BD-W | BD-U |
|---|---|---|
| Wt of black dross(g) | 10 | 10 |
| Wt of residue(g) | 8 | 4 |
| Wt of SA(g) | 19 | 17 |
| Colour of SA | white | Grey |
| Texture of SA | dry sandy | very moist |

It can be seen that the sodium aluminate produced from washed black dross has a white colour and sandy texture. Figure-4.2 and Figure-4.3 are the XRD spectra of analytical grade and sodium aluminate prepared from washed black dross respectively. Comparing these two spectra it can be confirmed that the product obtained from washed black dross is a pure sodium aluminate.

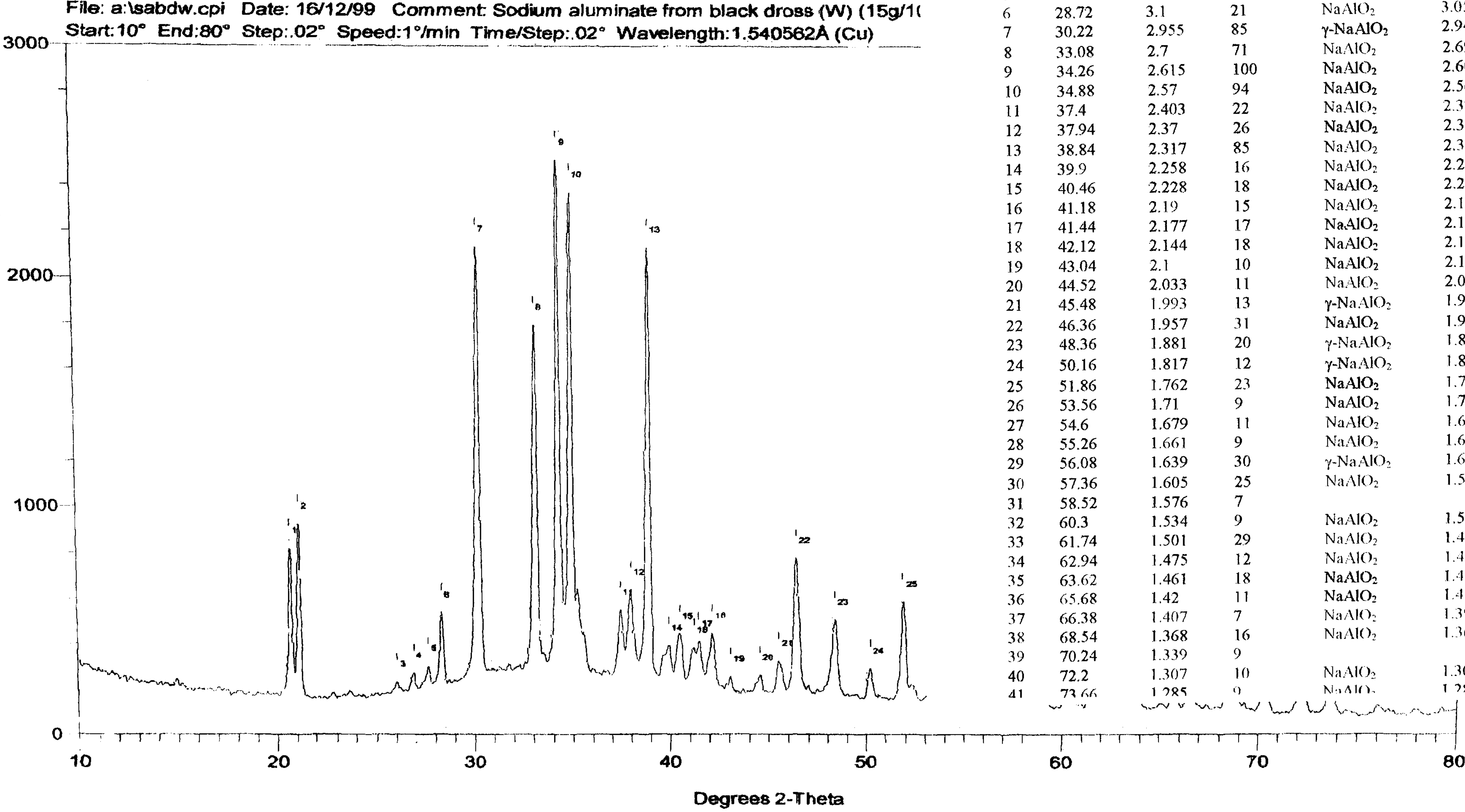


. Sodium aluminate, NaAlO$_2$
– Analytical grade

| No | Angle($^{0}$) | D Space | Rel I |
|---|---|---|---|
| 1 | 15.6 | 5.676 | 31 |
| 2 | 16.6 | 5.336 | 19 |
| 3 | 18.3 | 4.844 | 10 |
| 4 | 18.82 | 4.711 | 9 |
| 5 | 20.46 | 4.337 | 25 |
| 6 | 20.76 | 4.275 | 27 |
| 7 | 21.18 | 4.191 | 31 |
| 8 | 25.2 | 3.531 | 12 |
| 9 | 26.78 | 3.326 | 15 |
| 10 | 27.62 | 3.227 | 7 |
| 11 | 29.22 | 3.054 | 17 |
| 12 | 30.34 | 2.944 | 67 |
| 13 | 31.66 | 2.824 | 22 |
| 14 | 32.08 | 2.788 | 17 |
| 15 | 33.24 | 2.693 | 57 |
| 16 | 34.34 | 2.609 | 91 |
| 17 | 37.98 | 2.563 | 100 |
| 18 | 35.7 | 2.513 | 26 |
| 19 | 37.58 | 2.391 | 17 |
| 20 | 38.02 | 2.365 | 23 |
| 21 | 39876 | 2.321 | 19 |
| 22 | 39.08 | 2.303 | 27 |
| 23 | 39.98 | 2.253 | 14 |
| 24 | 40.48 | 2.227 | 9 |
| 25 | 41.14 | 2.192 | 11 |
| 26 | 41.52 | 2.173 | 17 |
| 27 | 41.96 | 2.151 | 13 |
| 28 | 42.22 | 2.139 | 13 |
| 29 | 43.8 | 2.065 | 8 |
| 30 | 44.56 | 2.032 | 22 |
| 31 | 45.58 | 1.989 | 10 |

| No | Angle($^{0}$) | D Space | Rel I |
|---|---|---|---|
| 32 | 46.46 | 1.953 | 28 |
| 33 | 48.54 | 1.874 | 15 |
| 34 | 50.46 | 1.807 | 8 |
| 35 | 51.96 | 1.758 | 19 |
| 36 | 52.84 | 1.731 | 11 |
| 37 | 53.54 | 1.71 | 8 |
| 38 | 54.3 | 1.688 | 8 |
| 39 | 55.52 | 1.654 | 13 |
| 40 | 57.58 | 1.599 | 24 |
| 41 | 60.56 | 1.528 | 10 |
| 42 | 61.92 | 1.497 | 28 |
| 43 | 63.08 | 1.473 | 10 |
| 44 | 63.76 | 1.458 | 18 |
| 45 | 64.34 | 1.447 | 8 |
| 46 | 64.96 | 1.434 | 6 |
| 47 | 65.84 | 1.417 | 9 |
| 48 | 66.96 | 1.396 | 7 |
| 49 | 68.8 | 1.363 | 15 |
| 50 | 72.4 | 1.304 | 9 |
| 51 | 73.86 | 1.282 | 6 |
| 52 | 81.76 | 1.177 | 8 |
| 53 | 86.98 | 1.119 | 8 |
| 54 | 94.7 | 1.047 | 3 |
| 55 | 96.76 | 1.03 | 3 |
| 56 | 96.84 | 1.03 | 3 |
| 57 | 99.26 | 1.011 | 5 |

**Figure-4.2. Analytical grade sodium aluminate.**



**Sample: Sodium aluminate from black dross (washed)**

| No | Angle(°) | D space | Relative intensity | Peak identity | ControlD space |
|---|---|---|---|---|---|
| 1 | 20.68 | 4.275 | 33 | $NaAlO_2$ | 4.275 |
| 2 | 21.12 | 4.203 | 37 | $NaAlO_2$ | 4.191 |
| 3 | 26.06 | 3.416 | 9 | | |
| 4 | 26.88 | 3.314 | 11 | $NaAlO_2$ | 3.326 |
| 5 | 27.62 | 3.227 | 12 | $NaAlO_2$ | 3.227 |
| 6 | 28.72 | 3.1 | 21 | $NaAlO_2$ | 3.054 |
| 7 | 30.22 | 2.955 | 85 | $\gamma$-$NaAlO_2$ | 2.94 |
| 8 | 33.08 | 2.7 | 71 | $NaAlO_2$ | 2.693 |
| 9 | 34.26 | 2.615 | 100 | $NaAlO_2$ | 2.609 |
| 10 | 34.88 | 2.57 | 94 | $NaAlO_2$ | 2.563 |
| 11 | 37.4 | 2.403 | 22 | $NaAlO_2$ | 2.391 |
| 12 | 37.94 | 2.37 | 26 | $NaAlO_2$ | 2.37 |
| 13 | 38.84 | 2.317 | 85 | $NaAlO_2$ | 2.303 |
| 14 | 39.9 | 2.258 | 16 | $NaAlO_2$ | 2.253 |
| 15 | 40.46 | 2.228 | 18 | $NaAlO_2$ | 2.228 |
| 16 | 41.18 | 2.19 | 15 | $NaAlO_2$ | 2.192 |
| 17 | 41.44 | 2.177 | 17 | $NaAlO_2$ | 2.173 |
| 18 | 42.12 | 2.144 | 18 | $NaAlO_2$ | 2.14 |
| 19 | 43.04 | 2.1 | 10 | $NaAlO_2$ | 2.1 |
| 20 | 44.52 | 2.033 | 11 | $NaAlO_2$ | 2.032 |
| 21 | 45.48 | 1.993 | 13 | $\gamma$-$NaAlO_2$ | 1.994 |
| 22 | 46.36 | 1.957 | 31 | $NaAlO_2$ | 1.953 |
| 23 | 48.36 | 1.881 | 20 | $\gamma$-$NaAlO_2$ | 1.881 |
| 24 | 50.16 | 1.817 | 12 | $\gamma$-$NaAlO_2$ | 1.816 |
| 25 | 51.86 | 1.762 | 23 | $NaAlO_2$ | 1.762 |
| 26 | 53.56 | 1.71 | 9 | $NaAlO_2$ | 1.71 |
| 27 | 54.6 | 1.679 | 11 | $NaAlO_2$ | 1.672 |
| 28 | 55.26 | 1.661 | 9 | $NaAlO_2$ | 1.654 |
| 29 | 56.08 | 1.639 | 30 | $\gamma$-$NaAlO_2$ | 1.636 |
| 30 | 57.36 | 1.605 | 25 | $NaAlO_2$ | 1.599 |
| 31 | 58.52 | 1.576 | 7 | | |
| 32 | 60.3 | 1.534 | 9 | $NaAlO_2$ | 1.528 |
| 33 | 61.74 | 1.501 | 29 | $NaAlO_2$ | 1.497 |
| 34 | 62.94 | 1.475 | 12 | $NaAlO_2$ | 1.473 |
| 35 | 63.62 | 1.461 | 18 | $NaAlO_2$ | 1.46 |
| 36 | 65.68 | 1.42 | 11 | $NaAlO_2$ | 1.417 |
| 37 | 66.38 | 1.407 | 7 | $NaAlO_2$ | 1.396 |
| 38 | 68.54 | 1.368 | 16 | $NaAlO_2$ | 1.363 |
| 39 | 70.24 | 1.339 | 9 | | |
| 40 | 72.2 | 1.307 | 10 | $NaAlO_2$ | 1.304 |
| 41 | 73.66 | 1.285 | 9 | $NaAlO_2$ | 1.282 |

Figure-4.3. Sodium aluminate produced from washed black dross.

Figure-4.4 is the XRF spectrum of the sodium aluminate produced from washed black dross. It can be seen that no impurities other than zinc are present in the product. Dissolving the sodium aluminate in de-ionised water and analysing by AAS, showed the zinc content was only 0.02%.

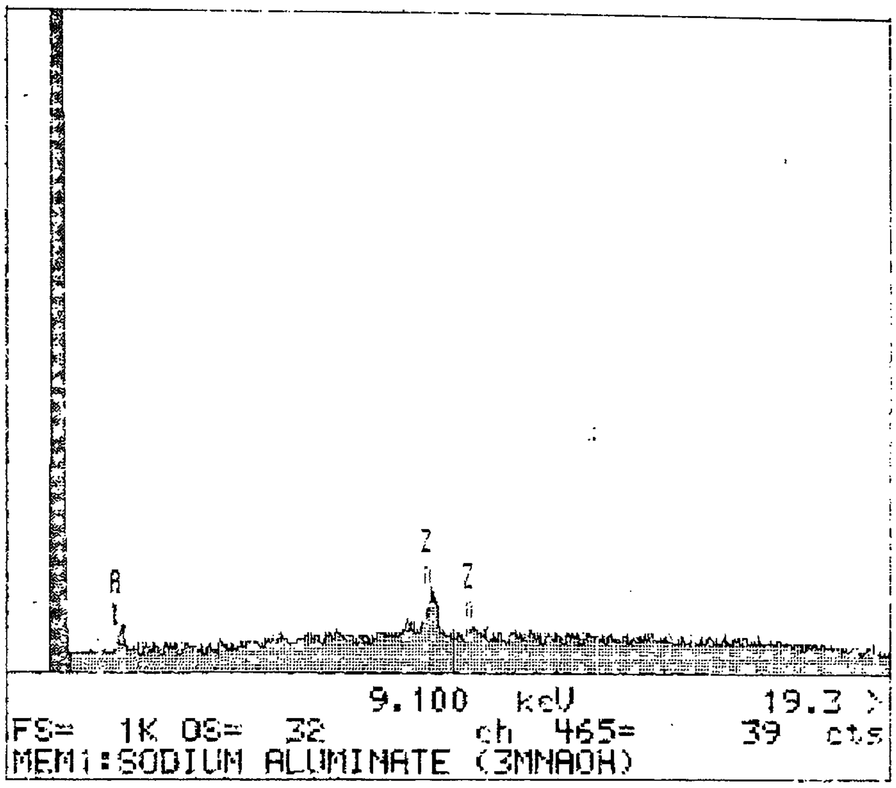
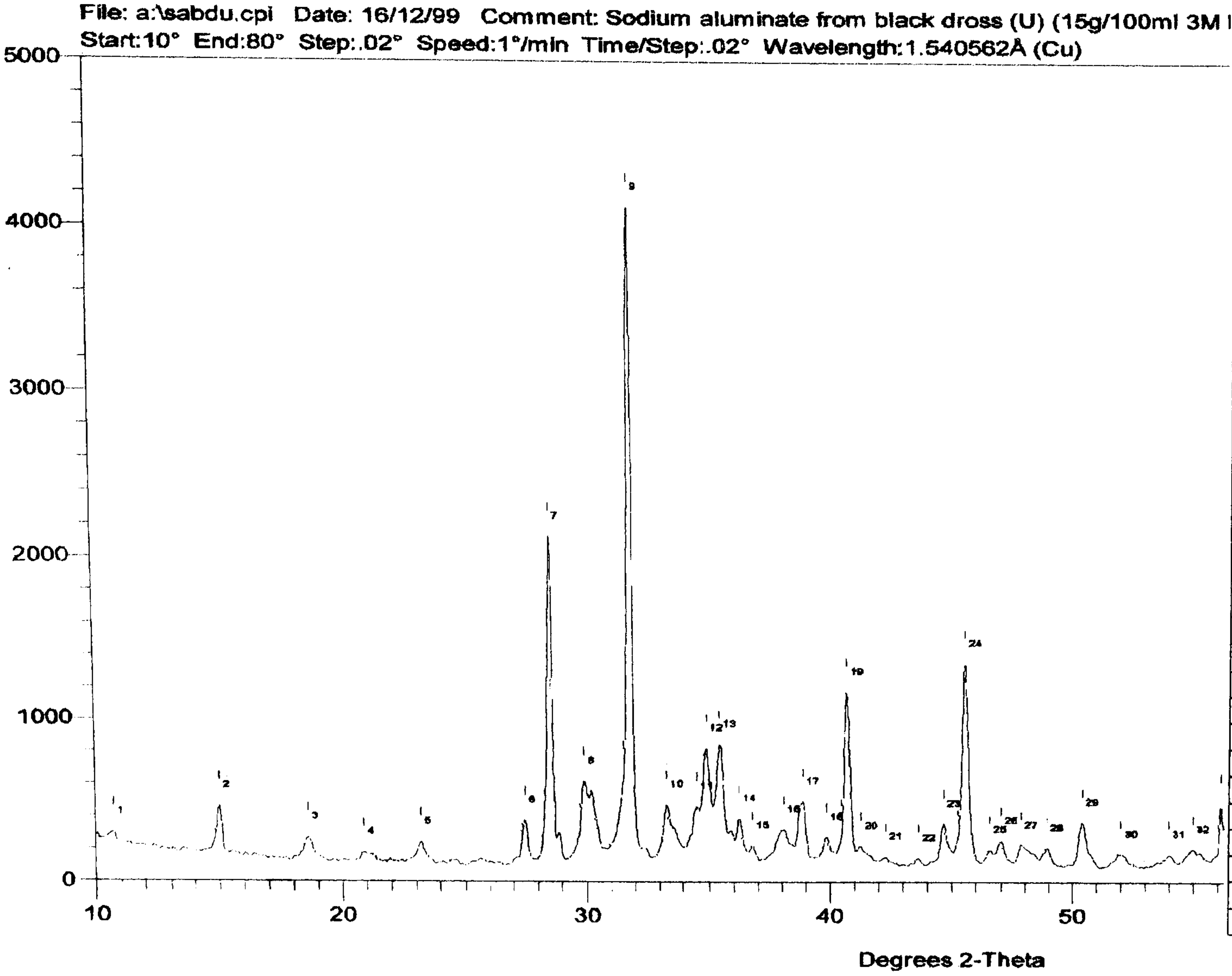


**Figure-4.4. XRF spectrum of sodium aluminate produced from washed black dross.**

Sodium aluminate produced from unwashed black dross is grey in colour and extremely hydrated even after keeping the compound in an oven at 120$^0$C for a week. The XRD spectrum (Figure-4.5) shows the compound to be and a mixture of salts (sodium chloride and potassium chloride) and sodium aluminate.

From Table-4.1, it can be seen that the undissolved residue of the unwashed black dross sample is only 4g whereas, the washed black dross sample residue was 8g. This is because unwashed black dross contains 50% salt which dissolved in the sodium hydroxide solution during the sodium aluminate preparation and contaminated the product. Comparing the three XRD spectra (Figure-4.2, 4.3 and 4.5) it can be confirmed that pure sodium aluminate can be produced from black dross only after washing the dross and removing the salt content.



**Sample:Sodium aluminate from black dross (unwashed)**

| No | Angle(°) | D space | Relative intensity | Peak identity | Control D space |
|---|---|---|---|---|---|
| 1 | 10.72 | 8.246 | 7 | | |
| 2 | 15. | 5.901 | 11 | | |
| 3 | 18.6 | 4.766 | 7 | | |
| 4 | 20.9 | 4.27 | 4 | γ-$NaAlO_2$ | 4.275 |
| 5 | 23.2 | 3.831 | 6 | | |
| 6 | 27.46 | 3.245 | 9 | | |
| 7 | 28.5 | 3.129 | 52 | | |
| 8 | 29.92 | 2.984 | 15 | γ-$NaAlO_2$ | 2.94 |
| 9 | 31.8 | 2.812 | 100 | NaCl | 2.82 |
| 10 | 33.28 | 2.69 | 12 | $NaAlO_2$ | 2.67 |
| 11 | 34.5 | 2.598 | 11 | $NaAlO_2$ | 2.59 |
| 12 | 34.88 | 2.57 | 20 | | |
| 13 | 35.44 | 2.531 | 21 | | |
| 14 | 36.24 | 2.477 | 10 | | |
| 15 | 36.78 | 2.442 | 5 | | |
| 16 | 38.08 | 2.361 | 8 | $NaAlO_2$ | 2.365 |
| 17 | 38.88 | 2.314 | 12 | | |
| 18 | 39.86 | 2.26 | 7 | $NaAlO_2$ | 2.26 |
| 19 | 40.72 | 2.214 | 29 | γ-$NaAlO_2$ | 2.21 |
| 20 | 41.28 | 2.185 | 5 | | |
| 21 | 42.3 | 2.135 | 4 | $NaAlO_2$ | 2.139 |
| 22 | 43.66 | 2.071 | 4 | | |
| 23 | 44.66 | 2.027 | 9 | | |
| 24 | 45.54 | 1.99 | 33 | NaCl | 1.994 |
| 25 | 46.56 | 1.949 | 5 | $NaAlO_2$ | 1.94 |
| 26 | 47.04 | 1.93 | 6 | | |
| 27 | 47.86 | 1.899 | 6 | KCl | 1.8972 |
| 28 | 48.92 | 1.86 | 5 | $NaAlO_2$ | 1.874 |
| 29 | 50.4 | 1.809 | 9 | $NaAlO_2$ | 1.807 |
| 30 | 52. | 1.757 | 4 | $NaAlO_2$ | 1.758 |
| 31 | 53.98 | 1.697 | 4 | | |
| 32 | 54.98 | 1.669 | 5 | | |
| 33 | 56.14 | 1.637 | 11 | γ-$NaAlO_2$ | 1.636 |
| 34 | 56.54 | 1.626 | 11 | NaCl | 1.628 |
| 35 | 58.88 | 1.567 | 5 | | |
| 36 | 62.02 | 1.495 | 4 | $NaAlO_2$ | 1.49 |
| 37 | 63.12 | 1.472 | 4 | $NaAlO_2$ | 1.47 |
| 38 | 65. | 1.434 | 4 | $NaAlO_2$ | 1.434 |
| 39 | 66.64 | 1.402 | 8 | KCl | 1.4071 |
| 40 | 70.32 | 1.338 | 6 | | |
| 41 | 73.98 | 1.28 | 5 | $NaAlO_2$ | 1.282 |
| 42 | 75.36 | 1.26 | 10 | NaCl | 1.261 |
| 43 | 78.1 | 1.223 | 4 | | |

Figure-4.5. Sodium aluminate produced from unwashed black dross

### 4.4.2. Preparation of Aluminium Hydroxide

Table-4.2 presents the results obtained after sodium aluminate solution was reacted with different volumes of hydrogen peroxide to produce aluminium hydroxide. The sodium aluminate solution was produced from washed black dross and the amount of sodium aluminate in the solution is 22%.

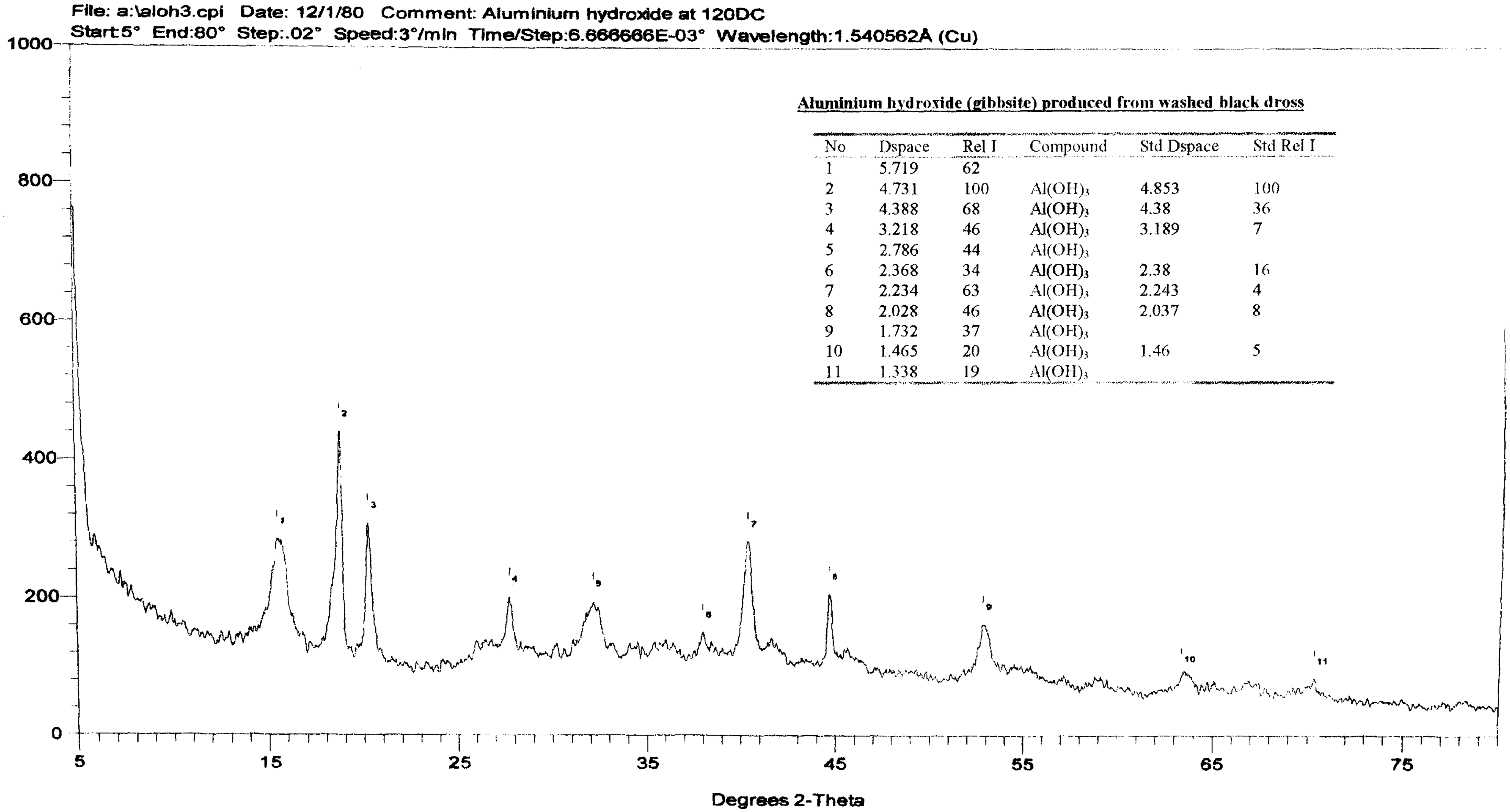
**Table-4.2. Production of aluminium hydroxide from sodium aluminate solution obtained from black dross**

| Sodium aluminate (ml) | 50 | 50 | 50 | 50 | 50 |
|---|---|---|---|---|---|
| $H_2O_2$ (ml) | 25 | 50 | 75 | 100 | 150 |
| Initial pH | 14.0 | 14.0 | 14.0 | 14.0 | 14.0 |
| Final pH | 13.0 | 11.5 | 10.34 | 9.96 | 9.5 |
| Wt of precipitate(g) | 11.1 | 16.1 | 16.19 | 17.2 | 17.62 |

It can be seen from Table 4.2 that as the amount of hydrogen peroxide is increased, the production of aluminium hydroxide does not increase proportionally. Using higher volume of hydrogen peroxide does not significantly increase weight of aluminium hydroxide produced. Figure-4.6 shows the XRD spectrum of the crystalline aluminium hydroxide. The XRD data in Figure-4.6 shows that the type of aluminium hydroxide is gibbsite [$\gamma$-Al($OH_3$)].

$$NaAlO_2 + H_2O_2 + 2H^+ \longrightarrow \gamma\text{-}Al(OH)_3 + NaOH$$

The XRF analysis (Figure-4.7) confirms that the presence of zinc in the aluminium hydroxide sample. Dissolving the aluminium hydroxide in 2M hydrochloric acid and analysing by AAS, revealed sodium and zinc concentration of 4% and 0.02% accordingly.



**Aluminium hydroxide (gibbsite) produced from washed black dross**

| No | Dspace | Rel I | Compound | Std Dspace | Std Rel I |
|---|---|---|---|---|---|
| 1 | 5.719 | 62 | | | |
| 2 | 4.731 | 100 | $Al(OH)_3$ | 4.853 | 100 |
| 3 | 4.388 | 68 | $Al(OH)_3$ | 4.38 | 36 |
| 4 | 3.218 | 46 | $Al(OH)_3$ | 3.189 | 7 |
| 5 | 2.786 | 44 | $Al(OH)_3$ | | |
| 6 | 2.368 | 34 | $Al(OH)_3$ | 2.38 | 16 |
| 7 | 2.234 | 63 | $Al(OH)_3$ | 2.243 | 4 |
| 8 | 2.028 | 46 | $Al(OH)_3$ | 2.037 | 8 |
| 9 | 1.732 | 37 | $Al(OH)_3$ | | |
| 10 | 1.465 | 20 | $Al(OH)_3$ | 1.46 | 5 |
| 11 | 1.338 | 19 | $Al(OH)_3$ | | |

**Figure-4.6. XRD spectrum of aluminium hydroxide (gibbsite) prepared from washed black dross (100ml $H_2O_2$ used).**

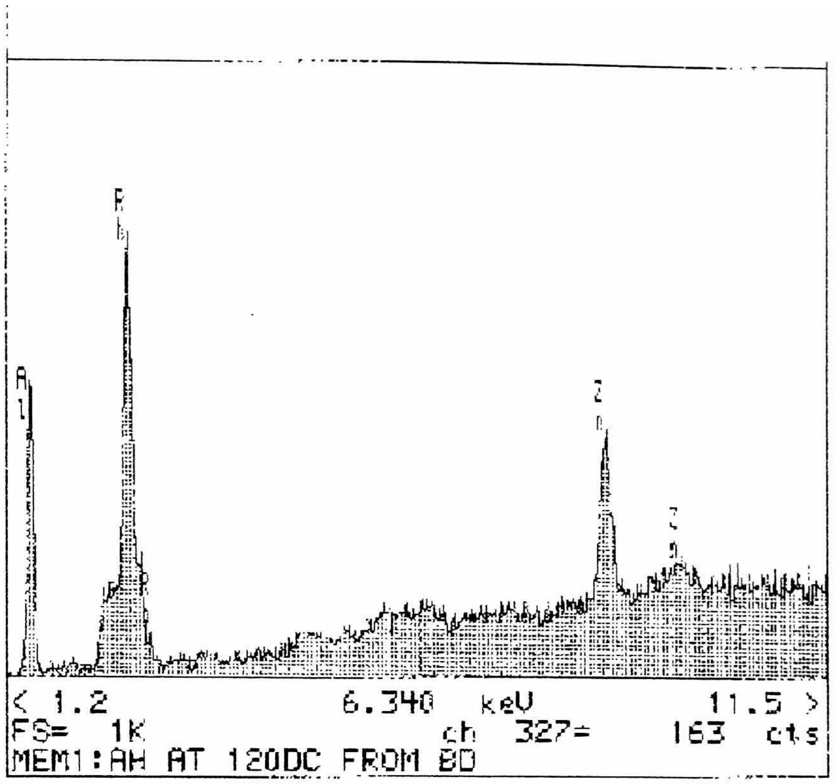
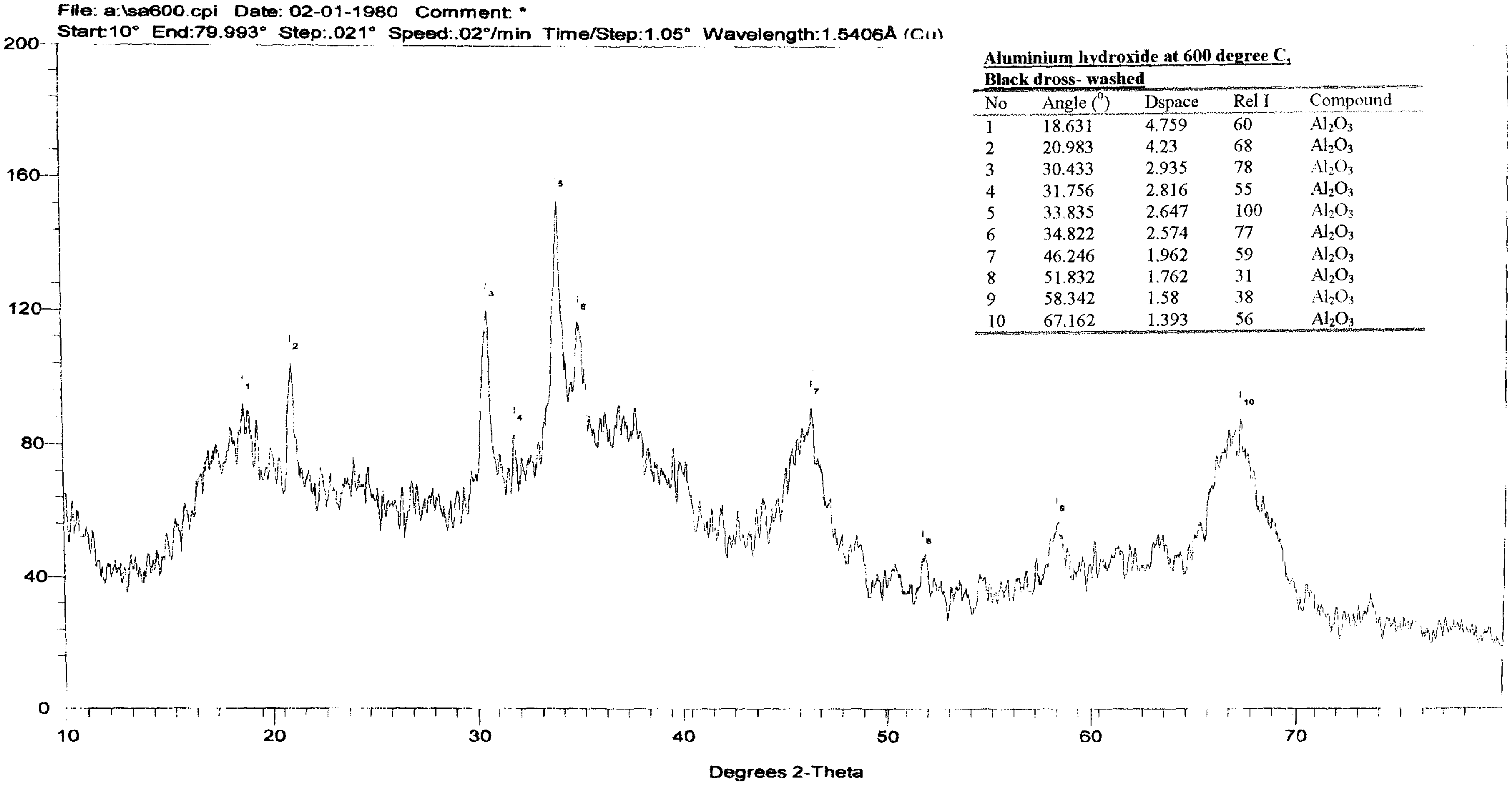


**Figure-4.7. XRD spectrum of aluminium hydroxide prepared from washed black dross.**

### 4.4.3. Preparation of Aluminium oxide (Alumina)

Once the aluminium hydroxide was achieved, the production of aluminium oxide or alumina was undertaken. Aluminium hydroxide produced from washed black dross, was calcined for four hours in a static atmosphere of air at different temperatures (600, 800, 900 and 1200$^{0}$C) using a temperature controlled muffle furnace. After calcination, the samples were cooled down to room temperature and crushed into fine powder using a pestle and mortar before being analysed by XRD. Figure-4.8-4.11 show the XRD spectra of the calcined samples. Using the "Powder Diffraction File" (USA, 1991) cards[8] all the samples have been analysed and the presence of compounds identified. It can be seen that gibbsite $\gamma$-Al(OH$_3$) produced by the $H_2O_2$ method was converted into $Al_2O_3$ (no name has given of this type of alumina)[8] at 600$^{0}$C, and into $\kappa$-$Al_2O_3$ at 800$^{0}$C. $\beta$-alumina along within some $\iota$-alumina dominated the XRD trace of the product achieved at 900$^{0}$C. A more crystalline product similar to the 900$^{0}$C was achieved at 1200$^{0}$C. Thus, the phase transition sequence of gibbsite can be summarised as:

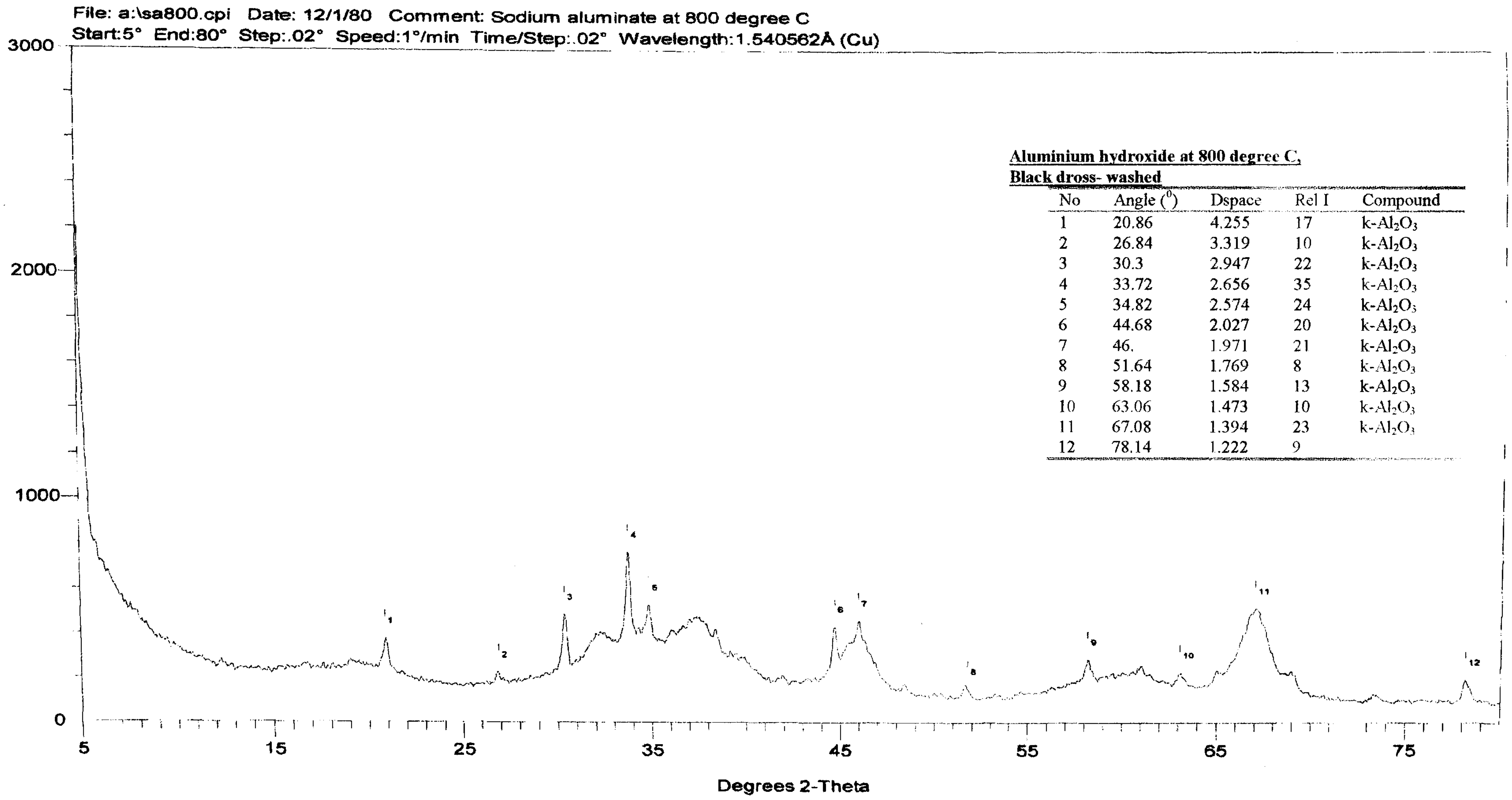
$$\text{Gibbsite} \xrightarrow{600^{0}\text{C}} Al_2O_3 \xrightarrow{800^{0}\text{C}} \kappa\text{-}Al_2O_3 \xrightarrow{900^{0}\text{C}} \beta\text{-}Al_2O_3/\iota\text{-}Al_2O_3 \xrightarrow{1200^{0}\text{C}} \beta\text{-}Al_2O_3/\iota\text{-}Al_2O_3$$



**Aluminium hydroxide at 600 degree C,**
**Black dross- washed**

| No | Angle (°) | Dspace | Rel I | Compound |
|---|---|---|---|---|
| 1 | 18.631 | 4.759 | 60 | $Al_2O_3$ |
| 2 | 20.983 | 4.23 | 68 | $Al_2O_3$ |
| 3 | 30.433 | 2.935 | 78 | $Al_2O_3$ |
| 4 | 31.756 | 2.816 | 55 | $Al_2O_3$ |
| 5 | 33.835 | 2.647 | 100 | $Al_2O_3$ |
| 6 | 34.822 | 2.574 | 77 | $Al_2O_3$ |
| 7 | 46.246 | 1.962 | 59 | $Al_2O_3$ |
| 8 | 51.832 | 1.762 | 31 | $Al_2O_3$ |
| 9 | 58.342 | 1.58 | 38 | $Al_2O_3$ |
| 10 | 67.162 | 1.393 | 56 | $Al_2O_3$ |

**Figure-4.8. XRD spectrum of aluminium hydroxide at $600^0$C.**



**Aluminium hydroxide at 800 degree C,**
**Black dross- washed**

| No | Angle ($^0$) | Dspace | Rel I | Compound |
|---|---|---|---|---|
| 1 | 20.86 | 4.255 | 17 | k-$Al_2O_3$ |
| 2 | 26.84 | 3.319 | 10 | k-$Al_2O_3$ |
| 3 | 30.3 | 2.947 | 22 | k-$Al_2O_3$ |
| 4 | 33.72 | 2.656 | 35 | k-$Al_2O_3$ |
| 5 | 34.82 | 2.574 | 24 | k-$Al_2O_3$ |
| 6 | 44.68 | 2.027 | 20 | k-$Al_2O_3$ |
| 7 | 46. | 1.971 | 21 | k-$Al_2O_3$ |
| 8 | 51.64 | 1.769 | 8 | k-$Al_2O_3$ |
| 9 | 58.18 | 1.584 | 13 | k-$Al_2O_3$ |
| 10 | 63.06 | 1.473 | 10 | k-$Al_2O_3$ |
| 11 | 67.08 | 1.394 | 23 | k-$Al_2O_3$ |
| 12 | 78.14 | 1.222 | 9 | |

Figure-4.9. XRD spectrum of aluminium hydroxide at 800$^0$C.

**Aluminium hydroxide at 900 degree C,**
**Black dross- washe**

| No | Angle ($^0$) | Dspace | Rel I | Compound |
|---|---|---|---|---|
| 1 | 7.84 | 11.267 | 24 | ß-$Al_2O_3$ |
| 2 | 15.74 | 5.626 | 14 | ß-$Al_2O_3$ |
| 3 | 20.92 | 4.243 | 40 | ß-$Al_2O_3$ |
| 4 | 23.7 | 3.751 | 9 | ß-$Al_2O_3$ |
| 5 | 26.9 | 3.312 | 14 | ι- $Al_2O_3$ |
| 6 | 30.38 | 2.94 | 64 | ι- $Al_2O_3$ |
| 7 | 32. | 2.795 | 14 | ι- $Al_2O_3$ |
| 8 | 33.76 | 2.653 | 100 | ß-$Al_2O_3$ |
| 9 | 34.86 | 2.572 | 42 | ι- $Al_2O_3$ |
| 10 | 35.86 | 2.502 | 15 | ß-$Al_2O_3$ |
| 11 | 37.3 | 2.409 | 14 | ß-$Al_2O_3$ |
| 12 | 40.08 | 2.248 | 11 | ß-$Al_2O_3$ |
| 13 | 41.94 | 2.152 | 9 | ι- $Al_2O_3$ |
| 14 | 44.66 | 2.027 | 10 | ß-$Al_2O_3$ |
| 15 | 45.42 | 1.995 | 16 | ι- $Al_2O_3$ |
| 16 | 46.02 | 1.971 | 28 | ß-$Al_2O_3$ |
| 17 | 48.44 | 1.878 | 12 | ß-$Al_2O_3$ |
| 18 | 51.74 | 1.765 | 14 | ß-$Al_2O_3$ |
| 19 | 53.3 | 1.717 | 5 | ι- $Al_2O_3$ |
| 20 | 54.7 | 1.677 | 6 | ß-$Al_2O_3$ |
| 21 | 58.24 | 1.583 | 25 | ß-$Al_2O_3$ |
| 22 | 61.04 | 1.517 | 13 | ι- $Al_2O_3$ |
| 23 | 63.14 | 1.471 | 15 | ß-$Al_2O_3$ |
| 24 | 65.84 | 1.417 | 12 | ß-$Al_2O_3$ |
| 25 | 66.9 | 1.397 | 18 | |
| 26 | 69. | 1.36 | 16 | ß-$Al_2O_3$ |
| 27 | 73.48 | 1.288 | 9 | ι- $Al_2O_3$ |

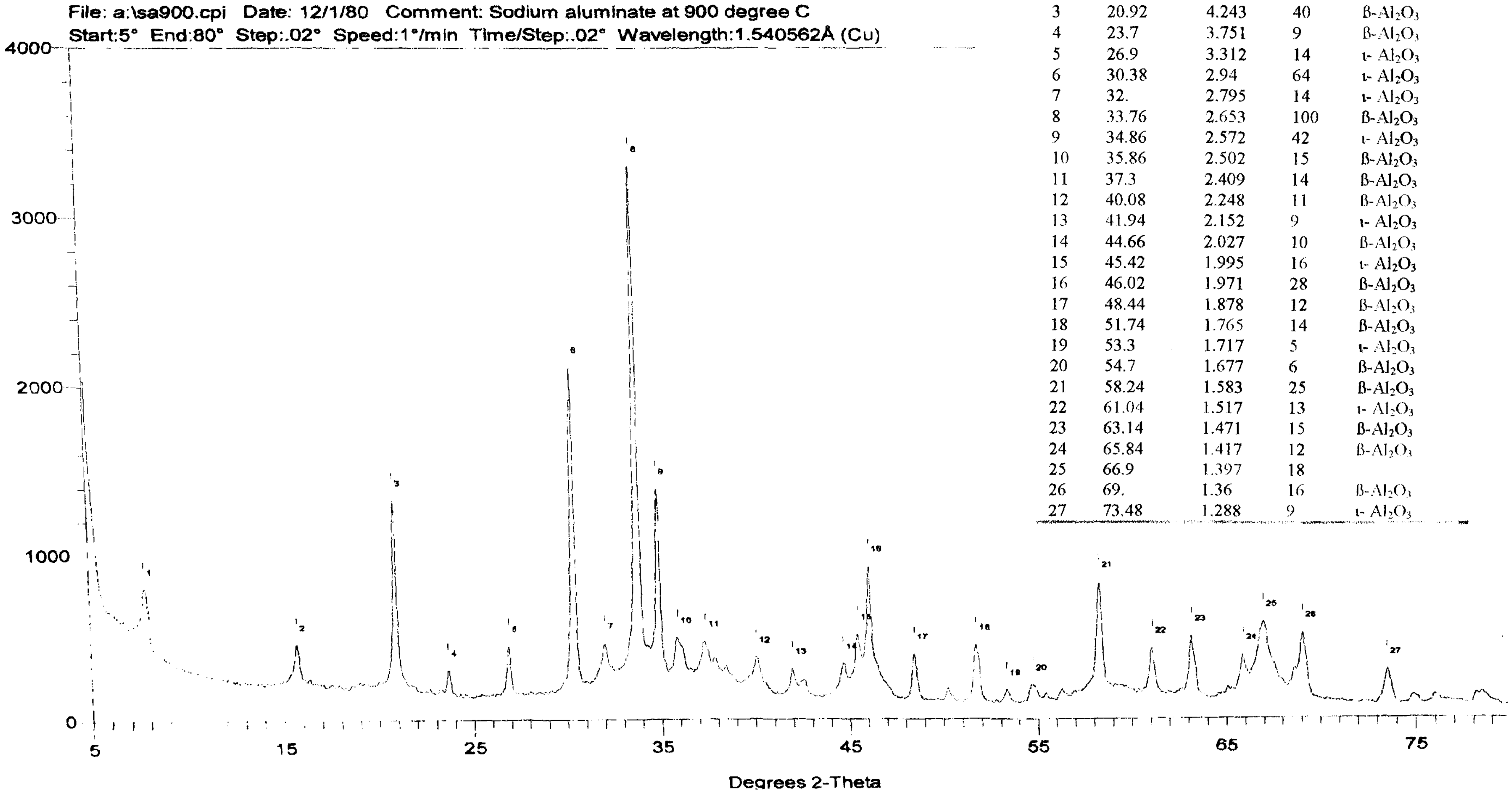


Figure-4.10. XRD spectrum of aluminium hydroxide at 900$^0$C.

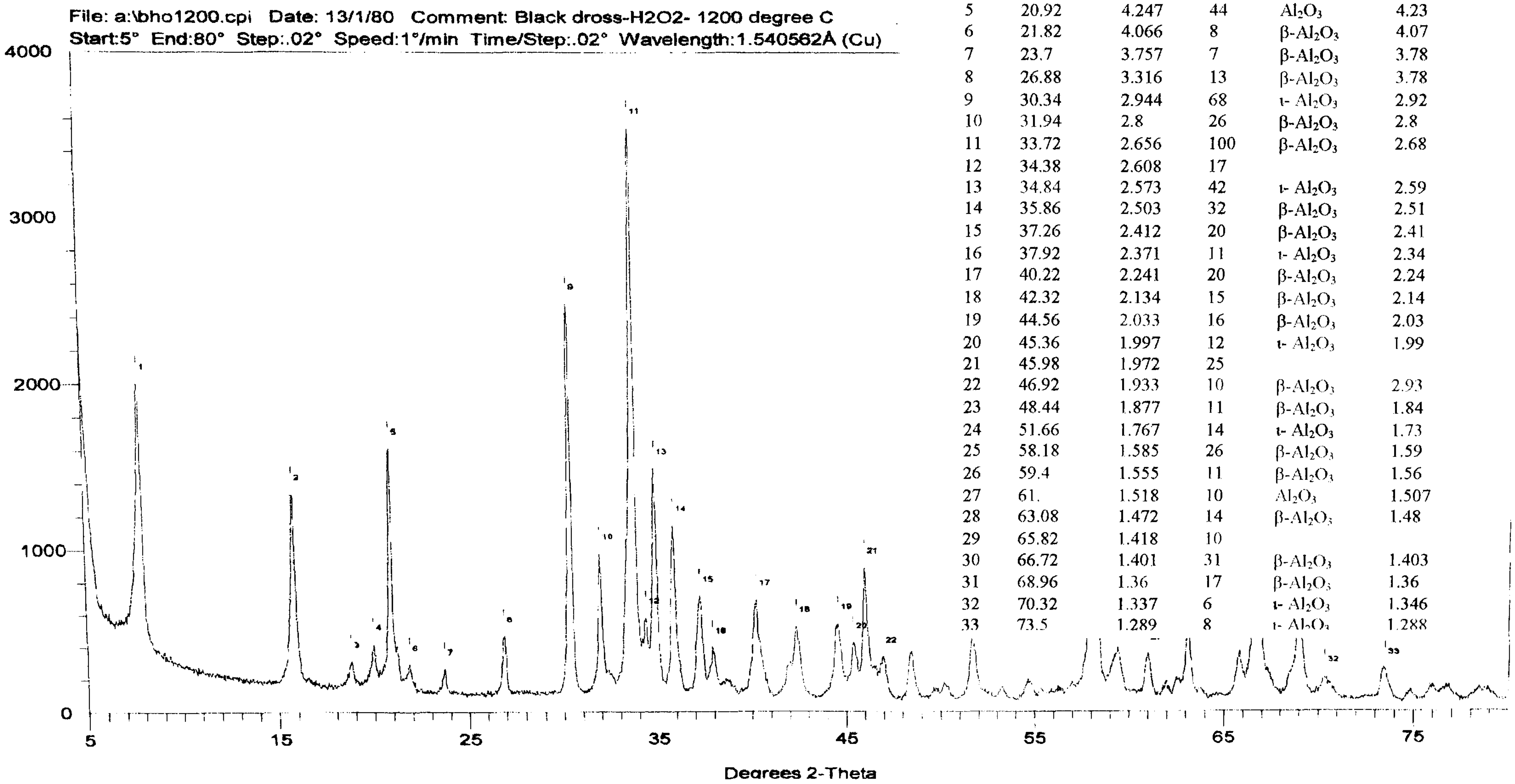


Figure-4.11. XRD spectrum of aluminium hydroxide at 1200$^0$C.

**Aluminium hydroxide at 1200 degree C: Black dross- washed**

| No | Angle ($^0$) | Dspace | Rel I | Compound | Std Dspace |
|---|---|---|---|---|---|
| 1 | 7.9 | 11.21 | 56 | $\beta$-$Al_2O_3$ | 11.9 |
| 2 | 15.82 | 5.597 | 38 | $\beta$-$Al_2O_3$ | 5.7 |
| 3 | 18.78 | 4.731 | 9 | | |
| 4 | 19.94 | 4.449 | 12 | $\beta$-$Al_2O_3$ | 4.45 |
| 5 | 20.92 | 4.247 | 44 | $Al_2O_3$ | 4.23 |
| 6 | 21.82 | 4.066 | 8 | $\beta$-$Al_2O_3$ | 4.07 |
| 7 | 23.7 | 3.757 | 7 | $\beta$-$Al_2O_3$ | 3.78 |
| 8 | 26.88 | 3.316 | 13 | $\beta$-$Al_2O_3$ | 3.78 |
| 9 | 30.34 | 2.944 | 68 | $\iota$- $Al_2O_3$ | 2.92 |
| 10 | 31.94 | 2.8 | 26 | $\beta$-$Al_2O_3$ | 2.8 |
| 11 | 33.72 | 2.656 | 100 | $\beta$-$Al_2O_3$ | 2.68 |
| 12 | 34.38 | 2.608 | 17 | | |
| 13 | 34.84 | 2.573 | 42 | $\iota$- $Al_2O_3$ | 2.59 |
| 14 | 35.86 | 2.503 | 32 | $\beta$-$Al_2O_3$ | 2.51 |
| 15 | 37.26 | 2.412 | 20 | $\beta$-$Al_2O_3$ | 2.41 |
| 16 | 37.92 | 2.371 | 11 | $\iota$- $Al_2O_3$ | 2.34 |
| 17 | 40.22 | 2.241 | 20 | $\beta$-$Al_2O_3$ | 2.24 |
| 18 | 42.32 | 2.134 | 15 | $\beta$-$Al_2O_3$ | 2.14 |
| 19 | 44.56 | 2.033 | 16 | $\beta$-$Al_2O_3$ | 2.03 |
| 20 | 45.36 | 1.997 | 12 | $\iota$- $Al_2O_3$ | 1.99 |
| 21 | 45.98 | 1.972 | 25 | | |
| 22 | 46.92 | 1.933 | 10 | $\beta$-$Al_2O_3$ | 2.93 |
| 23 | 48.44 | 1.877 | 11 | $\beta$-$Al_2O_3$ | 1.84 |
| 24 | 51.66 | 1.767 | 14 | $\iota$- $Al_2O_3$ | 1.73 |
| 25 | 58.18 | 1.585 | 26 | $\beta$-$Al_2O_3$ | 1.59 |
| 26 | 59.4 | 1.555 | 11 | $\beta$-$Al_2O_3$ | 1.56 |
| 27 | 61. | 1.518 | 10 | $Al_2O_3$ | 1.507 |
| 28 | 63.08 | 1.472 | 14 | $\beta$-$Al_2O_3$ | 1.48 |
| 29 | 65.82 | 1.418 | 10 | | |
| 30 | 66.72 | 1.401 | 31 | $\beta$-$Al_2O_3$ | 1.403 |
| 31 | 68.96 | 1.36 | 17 | $\beta$-$Al_2O_3$ | 1.36 |
| 32 | 70.32 | 1.337 | 6 | $\iota$- $Al_2O_3$ | 1.346 |
| 33 | 73.5 | 1.289 | 8 | $\iota$- $Al_2O_3$ | 1.288 |

Figure-4.12 shows the XRF spectrum of the alumina produced from black dross. There are no elements present apart from aluminium (Rhodium is present due to X-ray emission).

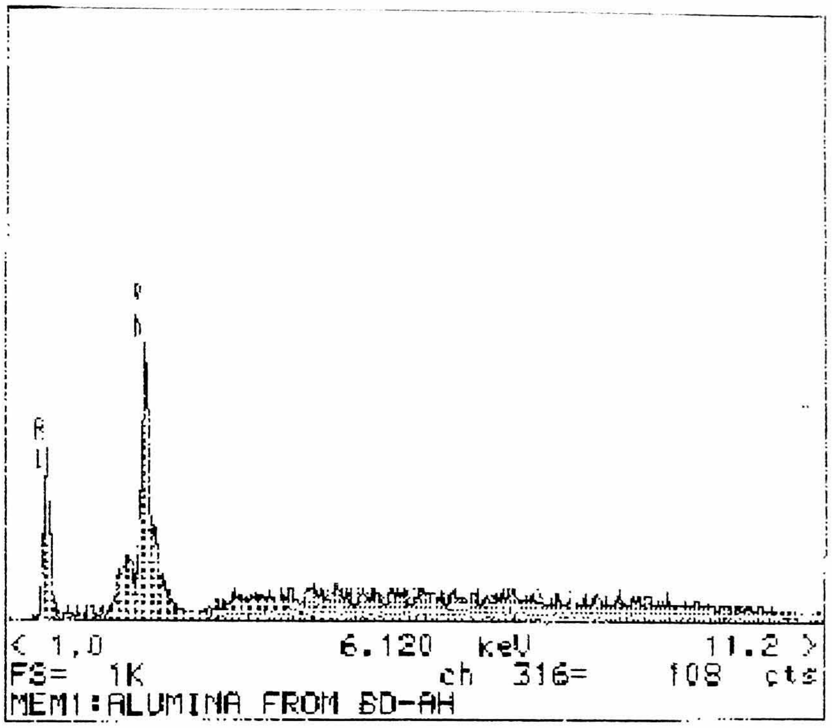


**Figure-4.12. XRF spectrum of alumina after calcination at 1200$^0$C, produced from black dross**

As mentioned in Section-4.2.3 there are different types of aluminium hydroxides and aluminas. The preparation of these aluminium hydroxides and the aluminas are very much dependent on several conditions. For example, production of different types of aluminium hydroxides depends on factors such as: preparation under vacuum or air, the speed of the addition of hydrogen peroxide, pH etc. Disturbance of the precipitate of aluminium hydroxide during filtration could also change the configuration of the molecules. Production of any types of alumina depend on the sort of aluminium hydroxide used for calcinations, their crystal sizes, surface areas etc. During calcination, alumina molecules change depending on the atmosphere (vacuum or air), presence of impurities, heating and cooling the compound slowly or rapidly, leaving the calcined compound in open air too long.

Under the experimental procedure described in this work, the aluminium hydroxide which has been produced is gibbsite, $\gamma$-$Al(OH)_3$. After the calcination at 1200$^0$C at atmospheric pressure, the final product is found to be a mixture of $\beta$-alumina and $\iota$-alumina. In Section-4.2.3 it has been mentioned that $\beta$-alumina contains sodium oxide, the common formula is $11Al_2O_3.Na_2O$. $\iota$-alumina is an active alumina, which is produced during the calcination process below 1000$^0$C. The presence of ι-alumina along with β-alumina at 1200$^0$C is due to rapid heating during the calcination process[8].

The purpose of this research is to reclaim the valuable aluminium from black dross, which is currently disposed in landfill. In this research, it has been successfully shown that it is possible to reclaim aluminium by producing pure quality aluminium compounds such as sodium aluminate, aluminium hydroxide and alumina. In order to produce certain types of aluminium hydroxide and alumina, more research work is needed as the preparation of these compounds needs very specific conditions. New research work has been set up in CER to investigate the production of different types of aluminium hydroxides and aluminas by optimising temperature, pressure and other conditions[9].

### 4.4.4. Preparation of Aluminium Sulphate

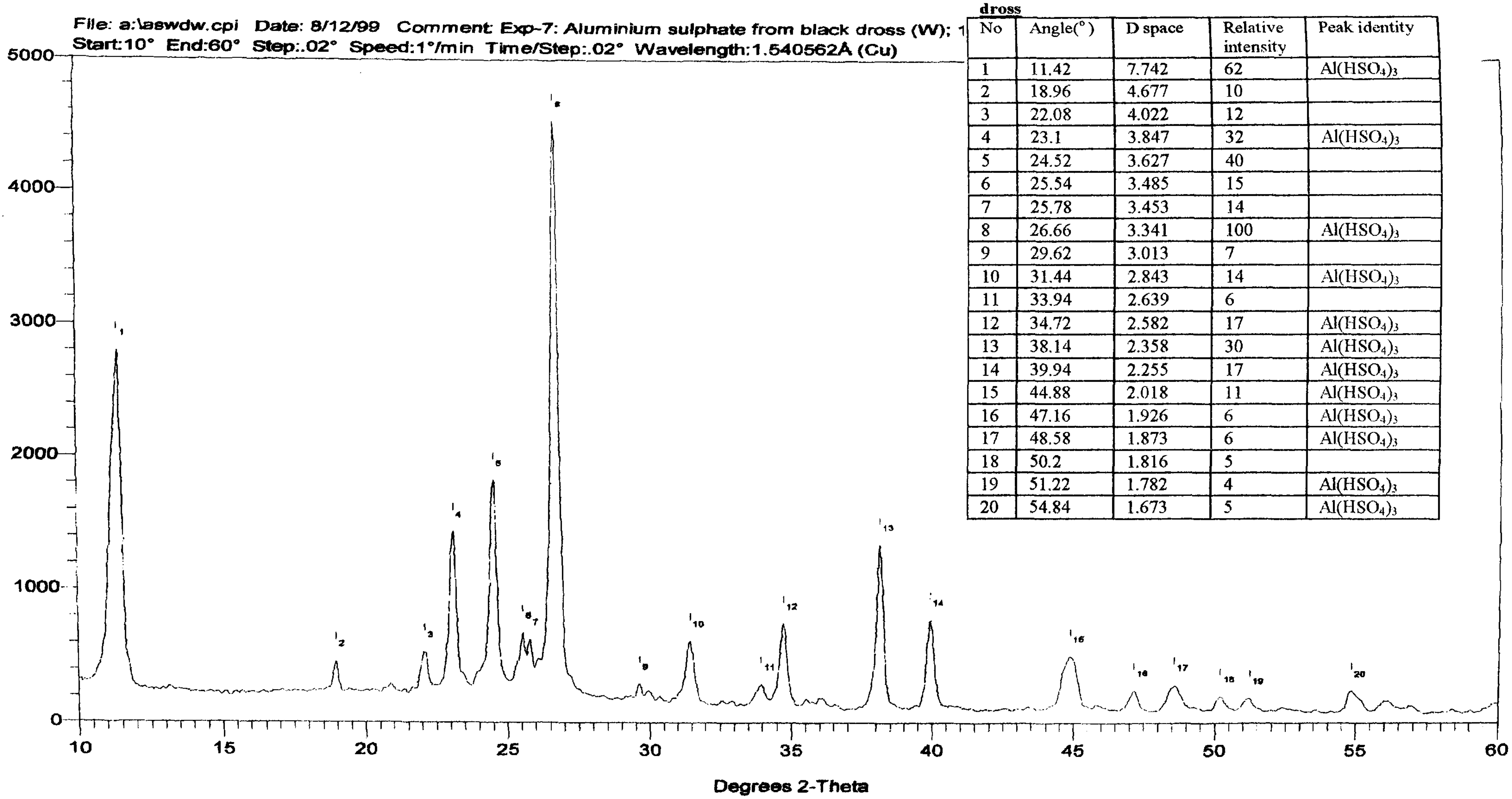
#### *4.4.4.1. Dissolution of dross in sulphuric acid*

In this experiment washed black dross and unwashed black dross were separately dissolved (straight) in sulphuric acid at 100$^0$C. Table-4.3 records the characteristics of the products obtained from the different types of dross samples.

**Table-4.3. Aluminium Sulphate (AS) produced from aluminium dross.**

| Dross | BD-W | BD-U |
|---|---|---|
| Wt of dross(g) | 10 | 10 |
| Wt of AS(g) | 38 | 37 |
| Wt of residue(g) | 5 | 2 |
| Colour of AS | light green | green |
| Texture of AS | viscous | Viscous |

It can be seen from Table-4.3 that aluminium sulphate obtained from washed black dross is light green is colour with a viscous texture at room temperature. The compound dries out after keeping it in an oven for a week, but does absorb moisture again at room temperature if left for one day. XRD analysis (Figure-4.13) of the dry product shows aluminium hydrogen sulphate [$Al(HSO_4)_3$]. However, the light green colour of the product and the XRF spectrum (Figure-4.14) confirm that the compound is contaminated with other elements. The compound produced from unwashed black dross is aluminium sulphate but contaminated with salt (Figure-4.15).



**XRD pattern of Aluminium sulphate from washed black dross**

| No | Angle(°) | D space | Relative intensity | Peak identity |
|---|---|---|---|---|
| 1 | 11.42 | 7.742 | 62 | $Al(HSO_4)_3$ |
| 2 | 18.96 | 4.677 | 10 | |
| 3 | 22.08 | 4.022 | 12 | |
| 4 | 23.1 | 3.847 | 32 | $Al(HSO_4)_3$ |
| 5 | 24.52 | 3.627 | 40 | |
| 6 | 25.54 | 3.485 | 15 | |
| 7 | 25.78 | 3.453 | 14 | |
| 8 | 26.66 | 3.341 | 100 | $Al(HSO_4)_3$ |
| 9 | 29.62 | 3.013 | 7 | |
| 10 | 31.44 | 2.843 | 14 | $Al(HSO_4)_3$ |
| 11 | 33.94 | 2.639 | 6 | |
| 12 | 34.72 | 2.582 | 17 | $Al(HSO_4)_3$ |
| 13 | 38.14 | 2.358 | 30 | $Al(HSO_4)_3$ |
| 14 | 39.94 | 2.255 | 17 | $Al(HSO_4)_3$ |
| 15 | 44.88 | 2.018 | 11 | $Al(HSO_4)_3$ |
| 16 | 47.16 | 1.926 | 6 | $Al(HSO_4)_3$ |
| 17 | 48.58 | 1.873 | 6 | $Al(HSO_4)_3$ |
| 18 | 50.2 | 1.816 | 5 | |
| 19 | 51.22 | 1.782 | 4 | $Al(HSO_4)_3$ |
| 20 | 54.84 | 1.673 | 5 | $Al(HSO_4)_3$ |

Figure-4.13. XRD spectrum of aluminium (hydrogen) sulphate produced from washed black dross

The physical characteristics and XRD spectra confirm that it is not possible to produce good quality aluminium sulphate by just dissolving the black dross in sulphuric acid. In washed black dross, most of the aluminium is in the alumina form, which is not very soluble in sulphuric acid. Therefore, this is not a very good method for recovering aluminium from the dross and preparing aluminium sulphate as most of the aluminium remain in the dross. Another problem with this method is the other impurities in the black dross are soluble in the sulphuric acid and will contaminate the product.

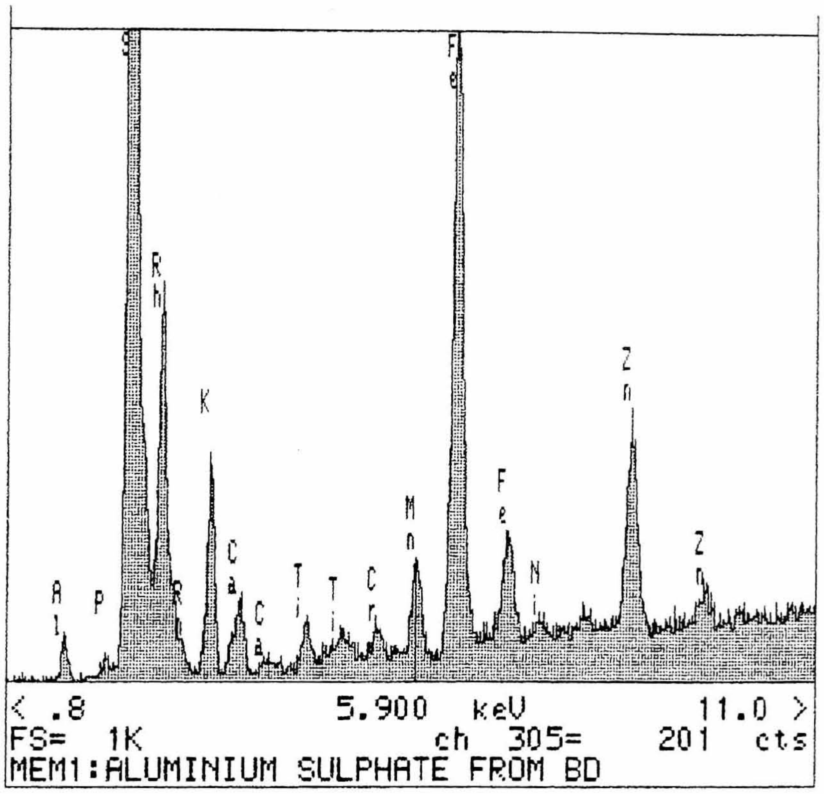
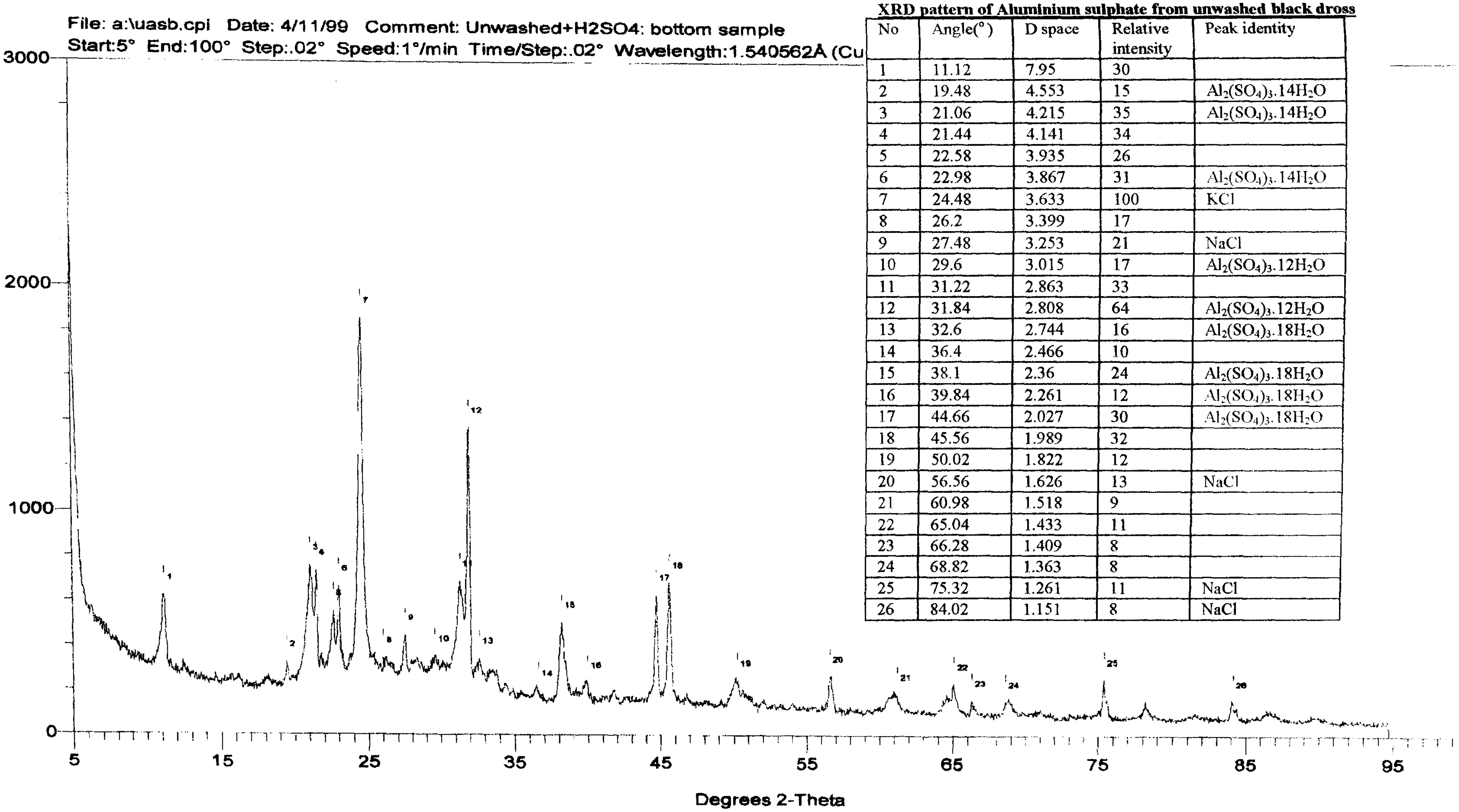


**Figure-4.14. XRF spectrum of aluminium hydrogen sulphate produced from washed black dross**

### *4.4.4.2. Dissolution of aluminium hydroxide (prepared from washed black dross) in sulphuric acid.*

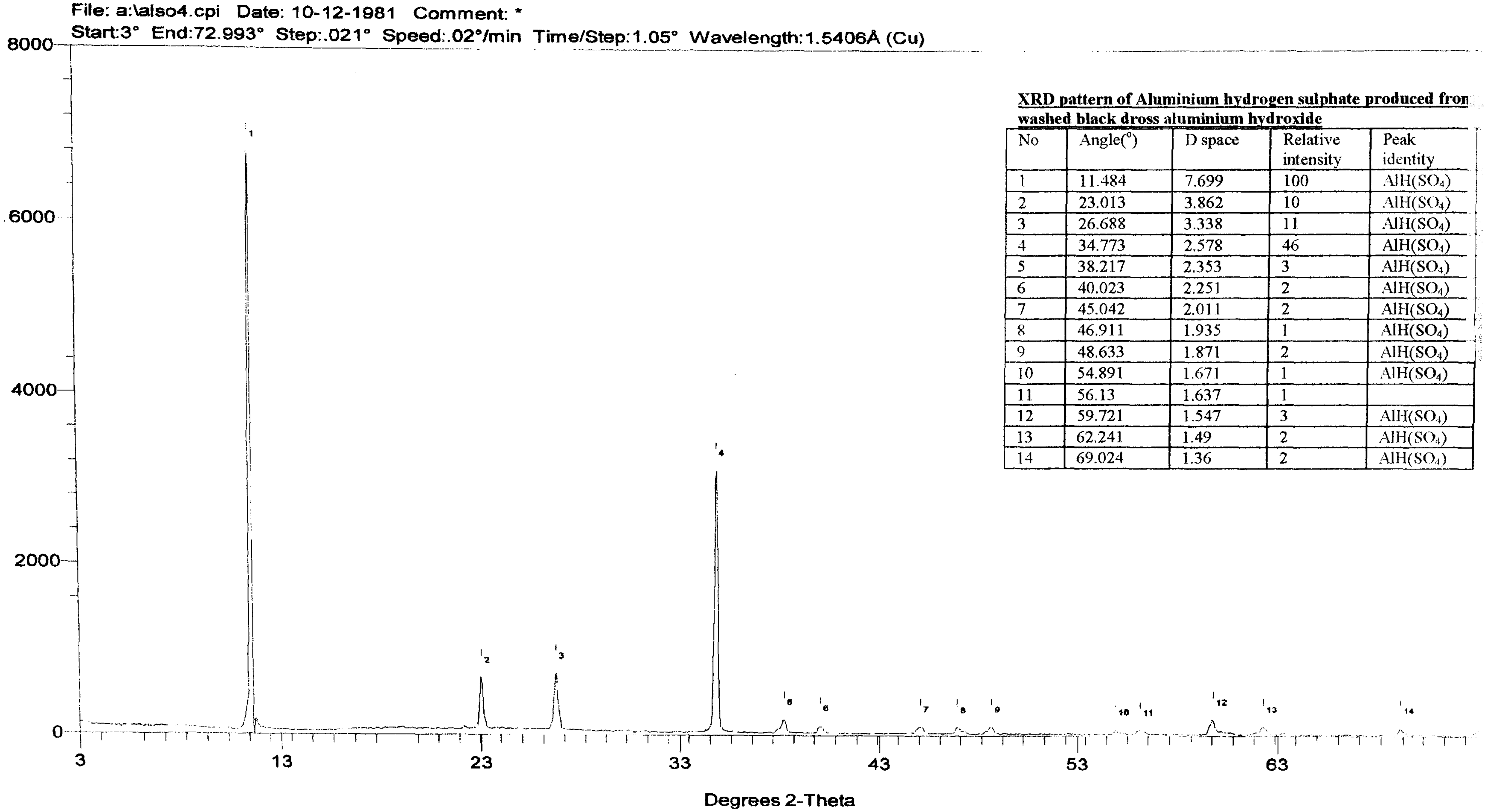
By dissolving 5g of aluminium hydroxide in 100ml of 2M sulphuric acid, the product yield was 26.62g. The XRD spectrum (Figure-4.16) of the compound obtained by dissolving aluminium hydroxide in sulphuric acid shows a pure aluminium hydrogen sulphate [$Al(HSO_4)_3$]. XRF spectrum (Figure-4.17) of the compound confirms the presence of only aluminium and sulphur with no other impurities. The colour of the aluminium sulphate is white, it has a sandy texture and dissolves in cold water. The compound is very hygroscopic, i.e., absorbs moister at room temperature. It remains stable[8] at 84$^0$C.



**XRD pattern of Aluminium sulphate from unwashed black dross**

| No | Angle(°) | D space | Relative intensity | Peak identity |
|---|---|---|---|---|
| 1 | 11.12 | 7.95 | 30 | |
| 2 | 19.48 | 4.553 | 15 | $Al_2(SO_4)_3.14H_2O$ |
| 3 | 21.06 | 4.215 | 35 | $Al_2(SO_4)_3.14H_2O$ |
| 4 | 21.44 | 4.141 | 34 | |
| 5 | 22.58 | 3.935 | 26 | |
| 6 | 22.98 | 3.867 | 31 | $Al_2(SO_4)_3.14H_2O$ |
| 7 | 24.48 | 3.633 | 100 | KCl |
| 8 | 26.2 | 3.399 | 17 | |
| 9 | 27.48 | 3.253 | 21 | NaCl |
| 10 | 29.6 | 3.015 | 17 | $Al_2(SO_4)_3.12H_2O$ |
| 11 | 31.22 | 2.863 | 33 | |
| 12 | 31.84 | 2.808 | 64 | $Al_2(SO_4)_3.12H_2O$ |
| 13 | 32.6 | 2.744 | 16 | $Al_2(SO_4)_3.18H_2O$ |
| 14 | 36.4 | 2.466 | 10 | |
| 15 | 38.1 | 2.36 | 24 | $Al_2(SO_4)_3.18H_2O$ |
| 16 | 39.84 | 2.261 | 12 | $Al_2(SO_4)_3.18H_2O$ |
| 17 | 44.66 | 2.027 | 30 | $Al_2(SO_4)_3.18H_2O$ |
| 18 | 45.56 | 1.989 | 32 | |
| 19 | 50.02 | 1.822 | 12 | |
| 20 | 56.56 | 1.626 | 13 | NaCl |
| 21 | 60.98 | 1.518 | 9 | |
| 22 | 65.04 | 1.433 | 11 | |
| 23 | 66.28 | 1.409 | 8 | |
| 24 | 68.82 | 1.363 | 8 | |
| 25 | 75.32 | 1.261 | 11 | NaCl |
| 26 | 84.02 | 1.151 | 8 | NaCl |

Figure-4.15. XRD spectrum of aluminium sulphate produced from unwashed black dross



**XRD pattern of Aluminium hydrogen sulphate produced fron washed black dross aluminium hydroxide**

| No | Angle(°) | D space | Relative intensity | Peak identity |
|---|---|---|---|---|
| 1 | 11.484 | 7.699 | 100 | $AlH(SO_4)$ |
| 2 | 23.013 | 3.862 | 10 | $AlH(SO_4)$ |
| 3 | 26.688 | 3.338 | 11 | $AlH(SO_4)$ |
| 4 | 34.773 | 2.578 | 46 | $AlH(SO_4)$ |
| 5 | 38.217 | 2.353 | 3 | $AlH(SO_4)$ |
| 6 | 40.023 | 2.251 | 2 | $AlH(SO_4)$ |
| 7 | 45.042 | 2.011 | 2 | $AlH(SO_4)$ |
| 8 | 46.911 | 1.935 | 1 | $AlH(SO_4)$ |
| 9 | 48.633 | 1.871 | 2 | $AlH(SO_4)$ |
| 10 | 54.891 | 1.671 | 1 | $AlH(SO_4)$ |
| 11 | 56.13 | 1.637 | 1 | |
| 12 | 59.721 | 1.547 | 3 | $AlH(SO_4)$ |
| 13 | 62.241 | 1.49 | 2 | $AlH(SO_4)$ |
| 14 | 69.024 | 1.36 | 2 | $AlH(SO_4)$ |

**Figure-4.16. XRD spectrum of Aluminium hydrogen sulphate produced from washed black dross aluminium hydroxide**

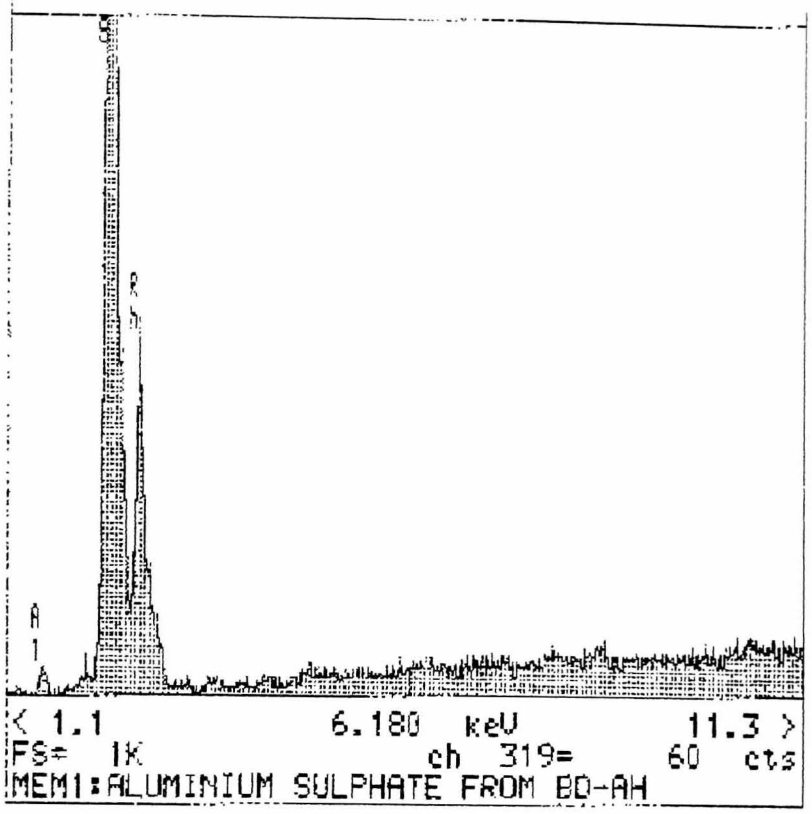


**Figure-4.17. XRF spectrum of aluminium sulphate produced from aluminium hydroxide made from washed black dross.**

## 4.4.5. Preparation of Aluminium Nitrate

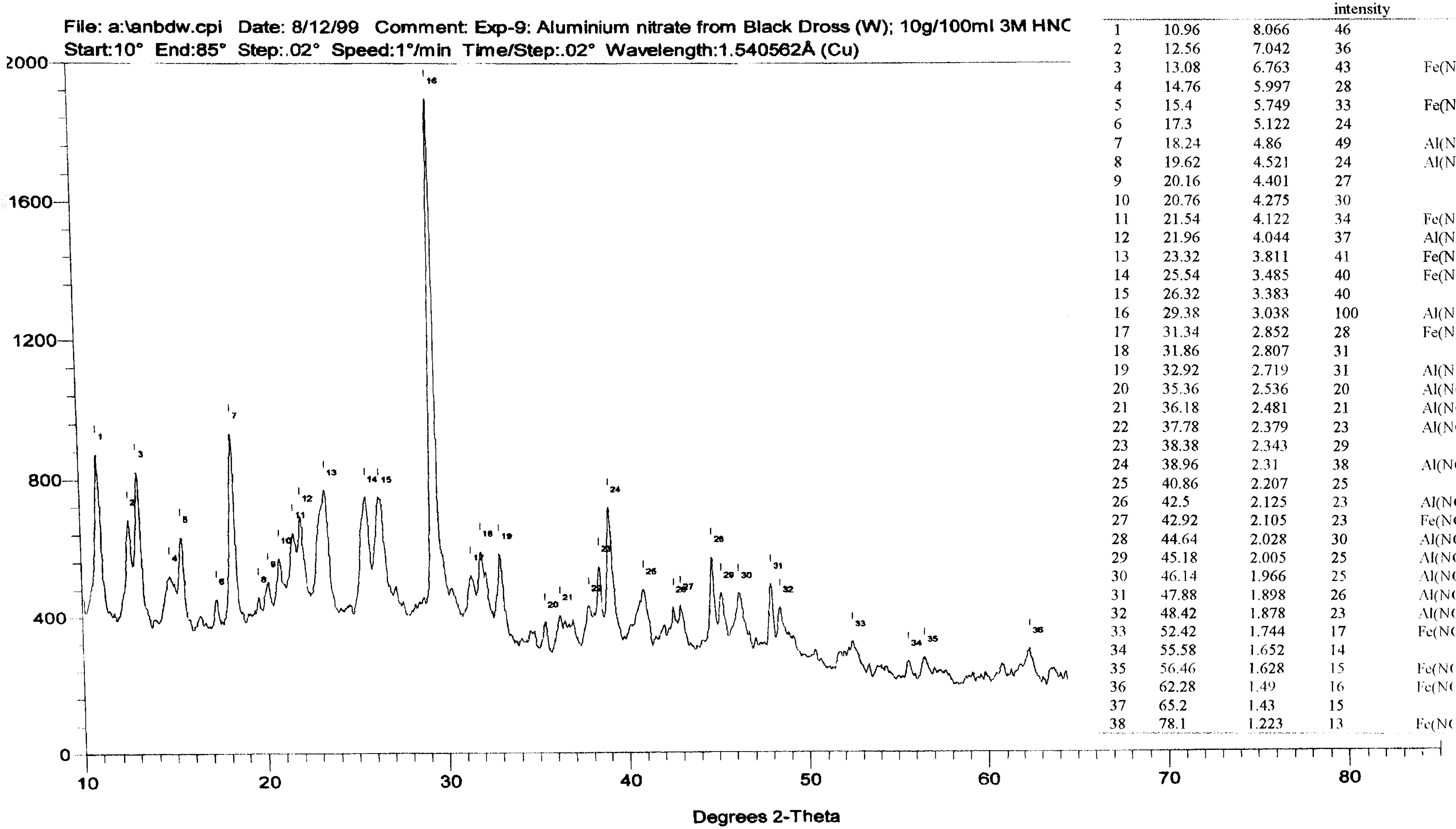
### *4.4.5.1. Dissolution of dross in nitric acid*

In this experiment washed black dross (BD-W) and unwashed black dross (BD-U) samples were leached with 2M nitric acid at 100$^0$C. Table-4.4 records the characteristic of the products obtained from the different types of dross samples.

**Table-4.4. Aluminium nitrate(AN) produced from aluminium dross.**

| Dross | BD-W | BD-U |
|---|---|---|
| Wt of black dross(g) | 10 | 10 |
| Wt of residue(g) | 5 | 2 |
| Wt of AN(g) | 15 | 14 |
| Colour of AN | yellow | brown |
| Texture of AN | sandy | sandy |

The XRD analysis of the product obtained from washed black dross shows (Figure-4.18) that the product is a mixture of aluminium nitrate and ferric nitrate.



**XRD pattern of Aluminium nitrate from washed black dross**

| No | Angle(°) | D space | Relative intensity | Peak identity |
|---|---|---|---|---|
| 1 | 10.96 | 8.066 | 46 | |
| 2 | 12.56 | 7.042 | 36 | |
| 3 | 13.08 | 6.763 | 43 | $Fe(NO_3)_3.9H_2O$ |
| 4 | 14.76 | 5.997 | 28 | |
| 5 | 15.4 | 5.749 | 33 | $Fe(NO_3)_3.9H_2O$ |
| 6 | 17.3 | 5.122 | 24 | |
| 7 | 18.24 | 4.86 | 49 | $Al(NO_3)_3.9H2O$ |
| 8 | 19.62 | 4.521 | 24 | $Al(NO_3)_3.9H2O$ |
| 9 | 20.16 | 4.401 | 27 | |
| 10 | 20.76 | 4.275 | 30 | |
| 11 | 21.54 | 4.122 | 34 | $Fe(NO_3)_3.9H_2O$ |
| 12 | 21.96 | 4.044 | 37 | $Al(NO_3)_3.9H2O$ |
| 13 | 23.32 | 3.811 | 41 | $Fe(NO_3)_3.9H_2O$ |
| 14 | 25.54 | 3.485 | 40 | $Fe(NO_3)_3.9H_2O$ |
| 15 | 26.32 | 3.383 | 40 | |
| 16 | 29.38 | 3.038 | 100 | $Al(NO_3)_3.9H2O$ |
| 17 | 31.34 | 2.852 | 28 | $Fe(NO_3)_3.9H_2O$ |
| 18 | 31.86 | 2.807 | 31 | |
| 19 | 32.92 | 2.719 | 31 | $Al(NO_3)_3.9H2O$ |
| 20 | 35.36 | 2.536 | 20 | $Al(NO_3)_3.9H2O$ |
| 21 | 36.18 | 2.481 | 21 | $Al(NO_3)_3.9H2O$ |
| 22 | 37.78 | 2.379 | 23 | $Al(NO_3)_3.9H2O$ |
| 23 | 38.38 | 2.343 | 29 | |
| 24 | 38.96 | 2.31 | 38 | $Al(NO_3)_3.9H2O$ |
| 25 | 40.86 | 2.207 | 25 | |
| 26 | 42.5 | 2.125 | 23 | $Al(NO_3)_3.9H2O$ |
| 27 | 42.92 | 2.105 | 23 | $Fe(NO_3)_3.9H_2O$ |
| 28 | 44.64 | 2.028 | 30 | $Al(NO_3)_3.9H2O$ |
| 29 | 45.18 | 2.005 | 25 | $Al(NO_3)_3.9H2O$ |
| 30 | 46.14 | 1.966 | 25 | $Al(NO_3)_3.9H2O$ |
| 31 | 47.88 | 1.898 | 26 | $Al(NO_3)_3.9H2O$ |
| 32 | 48.42 | 1.878 | 23 | $Al(NO_3)_3.9H2O$ |
| 33 | 52.42 | 1.744 | 17 | $Fe(NO_3)_3.9H_2O$ |
| 34 | 55.58 | 1.652 | 14 | |
| 35 | 56.46 | 1.628 | 15 | $Fe(NO_3)_3.9H_2O$ |
| 36 | 62.28 | 1.49 | 16 | $Fe(NO_3)_3.9H_2O$ |
| 37 | 65.2 | 1.43 | 15 | |
| 38 | 78.1 | 1.223 | 13 | $Fe(NO_3)_3.9H_2O$ |

Figure-4.18. XRD spectrum of aluminium nitrate produced from washed black dross.

Figure-4.19 presents the XRF spectrum of the aluminium nitrate produced from washed black dross which confirms the presence of several elements as well. The product obtained from unwashed black dross is contaminated with salt (Figure-4.20). Good quality aluminium nitrate cannot be produced by simply dissolving black dross with nitric acid as the other impurities dissolve in this medium and contaminate the product.

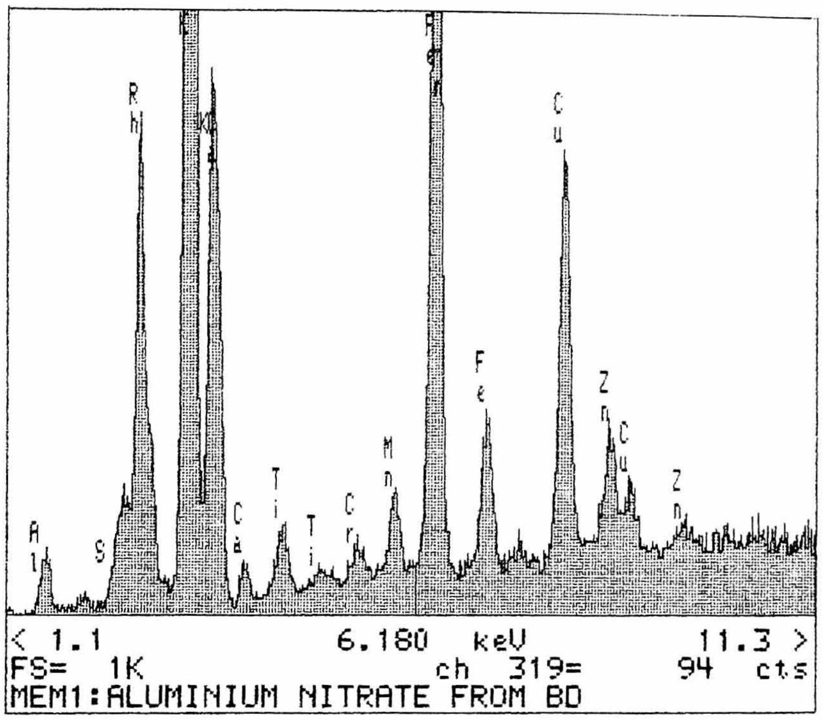
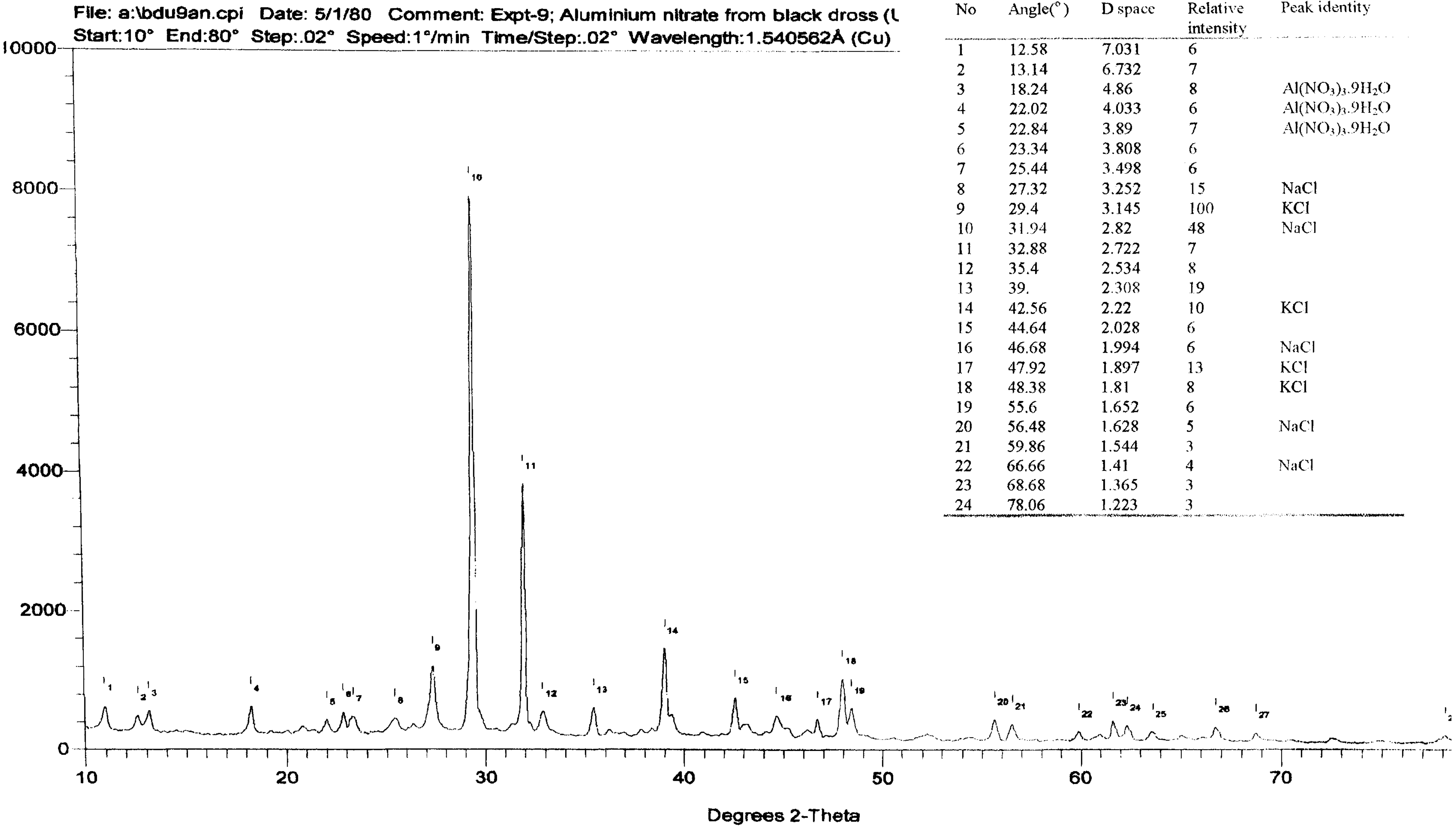


**Figure-4.19. XRF spectrum of aluminium nitrate produced from washed black dross.**

### *4.4.5.2. Dissolution of aluminium hydroxide (prepared from washed black dross) in nitric acid.*

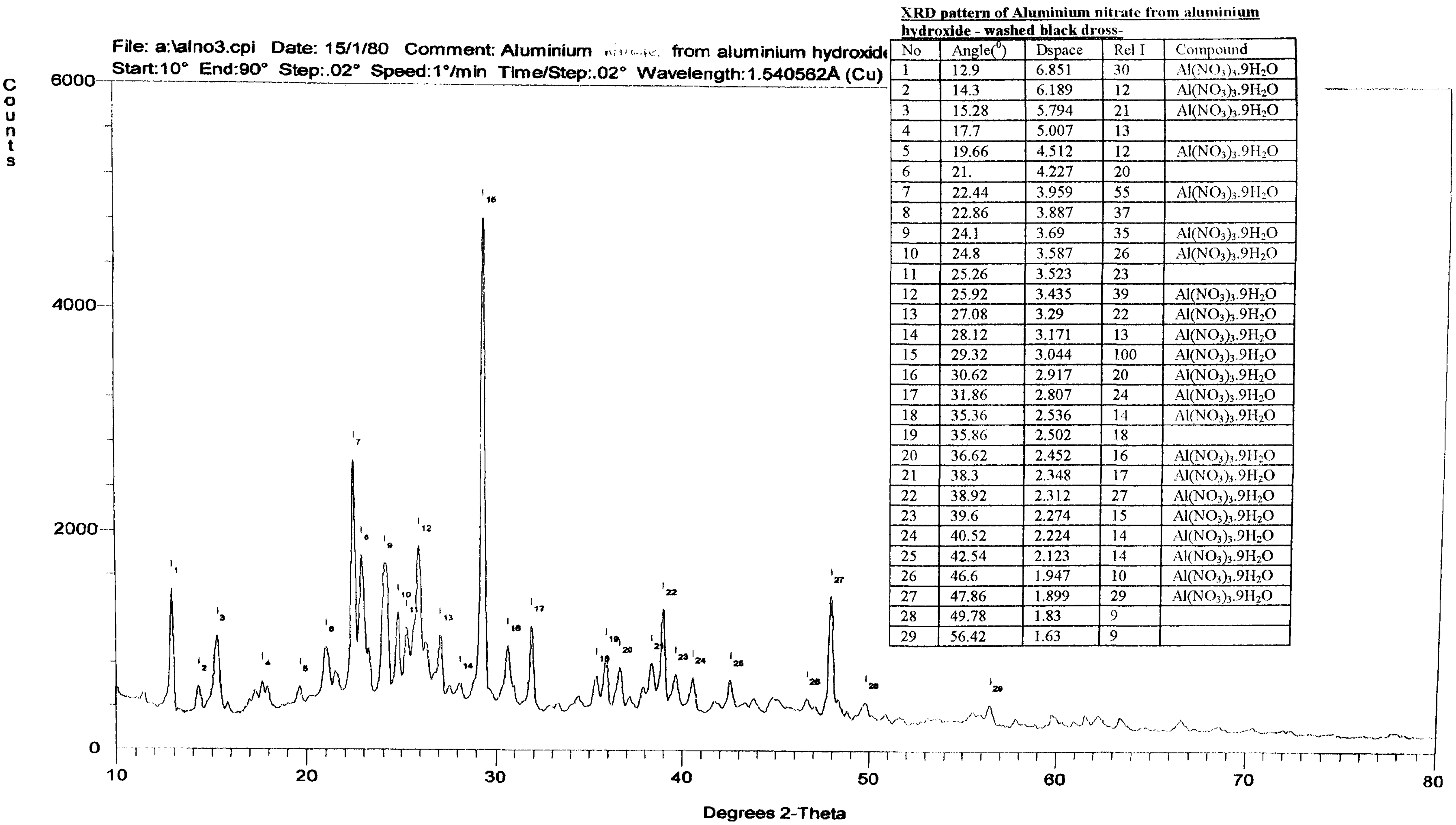
The XRD spectrum (Figure-4.21) of the compound obtained by dissolving aluminium hydroxide in nitric acid shows a pure aluminium nitrate [$Al(NO_3)_3.9H_2O$] compound. The product yield was 20g. XRF spectrum (Figure-4.22) of the compound confirms the presence of aluminium along with zinc impurities. The AAS analysis confirmed that the zinc content is 0.01%. The colour of the aluminium nitrate is white. The material has a sandy texture and dissolves in cold water.



**XRD pattern of Aluminium nitrate from unwashed black dross**

| No | Angle(°) | D space | Relative intensity | Peak identity |
|---|---|---|---|---|
| 1 | 12.58 | 7.031 | 6 | |
| 2 | 13.14 | 6.732 | 7 | |
| 3 | 18.24 | 4.86 | 8 | $Al(NO_3)_3.9H_2O$ |
| 4 | 22.02 | 4.033 | 6 | $Al(NO_3)_3.9H_2O$ |
| 5 | 22.84 | 3.89 | 7 | $Al(NO_3)_3.9H_2O$ |
| 6 | 23.34 | 3.808 | 6 | |
| 7 | 25.44 | 3.498 | 6 | |
| 8 | 27.32 | 3.252 | 15 | NaCl |
| 9 | 29.4 | 3.145 | 100 | KCl |
| 10 | 31.94 | 2.82 | 48 | NaCl |
| 11 | 32.88 | 2.722 | 7 | |
| 12 | 35.4 | 2.534 | 8 | |
| 13 | 39. | 2.308 | 19 | |
| 14 | 42.56 | 2.22 | 10 | KCl |
| 15 | 44.64 | 2.028 | 6 | |
| 16 | 46.68 | 1.994 | 6 | NaCl |
| 17 | 47.92 | 1.897 | 13 | KCl |
| 18 | 48.38 | 1.81 | 8 | KCl |
| 19 | 55.6 | 1.652 | 6 | |
| 20 | 56.48 | 1.628 | 5 | NaCl |
| 21 | 59.86 | 1.544 | 3 | |
| 22 | 66.66 | 1.41 | 4 | NaCl |
| 23 | 68.68 | 1.365 | 3 | |
| 24 | 78.06 | 1.223 | 3 | |

**Figure-4.20. XRD spectrum of aluminium nitrate produced from unwashed black dross.**



**XRD pattern of Aluminium nitrate from aluminium hydroxide - washed black dross-**

| No | Angle($^0$) | Dspace | Rel I | Compound |
|---|---|---|---|---|
| 1 | 12.9 | 6.851 | 30 | $Al(NO_3)_3.9H_2O$ |
| 2 | 14.3 | 6.189 | 12 | $Al(NO_3)_3.9H_2O$ |
| 3 | 15.28 | 5.794 | 21 | $Al(NO_3)_3.9H_2O$ |
| 4 | 17.7 | 5.007 | 13 | |
| 5 | 19.66 | 4.512 | 12 | $Al(NO_3)_3.9H_2O$ |
| 6 | 21. | 4.227 | 20 | |
| 7 | 22.44 | 3.959 | 55 | $Al(NO_3)_3.9H_2O$ |
| 8 | 22.86 | 3.887 | 37 | |
| 9 | 24.1 | 3.69 | 35 | $Al(NO_3)_3.9H_2O$ |
| 10 | 24.8 | 3.587 | 26 | $Al(NO_3)_3.9H_2O$ |
| 11 | 25.26 | 3.523 | 23 | |
| 12 | 25.92 | 3.435 | 39 | $Al(NO_3)_3.9H_2O$ |
| 13 | 27.08 | 3.29 | 22 | $Al(NO_3)_3.9H_2O$ |
| 14 | 28.12 | 3.171 | 13 | $Al(NO_3)_3.9H_2O$ |
| 15 | 29.32 | 3.044 | 100 | $Al(NO_3)_3.9H_2O$ |
| 16 | 30.62 | 2.917 | 20 | $Al(NO_3)_3.9H_2O$ |
| 17 | 31.86 | 2.807 | 24 | $Al(NO_3)_3.9H_2O$ |
| 18 | 35.36 | 2.536 | 14 | $Al(NO_3)_3.9H_2O$ |
| 19 | 35.86 | 2.502 | 18 | |
| 20 | 36.62 | 2.452 | 16 | $Al(NO_3)_3.9H_2O$ |
| 21 | 38.3 | 2.348 | 17 | $Al(NO_3)_3.9H_2O$ |
| 22 | 38.92 | 2.312 | 27 | $Al(NO_3)_3.9H_2O$ |
| 23 | 39.6 | 2.274 | 15 | $Al(NO_3)_3.9H_2O$ |
| 24 | 40.52 | 2.224 | 14 | $Al(NO_3)_3.9H_2O$ |
| 25 | 42.54 | 2.123 | 14 | $Al(NO_3)_3.9H_2O$ |
| 26 | 46.6 | 1.947 | 10 | $Al(NO_3)_3.9H_2O$ |
| 27 | 47.86 | 1.899 | 29 | $Al(NO_3)_3.9H_2O$ |
| 28 | 49.78 | 1.83 | 9 | |
| 29 | 56.42 | 1.63 | 9 | |

**Figure-4.21. XRD spectrum of aluminium nitrate produced from washed black dross aluminium hydroxide.**

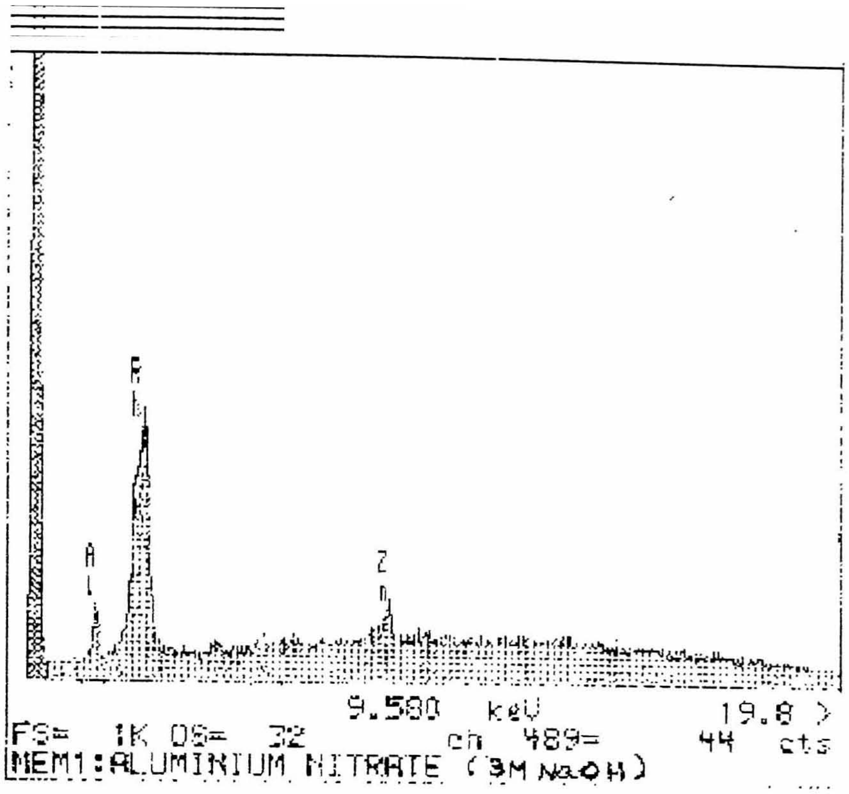


Figure-4.22. XRF spectrum of aluminium nitrate produced from aluminium hydroxide made from washed black dross.

## 4.4.6. Preparation of Aluminium Chloride

### 4.4.6.1. Dissolution of dross in hydrochloride acid

In this experiment washed black dross (BD-W) and unwashed black dross (BD-U) samples were leached with 2M hydrochloric acid at 100$^0$C. Table-4.5 records the characteristic of the products obtained from the different types of dross samples.

Table-4.5. Aluminium Chloride(AC) produced from aluminium dross.

| Dross | BD-W | BD-U |
|---|---|---|
| Wt of black dross(g) | 10 | 10 |
| Wt of residue(g) | 3 | 2 |
| Wt of AC(g) | 13 | 18 |
| Colour of AC | yellow | yellow |
| Texture of AC | sandy | sandy |

The XRD spectrum (Figure-4.23) of the compound prepared from washed black dross shows a mixture of anhydrous ($AlCl_3$) and hydrated ($AlCl_3.6H_2O$) aluminium chloride (because the metal extracted acid solution was heated to evaporate the liquid in open air not in vacuum or under pressure). Figure-4.24 is the XRF spectrum of the aluminium chloride compound extracted from washed black dross. It can be seen that the compound is not pure due to the presence of several impurities.

**Sample:Aluminium chloride from black dross (washed)**
**(filename:a:\alclbdw.cpi)**

| No | Angle(°) | D space | Relative intensity | Peak identity | Control D space |
|---|---|---|---|---|---|
| 1 | 14.9 | 5.941 | 37 | $AlCl_3.6H_2O$ | 5.901 |
| 2 | 15.48 | 5.719 | 51 | $AlCl_3$ | 5.8 |
| 3 | 15.82 | 5.597 | 33 | | |
| 4 | 17.12 | 5.175 | 58 | $AlCl_3$ | 5.1 |
| 5 | 22.88 | 3.884 | 44 | | |
| 6 | 23.3 | 3.815 | 20 | | |
| 7 | 24.12 | 3.687 | 21 | $AlCl_3.6H_2O$ | 3.66 |
| 8 | 26.06 | 3.416 | 22 | | |
| 9 | 27. | 3.3 | 70 | $AlCl_3.6H_2O$ | 3.29 |
| 10 | 29.02 | 3.074 | 20 | | |
| 11 | 29.92 | 2.984 | 51 | | |
| 12 | 31.34 | 2.852 | 28 | | |
| 13 | 34.08 | 2.629 | 17 | | |
| 14 | 34.32 | 2.611 | 18 | | |
| 15 | 35. | 2.562 | 100 | $AlCl_3.6H_2O$ | 2.559 |
| 16 | 36.7 | 2.447 | 15 | $AlCl_3$ | 2.46 |
| 17 | 38.28 | 2.349 | 17 | $AlCl_3.6H_2O$ | 2.349 |
| 18 | 38.98 | 2.309 | 38 | $AlCl_3.6H_2O$ | 2.302 |
| 19 | 39.7 | 2.268 | 14 | | |
| 20 | 41.24 | 2.187 | 13 | $AlCl_3.6H_2O$ | 2.182 |
| 21 | 41.78 | 2.16 | 13 | | |
| 22 | 44.66 | 2.027 | 24 | $AlCl_3.6H_2O$ | 2.027 |
| 23 | 46.72 | 1.943 | 19 | $AlCl_3.6H_2O$ | 1.945 |
| 24 | 47.72 | 1.904 | 19 | | |
| 25 | 51.98 | 1.758 | 39 | $AlCl_3.6H_2O$ | 1.757 |
| 26 | 54.82 | 1.673 | 9 | $AlCl_3.6H_2O$ | 1.673 |
| 27 | 55.72 | 1.648 | 17 | $AlCl_3.6H_2O$ | 1.646 |
| 28 | 56.76 | 1.621 | 11 | $AlCl_3.6H_2O$ | 1.622 |
| 29 | 59.06 | 1.563 | 9 | | |
| 30 | 61. | 1.518 | 10 | $AlCl_3.6H_2O$ | 1.515 |
| 31 | 62.28 | 1.49 | 10 | $AlCl_3.6H_2O$ | 1.48 |
| 32 | 63.84 | 1.457 | 8 | | |
| 33 | 67.64 | 1.384 | 9 | | |
| 34 | 67.86 | 1.38 | 10 | | |
| 35 | 73.38 | 1.289 | 8 | $AlCl_3$ | 1.28 |
| 36 | 78.16 | 1.222 | 9 | $AlCl_3.6H_2O$ | 1.221 |
| 37 | 82.76 | 1.165 | 6 | $AlCl_3$ | 1.17 |

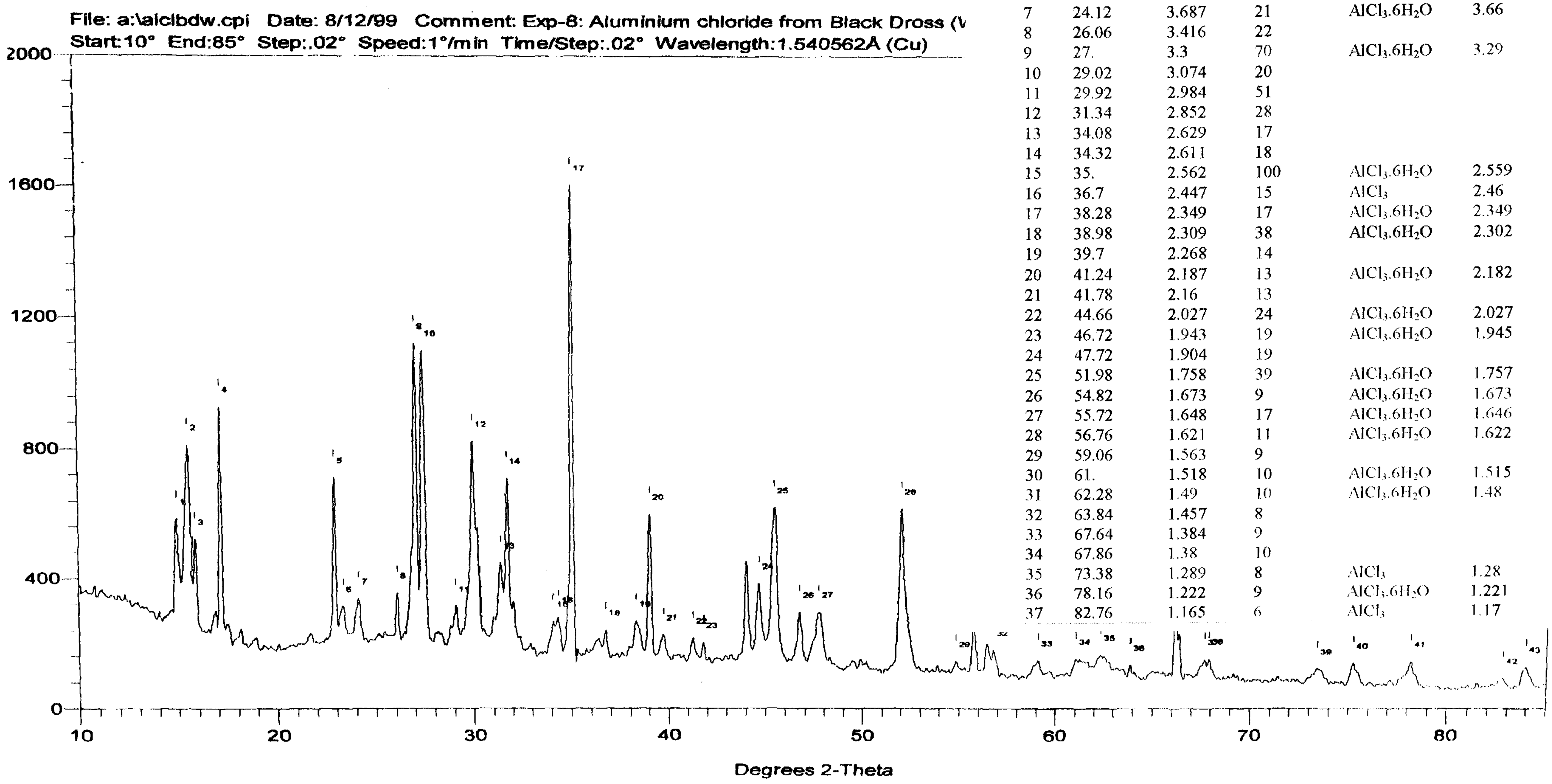
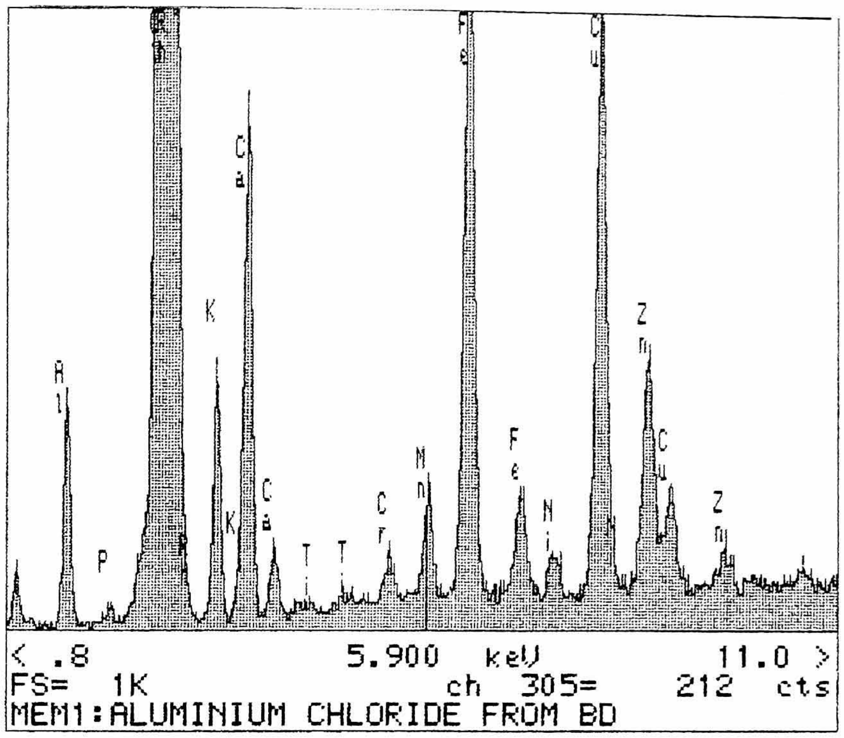


Figure-4.23. XRD spectrum of aluminium chloride produced from washed black dross.

Unwashed black dross is unsuitable for the production of pure aluminium chloride as the compound is contaminated with salts (Figure-4.25).



```
< .8                    5.900  keV          11.0 >
FS=  1K                   ch  305=         212  cts
MEM1:ALUMINIUM CHLORIDE FROM BD
```

**Figure-4.24. XRF spectrum of aluminium chloride extracted from washed black dross.**

### *4.4.6.2. Dissolution of aluminium hydroxide (prepared from washed black dross) in hydrochloric acid.*

The XRD spectrum (Figure-4.26) of the compound obtained a pure aluminium chloride [$AlCl_3.6H_2O$]. The product yield was 18g. The XRF spectrum (Figure-27) of the compound confirms the presence of only aluminium and chloride, with no other impurities. The colour of the aluminium chloride is white, with a sandy texture and it dissolves in cold water.

**XRD pattern of Aluminium chloride from unwashed black dross**

| No | Angle(°) | D space | Relative intensity | Peak identity | Std D space |
|---|---|---|---|---|---|
| 1 | 23.2 | 3.831 | 6 | | |
| 2 | 26.8 | 3.324 | 9 | | |
| 3 | 27.34 | 3.259 | 16 | NaCl | 3.258 |
| 4 | 28.34 | 3.147 | 58 | KCl | 3.146 |
| 5 | 29.98 | 2.978 | 7 | | |
| 6 | 31.7 | 2.82 | 100 | NaCl | 2.82 |
| 7 | 38.34 | 2.346 | 5 | | |
| 8 | 40.5 | 2.225 | 22 | KCl | 2.2251 |
| 9 | 44.64 | 2.028 | 7 | | |
| 10 | 45.42 | 1.995 | 47 | NaCl | 1.994 |
| 11 | 50.12 | 1.897 | 6 | KCl | 1.8972 |
| 12 | 53.84 | 1.701 | 4 | NaCl | 1.701 |
| 13 | 56.44 | 1.629 | 28 | NaCl | 1.628 |
| 14 | 58.58 | 1.574 | 4 | KCl | 1.573 |
| 15 | 65.02 | 1.433 | 3 | | |
| 16 | 66.2 | 1.411 | 15 | NaCl | 1.41 |
| 17 | 73.04 | 1.294 | 3 | | |
| 18 | 73.7 | 1.284 | 4 | KCl | 1.2839 |
| 19 | 75.24 | 1.262 | 25 | NaCl | 1.261 |
| 20 | 75.46 | 1.259 | 15 | | |
| 21 | 78.08 | 1.223 | 3 | | |

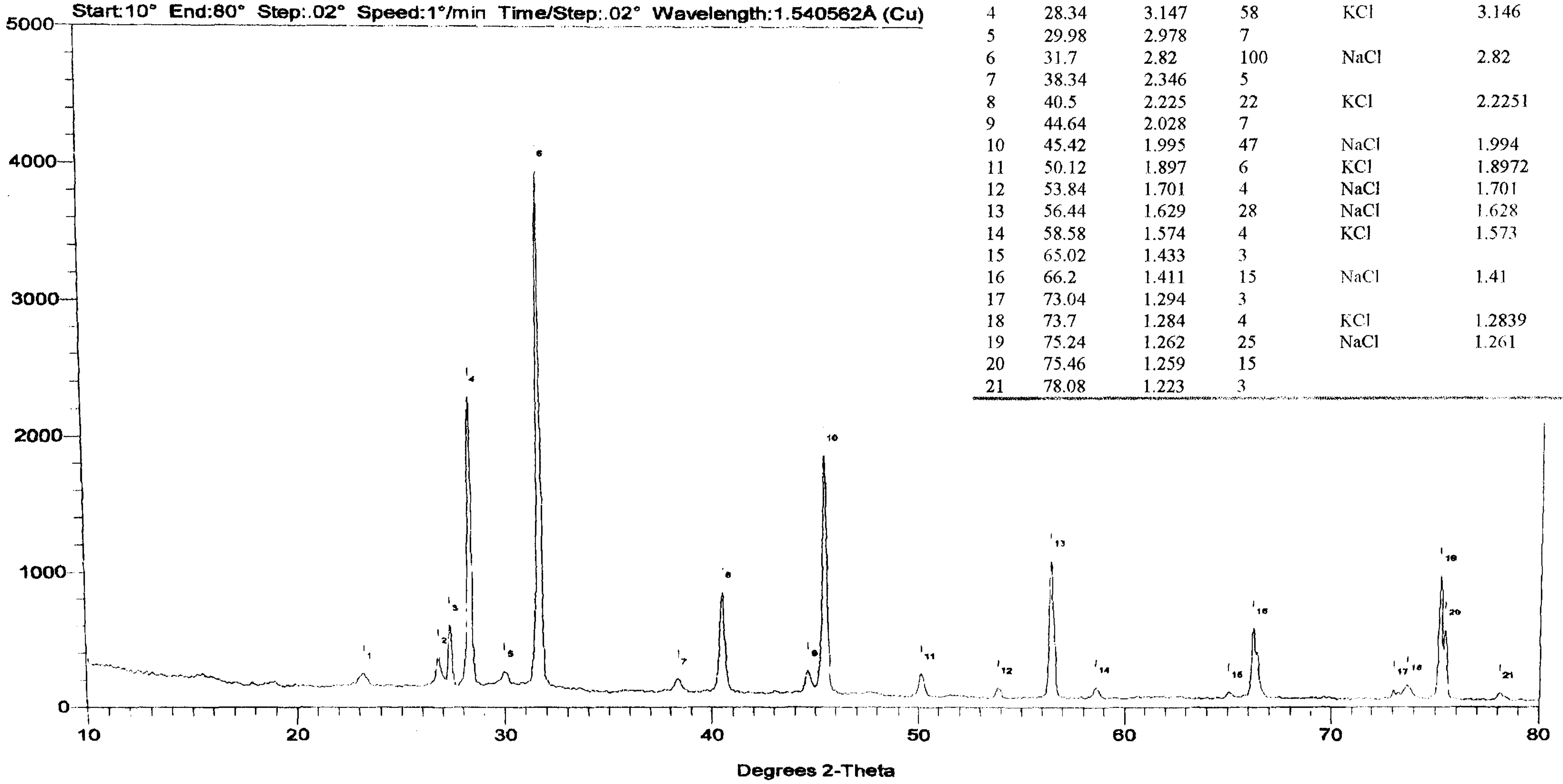


Figure-4.25. XRD spectrum of aluminium chloride produced from unwashed black dross.

**XRD pattern of Aluminium chloride from aluminium hydroxide -washed black dross**

| No | Dspace | Rel I | Compound | Std Dspace |
|---|---|---|---|---|
| 1 | 5.917 | 52 | $AlCl_3.6H_2O$ | 5.901 |
| 2 | 5.151 | 31 | $AlCl_3.6H_2O$ | 5.139 |
| 3 | 3.887 | 42 | $AlCl_3.6H_2O$ | 3.87 |
| 4 | 3.681 | 81 | $AlCl_3.6H_2O$ | 3.669 |
| 5 | 3.416 | 36 | $AlCl_3.6H_2O$ | 3.401 |
| 6 | 3.297 | 86 | $AlCl_3.6H_2O$ | 3.29 |
| 7 | 3.248 | 100 | $AlCl_3.6H_2O$ | 3.236 |
| 8 | 2.959 | 25 | $AlCl_3.6H_2O$ | 2.951 |
| 10 | 2.764 | 10 | $AlCl_3.6H_2O$ | 2.759 |
| 11 | 2.564 | 24 | $AlCl_3.6H_2O$ | 2.559 |
| 12 | 2.371 | 7 | | |
| 13 | 2.353 | 6 | $AlCl_3.6H_2O$ | 2.349 |
| 14 | 2.306 | 46 | $AlCl_3.6H_2O$ | 2.302 |
| 15 | 2.187 | 22 | $AlCl_3.6H_2O$ | 2.182 |
| 16 | 2.056 | 32 | $AlCl_3.6H_2O$ | 2.052 |
| 17 | 2.029 | 8 | $AlCl_3.6H_2O$ | 2.027 |
| 18 | 1.986 | 20 | $AlCl_3.6H_2O$ | 1.982 |
| 19 | 1.912 | 6 | $AlCl_3$ | 1.92 |
| 20 | 1.883 | 4 | | |
| 21 | 1.841 | 4 | $AlCl_3.6H_2O$ | 1.839 |
| 22 | 1.819 | 8 | $AlCl_3.6H_2O$ | 1.817 |
| 23 | 1.759 | 21 | $AlCl_3.6H_2O$ | 1.757 |
| 24 | 1.689 | 6 | $AlCl_3.6H_2O$ | 1.687 |
| 25 | 1.674 | 8 | $AlCl_3.6H_2O$ | 1.673 |
| 26 | 1.649 | 8 | $AlCl_3.6H_2O$ | 1.646 |
| 27 | 1.565 | 4 | | |
| 28 | 1.549 | 8 | $AlCl_3.6H_2O$ | 1.549 |
| 29 | 1.517 | 7 | | |
| 30 | 1.479 | 18 | $AlCl_3.6H_2O$ | 1.48 |
| 31 | 1.467 | 7 | $AlCl_3.6H_2O$ | 1.465 |
| 32 | 1.411 | 8 | $AlCl_3.6H_2O$ | 1.41 |
| 33 | 1.382 | 6 | $AlCl_3.6H_2O$ | 1.377 |
| 34 | 1.358 | 5 | $AlCl_3.6H_2O$ | 1.356 |
| 35 | 1.314 | 4 | | |
| 37 | 1.282 | 4 | $AlCl_3$ | 1.28 |
| 39 | 1.228 | 5 | $AlCl_3.6H_2O$ | 1.227 |

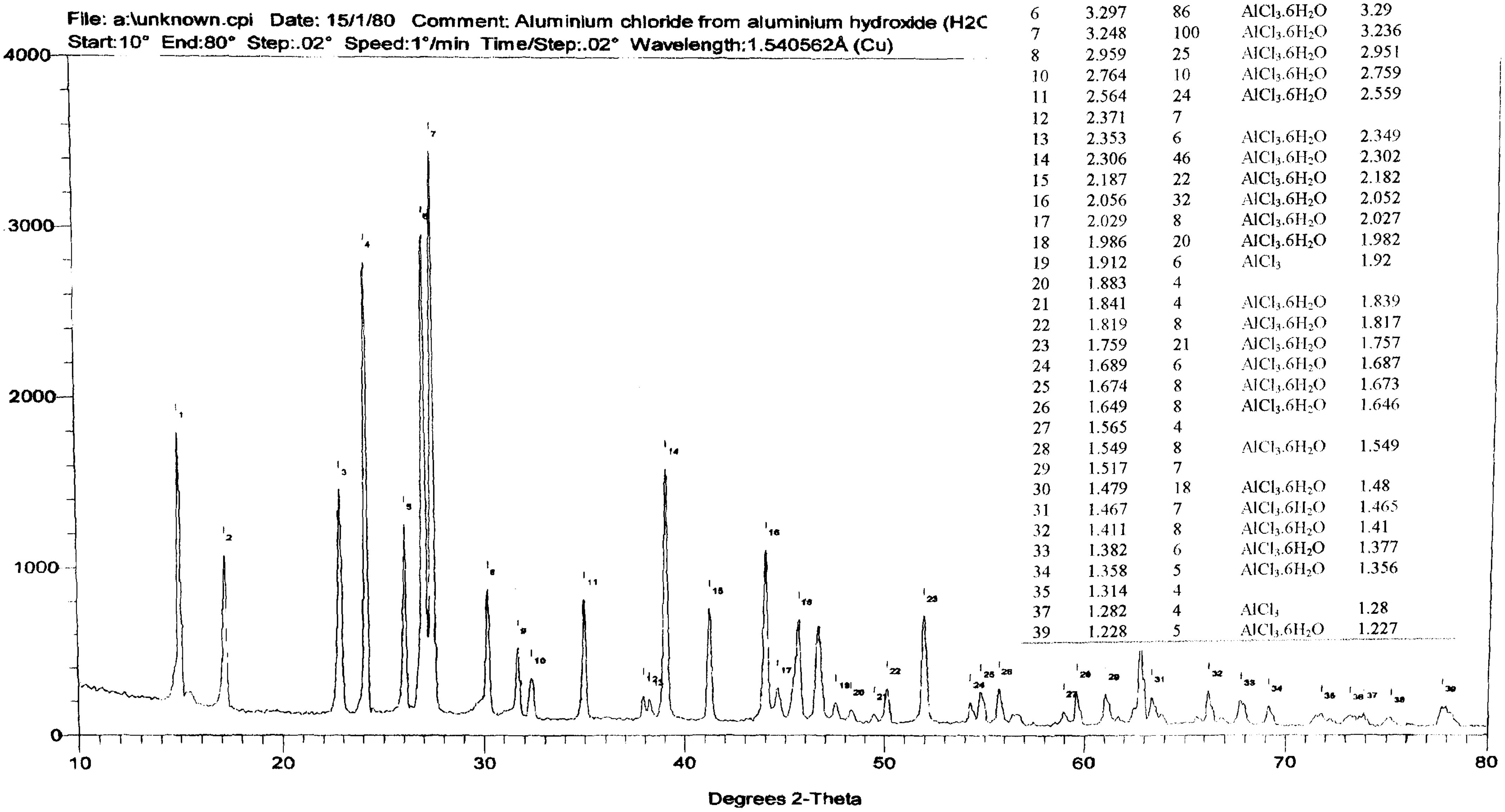


Figure-4.26. XRD spectrum of Aluminium chloride produced from washed black dross aluminium hydroxide

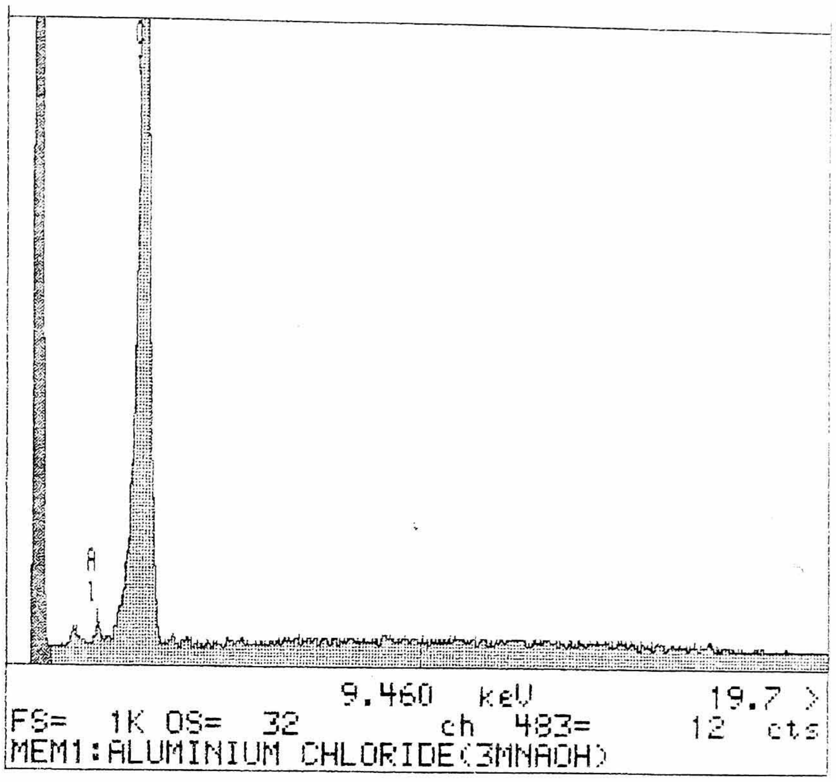


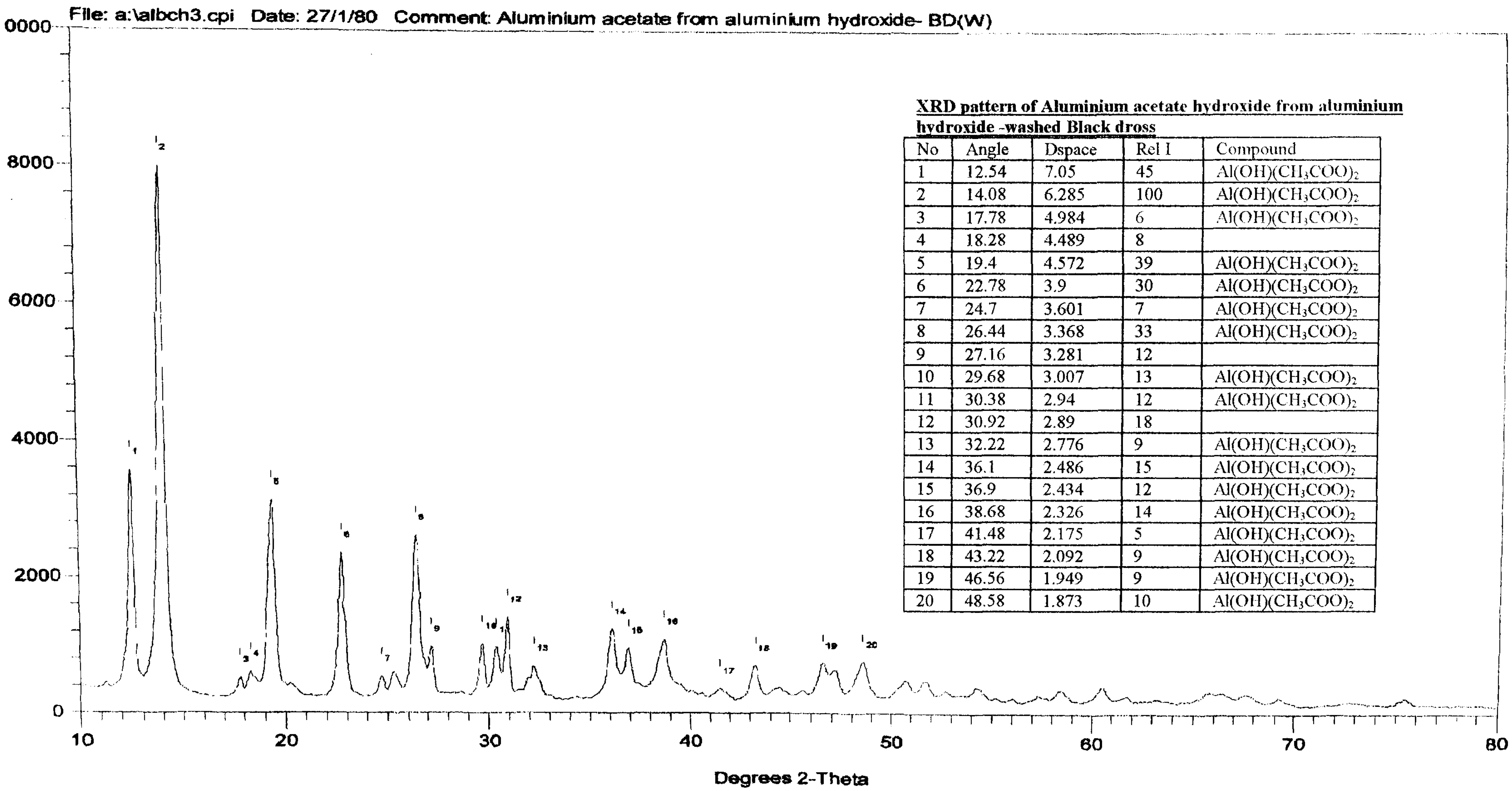
**Figure-4.27. Aluminium chloride produced from aluminium hydroxide, extracted from washed black dross.**

### 4.4.7. Preparation of Aluminium Acetate and Aluminium Formate

Aluminium acetate and aluminium formate were prepared by dissolving aluminium hydroxide in acetic acid and formic acid respectively at $100^0$C. The products obtained 7g aluminium acetate and 8g aluminium formate. The compounds were analysed by XRD and identified using the "Powder Diffraction File". Comparing the data cards shows that a very good quality aluminium acetate hydroxide [$Al(OH)(CH_3COO)_2$] (Figure-4.28) and aluminium formate hydroxide [$Al(OH)(HCOO)_2$] (Figure-4.29) have been produced. XRF spectra (Figure-4.30 and 31) of both compounds show presence of zinc impurity. The AAS confirms the zinc content is 0.02%. Both compounds are white in colour with a talcum powder texture and are not soluble in water.

### 4.4.8. Preparation of Sodium Aluminate from Bulk Content of Washed Black Dross

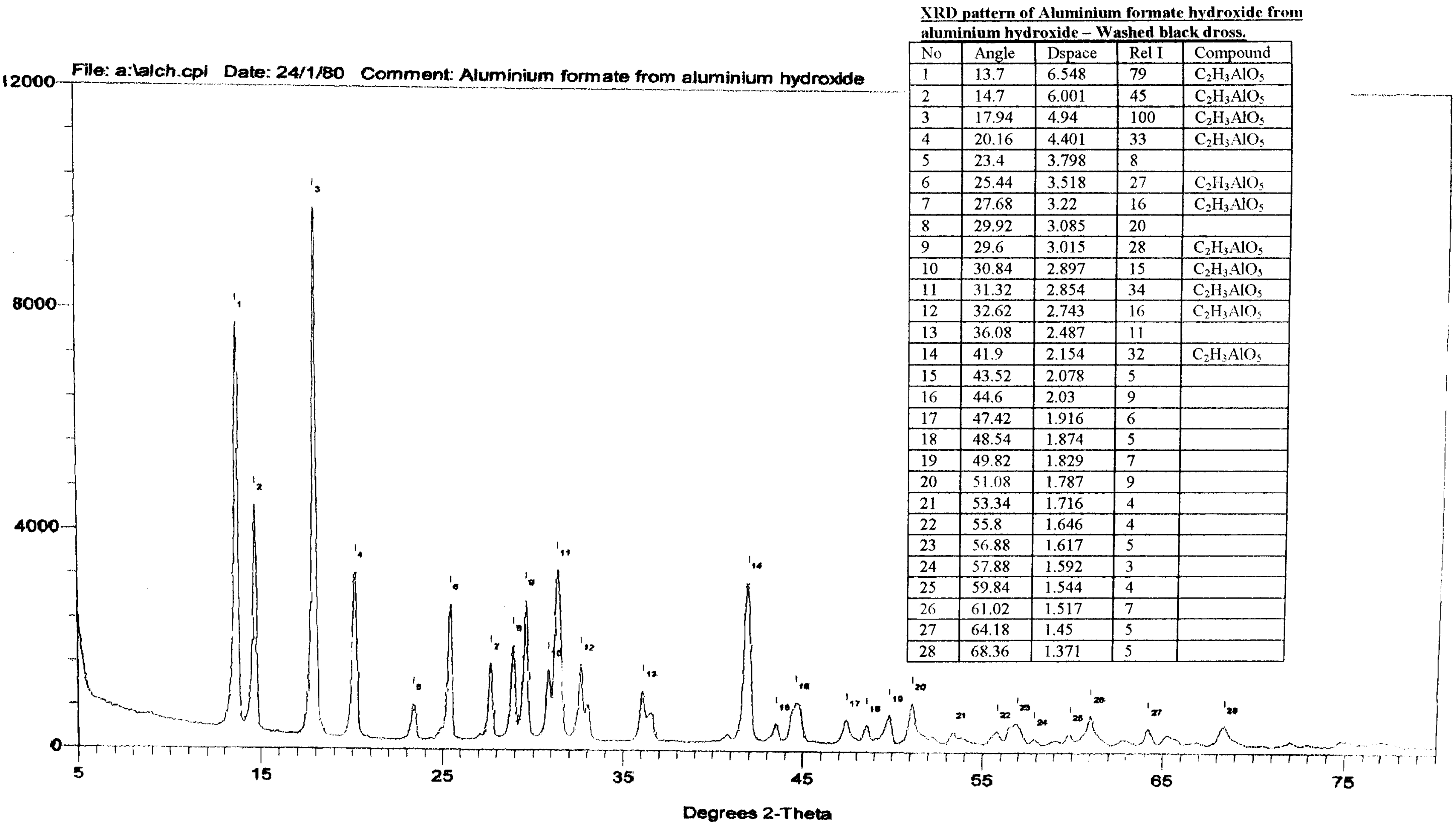
A large amount of washed black dross was used to prepare a good quality sodium aluminate in order to develop an industrial based preparation and also to perform the economic calculations. Table-4.6 shows the effect of different concentrations of sodium hydroxide solution on the leaching of washed aluminium black dross.



**XRD pattern of Aluminium acetate hydroxide from aluminium hydroxide -washed Black dross**

| No | Angle | Dspace | Rel I | Compound |
|---|---|---|---|---|
| 1 | 12.54 | 7.05 | 45 | $Al(OH)(CH_3COO)_2$ |
| 2 | 14.08 | 6.285 | 100 | $Al(OH)(CH_3COO)_2$ |
| 3 | 17.78 | 4.984 | 6 | $Al(OH)(CH_3COO)_2$ |
| 4 | 18.28 | 4.489 | 8 | |
| 5 | 19.4 | 4.572 | 39 | $Al(OH)(CH_3COO)_2$ |
| 6 | 22.78 | 3.9 | 30 | $Al(OH)(CH_3COO)_2$ |
| 7 | 24.7 | 3.601 | 7 | $Al(OH)(CH_3COO)_2$ |
| 8 | 26.44 | 3.368 | 33 | $Al(OH)(CH_3COO)_2$ |
| 9 | 27.16 | 3.281 | 12 | |
| 10 | 29.68 | 3.007 | 13 | $Al(OH)(CH_3COO)_2$ |
| 11 | 30.38 | 2.94 | 12 | $Al(OH)(CH_3COO)_2$ |
| 12 | 30.92 | 2.89 | 18 | |
| 13 | 32.22 | 2.776 | 9 | $Al(OH)(CH_3COO)_2$ |
| 14 | 36.1 | 2.486 | 15 | $Al(OH)(CH_3COO)_2$ |
| 15 | 36.9 | 2.434 | 12 | $Al(OH)(CH_3COO)_2$ |
| 16 | 38.68 | 2.326 | 14 | $Al(OH)(CH_3COO)_2$ |
| 17 | 41.48 | 2.175 | 5 | $Al(OH)(CH_3COO)_2$ |
| 18 | 43.22 | 2.092 | 9 | $Al(OH)(CH_3COO)_2$ |
| 19 | 46.56 | 1.949 | 9 | $Al(OH)(CH_3COO)_2$ |
| 20 | 48.58 | 1.873 | 10 | $Al(OH)(CH_3COO)_2$ |

**Figure-4.28. XRD spectrum of aluminium acetate produced from washed black dross aluminium hydroxide.**



**XRD pattern of Aluminium formate hydroxide from aluminium hydroxide – Washed black dross.**

| No | Angle | Dspace | Rel I | Compound |
|---|---|---|---|---|
| 1 | 13.7 | 6.548 | 79 | $C_2H_3AlO_5$ |
| 2 | 14.7 | 6.001 | 45 | $C_2H_3AlO_5$ |
| 3 | 17.94 | 4.94 | 100 | $C_2H_3AlO_5$ |
| 4 | 20.16 | 4.401 | 33 | $C_2H_3AlO_5$ |
| 5 | 23.4 | 3.798 | 8 | |
| 6 | 25.44 | 3.518 | 27 | $C_2H_3AlO_5$ |
| 7 | 27.68 | 3.22 | 16 | $C_2H_3AlO_5$ |
| 8 | 29.92 | 3.085 | 20 | |
| 9 | 29.6 | 3.015 | 28 | $C_2H_3AlO_5$ |
| 10 | 30.84 | 2.897 | 15 | $C_2H_3AlO_5$ |
| 11 | 31.32 | 2.854 | 34 | $C_2H_3AlO_5$ |
| 12 | 32.62 | 2.743 | 16 | $C_2H_3AlO_5$ |
| 13 | 36.08 | 2.487 | 11 | |
| 14 | 41.9 | 2.154 | 32 | $C_2H_3AlO_5$ |
| 15 | 43.52 | 2.078 | 5 | |
| 16 | 44.6 | 2.03 | 9 | |
| 17 | 47.42 | 1.916 | 6 | |
| 18 | 48.54 | 1.874 | 5 | |
| 19 | 49.82 | 1.829 | 7 | |
| 20 | 51.08 | 1.787 | 9 | |
| 21 | 53.34 | 1.716 | 4 | |
| 22 | 55.8 | 1.646 | 4 | |
| 23 | 56.88 | 1.617 | 5 | |
| 24 | 57.88 | 1.592 | 3 | |
| 25 | 59.84 | 1.544 | 4 | |
| 26 | 61.02 | 1.517 | 7 | |
| 27 | 64.18 | 1.45 | 5 | |
| 28 | 68.36 | 1.371 | 5 | |

**Figure-4.29. XRD spectrum of aluminium formate hydroxide produced from washed black dross aluminium hydroxide.**

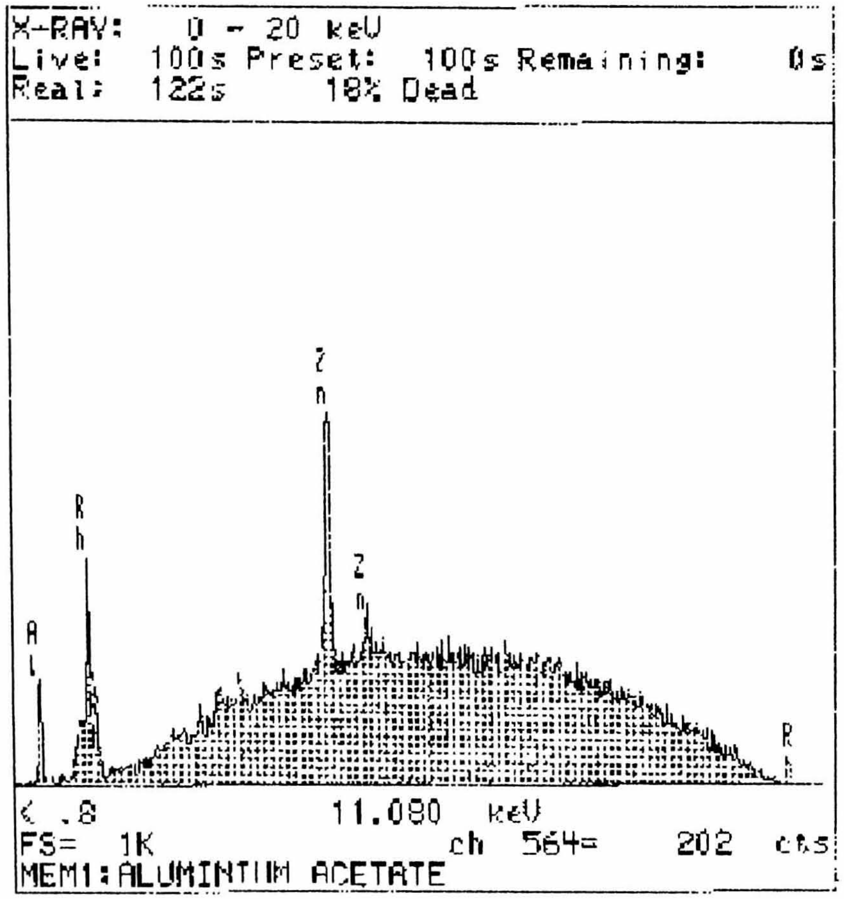


**Figure-4.30. XRF spectrum of Aluminium acetate hydroxide produced from aluminium hydroxide, prepared from black dross**

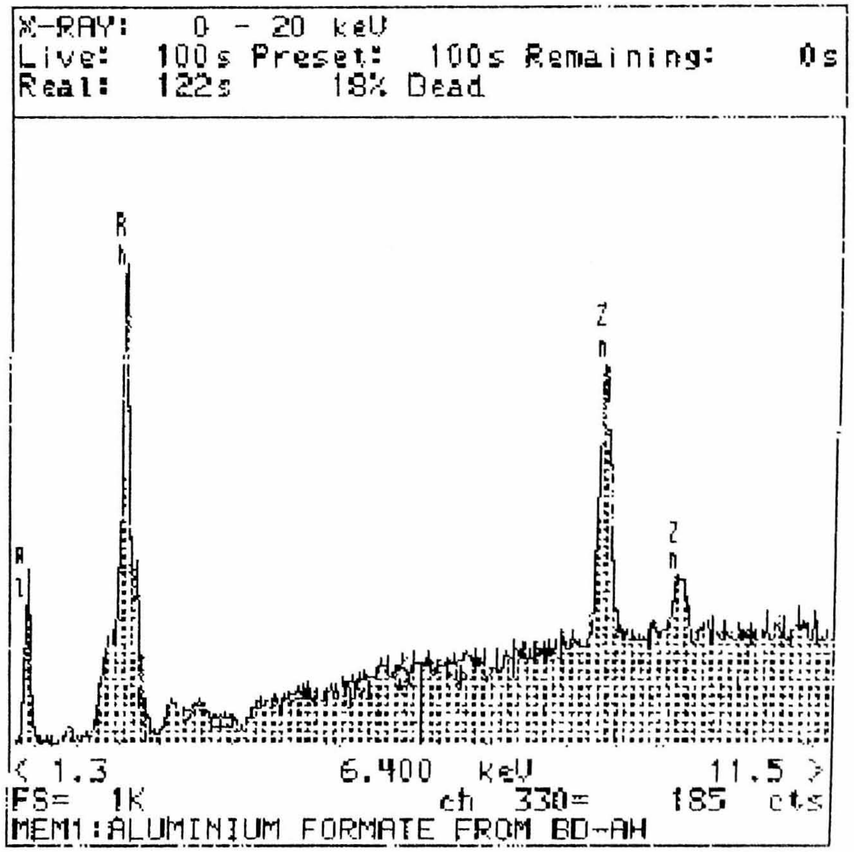


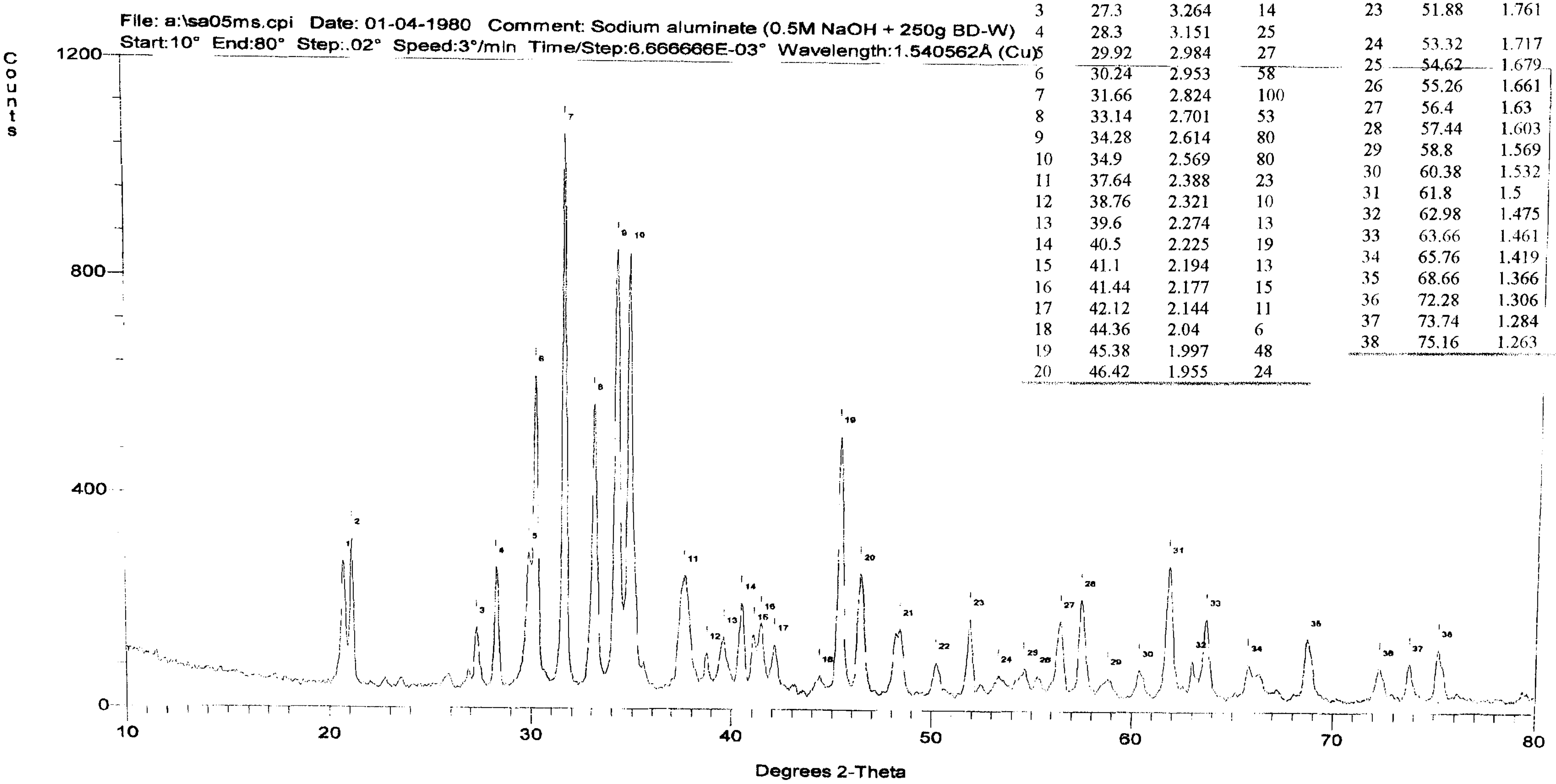
**Figure-4.31. XRF spectrum of Aluminium formate hydroxide produced from aluminium hydroxide, prepared from black dro**

**Table-4.6. Effect of sodium hydroxide concentration on the leaching of washed black dross**

| Sodium hydroxide concentration (mol dm$^{-3}$) | Weight of black dross (g) | Weight of dried residue (g) | Wt. of sodium aluminate recovered (g) |
|---|---|---|---|
| 0.5 | 250 | 262 | 17 |
| 1.0 | 250 | 214 | 34 |
| 2.0 | 250 | 232 | 64 |
| 3.0 | 250 | 267 | 53 |
| 4.0 | 250 | 268 | 115 |
| 5.0 | 250 | 270 | 162 |

The results in Table-4.6 show that, in most cases, the weight of the dried residue is higher than the amount of black dross (250g) used to leach the aluminium. This arises because, during sodium hydroxide leaching, only aluminium is soluble but other metal impurities (Fe, Cu, Cr, Ni etc) precipitate as hydroxides and ultimately increase the weight of the residue.

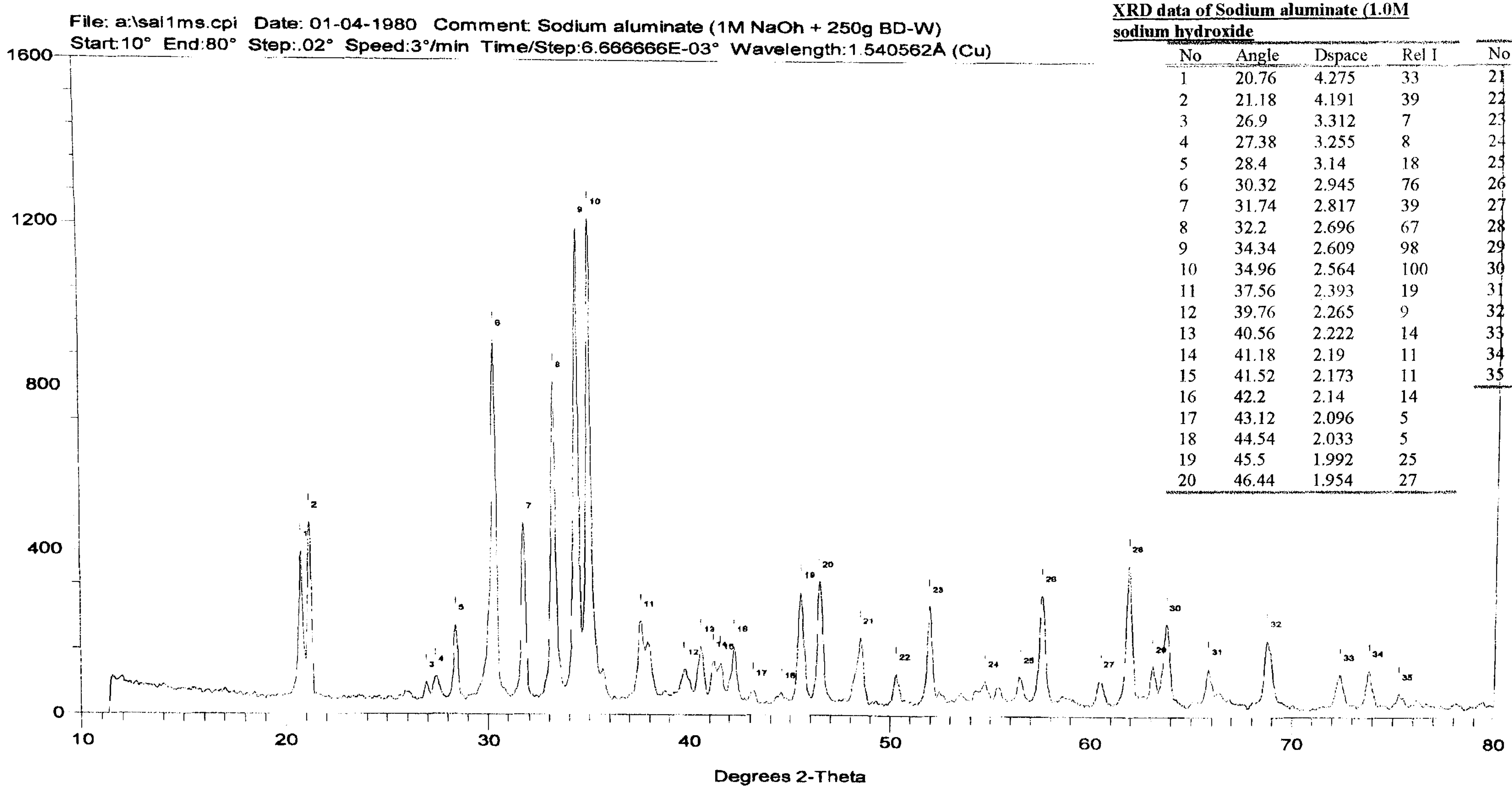
Sodium aluminate samples were characterised using the XRD technique. Compared with the analytical grade sodium aluminate (Figure-4.2), the XRD spectra of the sodium aluminate prepared from black dross samples (figure-4.32-4.36) show that a good quality sodium aluminate can be obtained using 0.5 – 4.0M sodium hydroxide solution. The use of a 5.0M sodium hydroxide solution, however, leads to the formation of a contaminated sodium aluminate (Figure-4.37). The results show that 4M sodium hydroxide solution (500ml) is the optimum concentration for the complete recovery of aluminium from 250g of washed black dross sample, as the yield is high. The XRF spectrum (Figure-4.38) shows that the product contains zinc as an impurity. The concentration analysed by AAS was found to be 0.02%.



**XRD data of Sodium aluminate (0.5M sodium hydroxide**

| No | Angle | Dspace | Rel I |
|---|---|---|---|
| 1 | 20.68 | 4.292 | 25 |
| 2 | 21.12 | 4.203 | 30 |
| 3 | 27.3 | 3.264 | 14 |
| 4 | 28.3 | 3.151 | 25 |
| 5 | 29.92 | 2.984 | 27 |
| 6 | 30.24 | 2.953 | 58 |
| 7 | 31.66 | 2.824 | 100 |
| 8 | 33.14 | 2.701 | 53 |
| 9 | 34.28 | 2.614 | 80 |
| 10 | 34.9 | 2.569 | 80 |
| 11 | 37.64 | 2.388 | 23 |
| 12 | 38.76 | 2.321 | 10 |
| 13 | 39.6 | 2.274 | 13 |
| 14 | 40.5 | 2.225 | 19 |
| 15 | 41.1 | 2.194 | 13 |
| 16 | 41.44 | 2.177 | 15 |
| 17 | 42.12 | 2.144 | 11 |
| 18 | 44.36 | 2.04 | 6 |
| 19 | 45.38 | 1.997 | 48 |
| 20 | 46.42 | 1.955 | 24 |
| 21 | 48.4 | 1.879 | 14 |
| 22 | 50.2 | 1.816 | 9 |
| 23 | 51.88 | 1.761 | 16 |
| 24 | 53.32 | 1.717 | 6 |
| 25 | 54.62 | 1.679 | 8 |
| 26 | 55.26 | 1.661 | 6 |
| 27 | 56.4 | 1.63 | 16 |
| 28 | 57.44 | 1.603 | 20 |
| 29 | 58.8 | 1.569 | 6 |
| 30 | 60.38 | 1.532 | 7 |
| 31 | 61.8 | 1.5 | 26 |
| 32 | 62.98 | 1.475 | 9 |
| 33 | 63.66 | 1.461 | 16 |
| 34 | 65.76 | 1.419 | 8 |
| 35 | 68.66 | 1.366 | 13 |
| 36 | 72.28 | 1.306 | 8 |
| 37 | 73.74 | 1.284 | 9 |
| 38 | 75.16 | 1.263 | 11 |

**Figure-4.32. XRD spectrum of sodium aluminate produced from bulk amount washed black dross using 0.5M sodium hydroxide**

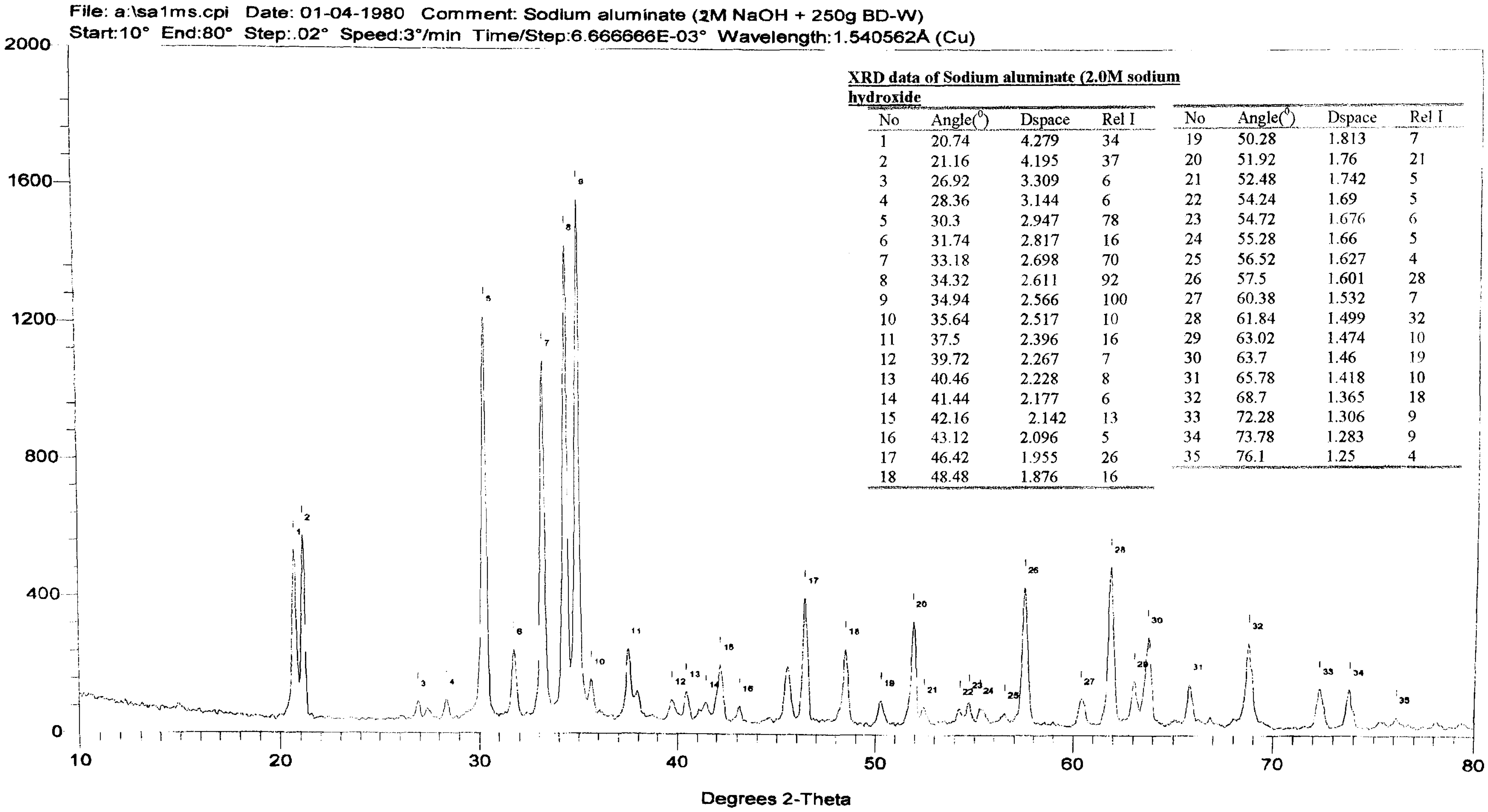


**XRD data of Sodium aluminate (1.0M sodium hydroxide**

| No | Angle | Dspace | Rel I |
|---|---|---|---|
| 1 | 20.76 | 4.275 | 33 |
| 2 | 21.18 | 4.191 | 39 |
| 3 | 26.9 | 3.312 | 7 |
| 4 | 27.38 | 3.255 | 8 |
| 5 | 28.4 | 3.14 | 18 |
| 6 | 30.32 | 2.945 | 76 |
| 7 | 31.74 | 2.817 | 39 |
| 8 | 32.2 | 2.696 | 67 |
| 9 | 34.34 | 2.609 | 98 |
| 10 | 34.96 | 2.564 | 100 |
| 11 | 37.56 | 2.393 | 19 |
| 12 | 39.76 | 2.265 | 9 |
| 13 | 40.56 | 2.222 | 14 |
| 14 | 41.18 | 2.19 | 11 |
| 15 | 41.52 | 2.173 | 11 |
| 16 | 42.2 | 2.14 | 14 |
| 17 | 43.12 | 2.096 | 5 |
| 18 | 44.54 | 2.033 | 5 |
| 19 | 45.5 | 1.992 | 25 |
| 20 | 46.44 | 1.954 | 27 |

| No | Angle | Dspace | |
|---|---|---|---|
| 21 | 48.5 | 1.875 | |
| 22 | 50.28 | 1.813 | |
| 23 | 51.94 | 1.759 | |
| 24 | 54.7 | 1.677 | |
| 25 | 56.46 | 1.628 | |
| 26 | 57.54 | 1.6 | |
| 27 | 60.46 | 1.53 | |
| 28 | 61.88 | 1.498 | |
| 29 | 63.06 | 1.473 | |
| 30 | 63.72 | 1.459 | |
| 31 | 65.82 | 1.418 | |
| 32 | 68.72 | 1.365 | 1 |
| 33 | 72.36 | 1.305 | 9 |
| 34 | 73.78 | 1.283 | 1 |
| 35 | 75.26 | 1.262 | 5 |

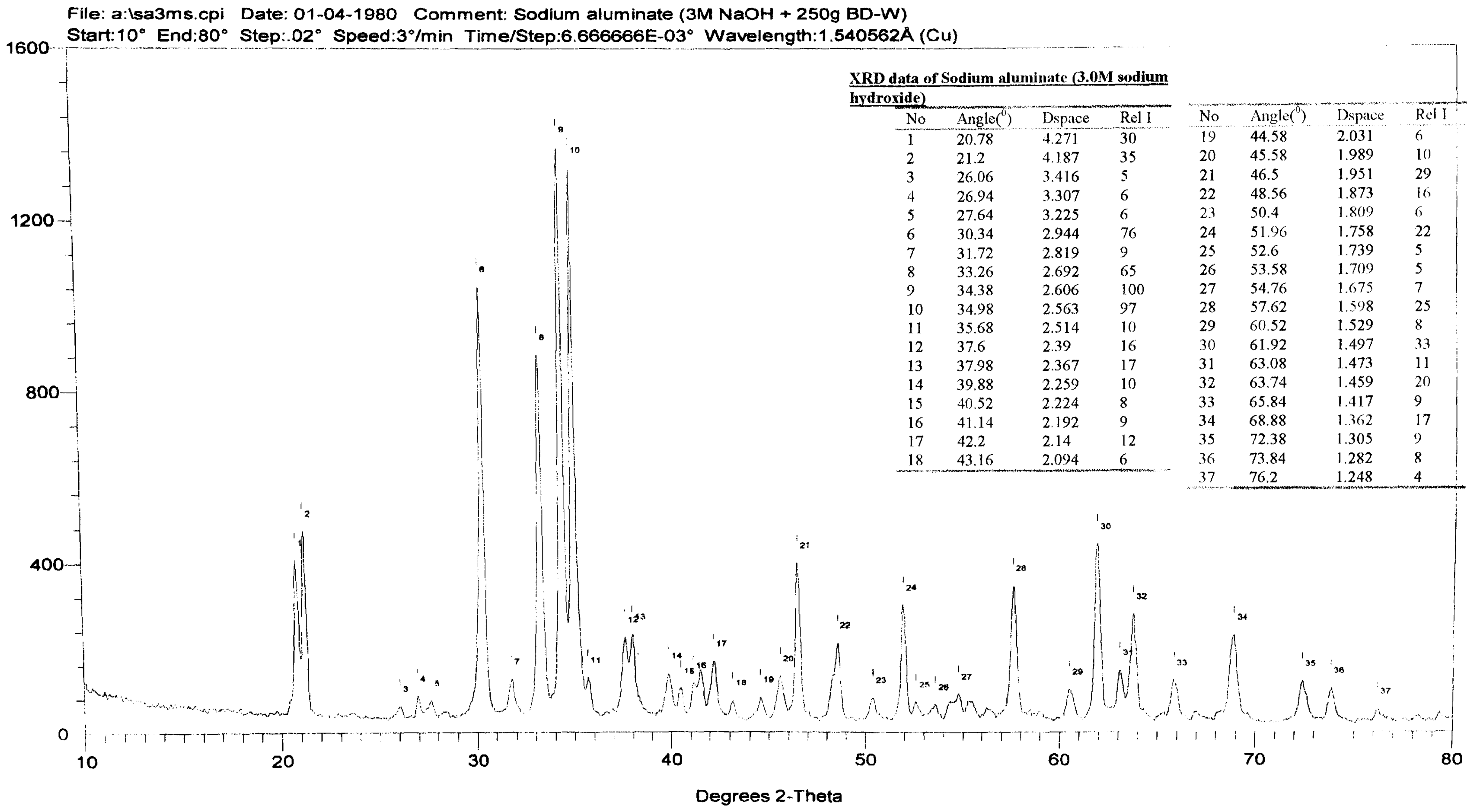
**Figure-4.33. XRD spectrum of sodium aluminate produced from bulk amount washed black dross using 1M sodium hydroxide**



**XRD data of Sodium aluminate (2.0M sodium hydroxide**

| No | Angle(⁰) | Dspace | Rel I |
|---|---|---|---|
| 1 | 20.74 | 4.279 | 34 |
| 2 | 21.16 | 4.195 | 37 |
| 3 | 26.92 | 3.309 | 6 |
| 4 | 28.36 | 3.144 | 6 |
| 5 | 30.3 | 2.947 | 78 |
| 6 | 31.74 | 2.817 | 16 |
| 7 | 33.18 | 2.698 | 70 |
| 8 | 34.32 | 2.611 | 92 |
| 9 | 34.94 | 2.566 | 100 |
| 10 | 35.64 | 2.517 | 10 |
| 11 | 37.5 | 2.396 | 16 |
| 12 | 39.72 | 2.267 | 7 |
| 13 | 40.46 | 2.228 | 8 |
| 14 | 41.44 | 2.177 | 6 |
| 15 | 42.16 | 2.142 | 13 |
| 16 | 43.12 | 2.096 | 5 |
| 17 | 46.42 | 1.955 | 26 |
| 18 | 48.48 | 1.876 | 16 |
| 19 | 50.28 | 1.813 | 7 |
| 20 | 51.92 | 1.76 | 21 |
| 21 | 52.48 | 1.742 | 5 |
| 22 | 54.24 | 1.69 | 5 |
| 23 | 54.72 | 1.676 | 6 |
| 24 | 55.28 | 1.66 | 5 |
| 25 | 56.52 | 1.627 | 4 |
| 26 | 57.5 | 1.601 | 28 |
| 27 | 60.38 | 1.532 | 7 |
| 28 | 61.84 | 1.499 | 32 |
| 29 | 63.02 | 1.474 | 10 |
| 30 | 63.7 | 1.46 | 19 |
| 31 | 65.78 | 1.418 | 10 |
| 32 | 68.7 | 1.365 | 18 |
| 33 | 72.28 | 1.306 | 9 |
| 34 | 73.78 | 1.283 | 9 |
| 35 | 76.1 | 1.25 | 4 |

Figure-4.34. XRD spectrum of sodium aluminate produced from bulk amount washed black dross using 2M sodium hydroxide



**XRD data of Sodium aluminate (3.0M sodium hydroxide)**

| No | Angle(⁰) | Dspace | Rel I |
|---|---|---|---|
| 1 | 20.78 | 4.271 | 30 |
| 2 | 21.2 | 4.187 | 35 |
| 3 | 26.06 | 3.416 | 5 |
| 4 | 26.94 | 3.307 | 6 |
| 5 | 27.64 | 3.225 | 6 |
| 6 | 30.34 | 2.944 | 76 |
| 7 | 31.72 | 2.819 | 9 |
| 8 | 33.26 | 2.692 | 65 |
| 9 | 34.38 | 2.606 | 100 |
| 10 | 34.98 | 2.563 | 97 |
| 11 | 35.68 | 2.514 | 10 |
| 12 | 37.6 | 2.39 | 16 |
| 13 | 37.98 | 2.367 | 17 |
| 14 | 39.88 | 2.259 | 10 |
| 15 | 40.52 | 2.224 | 8 |
| 16 | 41.14 | 2.192 | 9 |
| 17 | 42.2 | 2.14 | 12 |
| 18 | 43.16 | 2.094 | 6 |
| 19 | 44.58 | 2.031 | 6 |
| 20 | 45.58 | 1.989 | 10 |
| 21 | 46.5 | 1.951 | 29 |
| 22 | 48.56 | 1.873 | 16 |
| 23 | 50.4 | 1.809 | 6 |
| 24 | 51.96 | 1.758 | 22 |
| 25 | 52.6 | 1.739 | 5 |
| 26 | 53.58 | 1.709 | 5 |
| 27 | 54.76 | 1.675 | 7 |
| 28 | 57.62 | 1.598 | 25 |
| 29 | 60.52 | 1.529 | 8 |
| 30 | 61.92 | 1.497 | 33 |
| 31 | 63.08 | 1.473 | 11 |
| 32 | 63.74 | 1.459 | 20 |
| 33 | 65.84 | 1.417 | 9 |
| 34 | 68.88 | 1.362 | 17 |
| 35 | 72.38 | 1.305 | 9 |
| 36 | 73.84 | 1.282 | 8 |
| 37 | 76.2 | 1.248 | 4 |

**Figure-4.35. XRD spectrum of sodium aluminate produced from bulk amount washed black dross using 3M sodium hydroxide**

**XRD data of Sodium aluminate (4.0M sodium hydroxide**

| No | Angle($^0$) | Dspace | Rel I |
|---|---|---|---|
| 1 | 20.74 | 4.279 | 36 |
| 2 | 21.14 | 4.199 | 38 |
| 3 | 26. | 3.424 | 7 |
| 4 | 26.9 | 3.312 | 7 |
| 5 | 27.58 | 3.232 | 8 |
| 6 | 28.32 | 3.149 | 6 |
| 7 | 30.26 | 2.951 | 81 |
| 8 | 31.7 | 2.82 | 13 |
| 9 | 33.18 | 2.698 | 71 |
| 10 | 34.3 | 2.612 | 98 |
| 11 | 34.92 | 2.567 | 100 |
| 12 | 37.5 | 2.396 | 19 |
| 13 | 37.94 | 2.37 | 26 |
| 14 | 39.86 | 2.26 | 18 |
| 15 | 40.42 | 2.23 | 9 |
| 16 | 41.1 | 2.194 | 12 |
| 17 | 41.44 | 2.177 | 15 |
| 18 | 42.16 | 2.142 | 15 |
| 19 | 43.08 | 2.098 | 6 |
| 20 | 44.44 | 2.037 | 7 |
| 21 | 45.52 | 1.991 | 11 |
| 22 | 46.4 | 1.955 | 31 |
| 23 | 48.46 | 1.877 | 17 |
| 24 | 50.26 | 1.814 | 7 |
| 25 | 51.88 | 1.761 | 22 |

| No | Angle($^0$) | Dspace | Rel I |
|---|---|---|---|
| 26 | 52.5 | 1.742 | 6 |
| 27 | 53.48 | 1.712 | 8 |
| 28 | 54.6 | 1.679 | 9 |
| 29 | 55.28 | 1.66 | 7 |
| 30 | 56.22 | 1.635 | 5 |
| 31 | 57.5 | 1.601 | 26 |
| 32 | 58.4 | 1.579 | 5 |
| 33 | 58.96 | 1.565 | 5 |
| 34 | 60.44 | 1.53 | 9 |
| 35 | 61.84 | 1.499 | 32 |
| 36 | 63. | 1.474 | 10 |
| 37 | 63.68 | 1.46 | 21 |
| 38 | 65.78 | 1.418 | 11 |
| 39 | 68.7 | 1.365 | 17 |
| 40 | 72.32 | 1.305 | 9 |
| 41 | 73.74 | 1.284 | 9 |
| 42 | 74.46 | 1.273 | 4 |
| 43 | 76.18 | 1.249 | 4 |

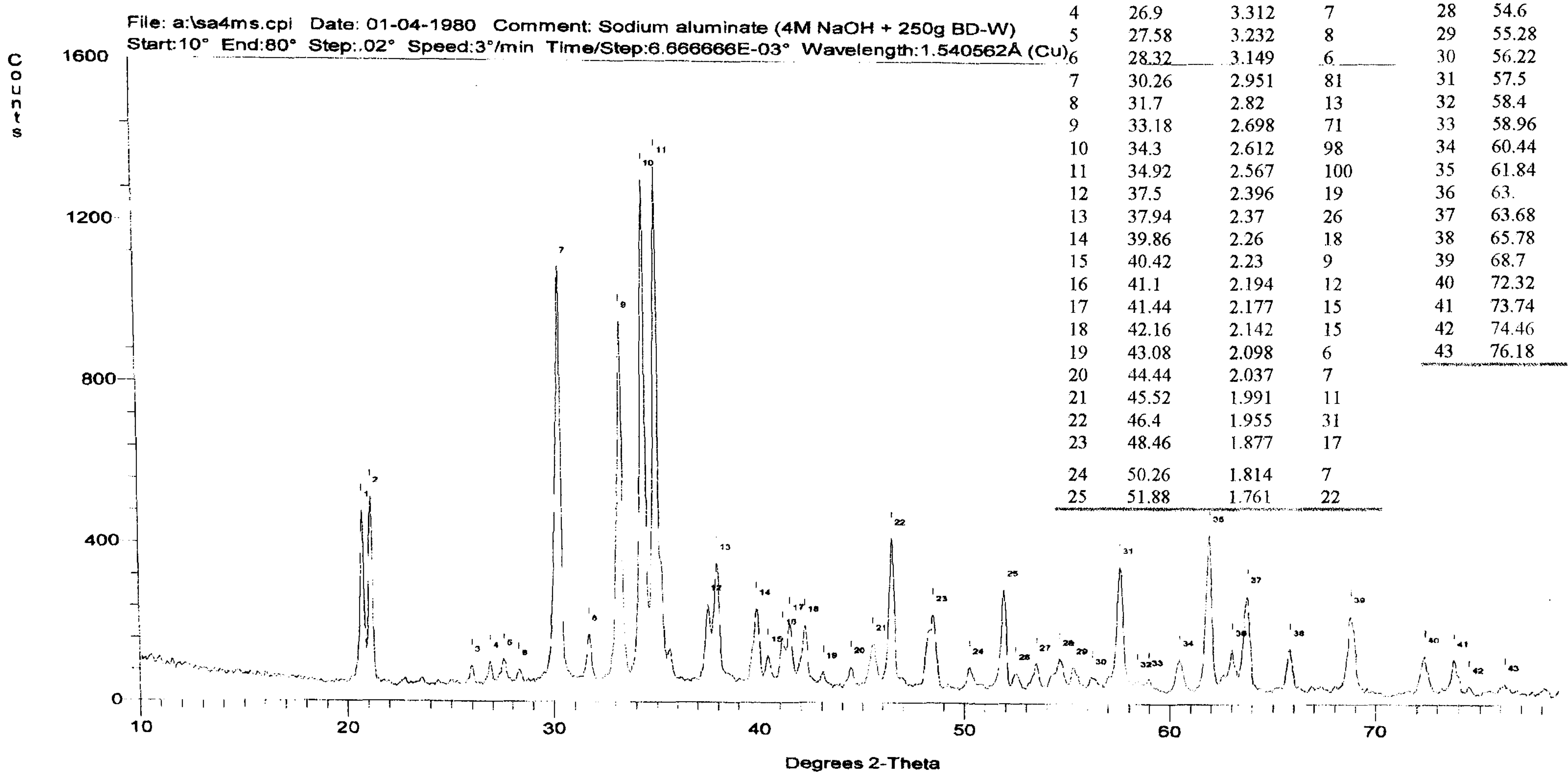
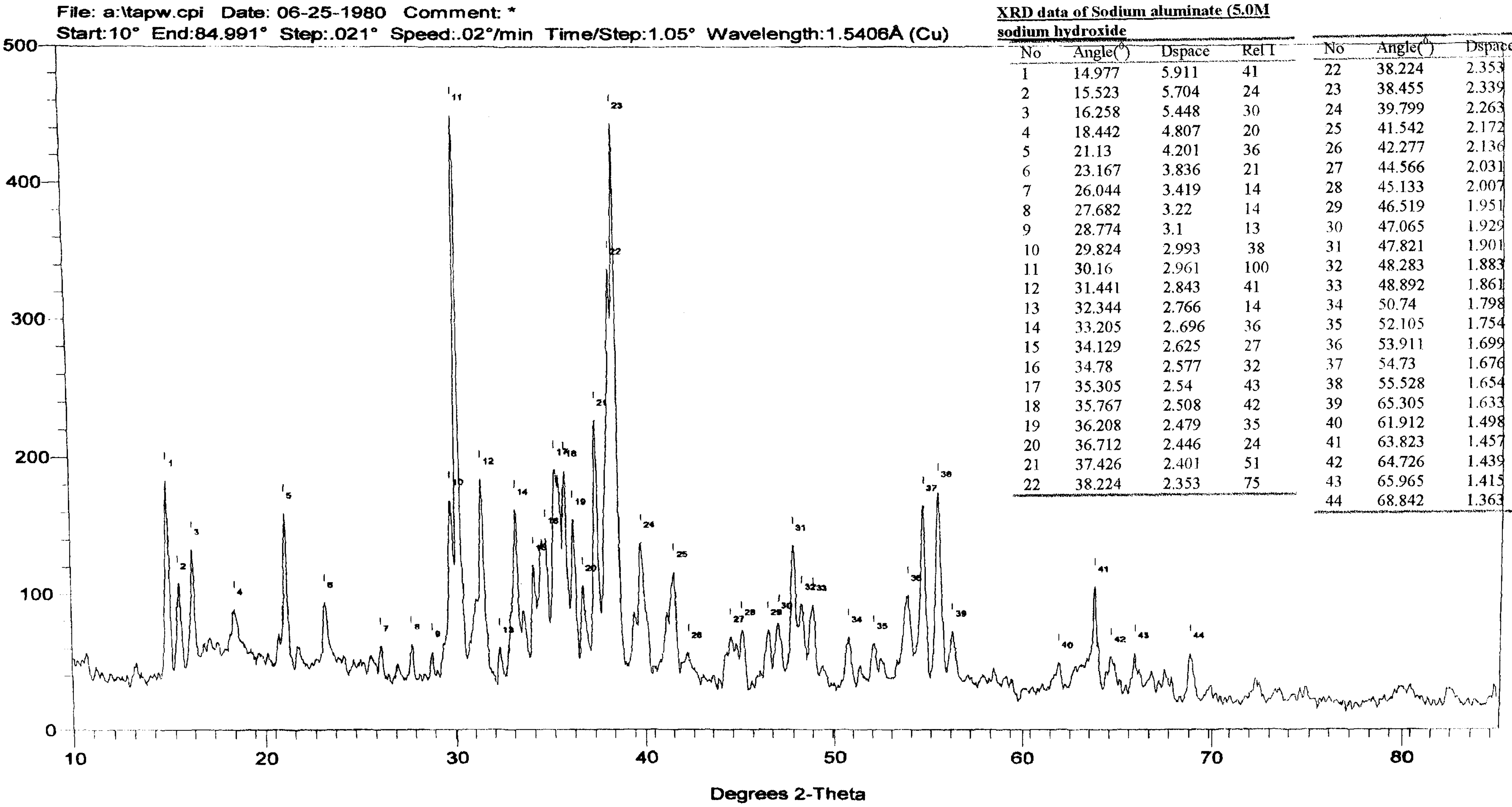


Figure-4.36. XRD spectrum of sodium aluminate produced from bulk amount washed black dross using 4M sodium hydroxide


File: a:\tapw.cpi Date: 06-25-1980 Comment: *
Start:10° End:84.991° Step:.021° Speed:.02°/min Time/Step:1.05° Wavelength:1.5406Å (Cu)

**XRD data of Sodium aluminate (5.0M sodium hydroxide**

| No | Angle(°) | Dspace | Rel I |
|---|---|---|---|
| 1 | 14.977 | 5.911 | 41 |
| 2 | 15.523 | 5.704 | 24 |
| 3 | 16.258 | 5.448 | 30 |
| 4 | 18.442 | 4.807 | 20 |
| 5 | 21.13 | 4.201 | 36 |
| 6 | 23.167 | 3.836 | 21 |
| 7 | 26.044 | 3.419 | 14 |
| 8 | 27.682 | 3.22 | 14 |
| 9 | 28.774 | 3.1 | 13 |
| 10 | 29.824 | 2.993 | 38 |
| 11 | 30.16 | 2.961 | 100 |
| 12 | 31.441 | 2.843 | 41 |
| 13 | 32.344 | 2.766 | 14 |
| 14 | 33.205 | 2..696 | 36 |
| 15 | 34.129 | 2.625 | 27 |
| 16 | 34.78 | 2.577 | 32 |
| 17 | 35.305 | 2.54 | 43 |
| 18 | 35.767 | 2.508 | 42 |
| 19 | 36.208 | 2.479 | 35 |
| 20 | 36.712 | 2.446 | 24 |
| 21 | 37.426 | 2.401 | 51 |
| 22 | 38.224 | 2.353 | 75 |
| 22 | 38.224 | 2.353 | 75 |
| 23 | 38.455 | 2.339 | 99 |
| 24 | 39.799 | 2.263 | 31 |
| 25 | 41.542 | 2.172 | 26 |
| 26 | 42.277 | 2.136 | 13 |
| 27 | 44.566 | 2.031 | 15 |
| 28 | 45.133 | 2.007 | 16 |
| 29 | 46.519 | 1.951 | 16 |
| 30 | 47.065 | 1.929 | 18 |
| 31 | 47.821 | 1.901 | 30 |
| 32 | 48.283 | 1.883 | 21 |
| 33 | 48.892 | 1.861 | 20 |
| 34 | 50.74 | 1.798 | 15 |
| 35 | 52.105 | 1.754 | 14 |
| 36 | 53.911 | 1.699 | 22 |
| 37 | 54.73 | 1.676 | 37 |
| 38 | 55.528 | 1.654 | 39 |
| 39 | 65.305 | 1.633 | 16 |
| 40 | 61.912 | 1.498 | 11 |
| 41 | 63.823 | 1.457 | 24 |
| 42 | 64.726 | 1.439 | 12 |
| 43 | 65.965 | 1.415 | 13 |
| 44 | 68.842 | 1.363 | 13 |

Figure-4.37. XRD spectrum of sodium aluminate produced from bulk amount washed black dross using 5M sodium hydroxide

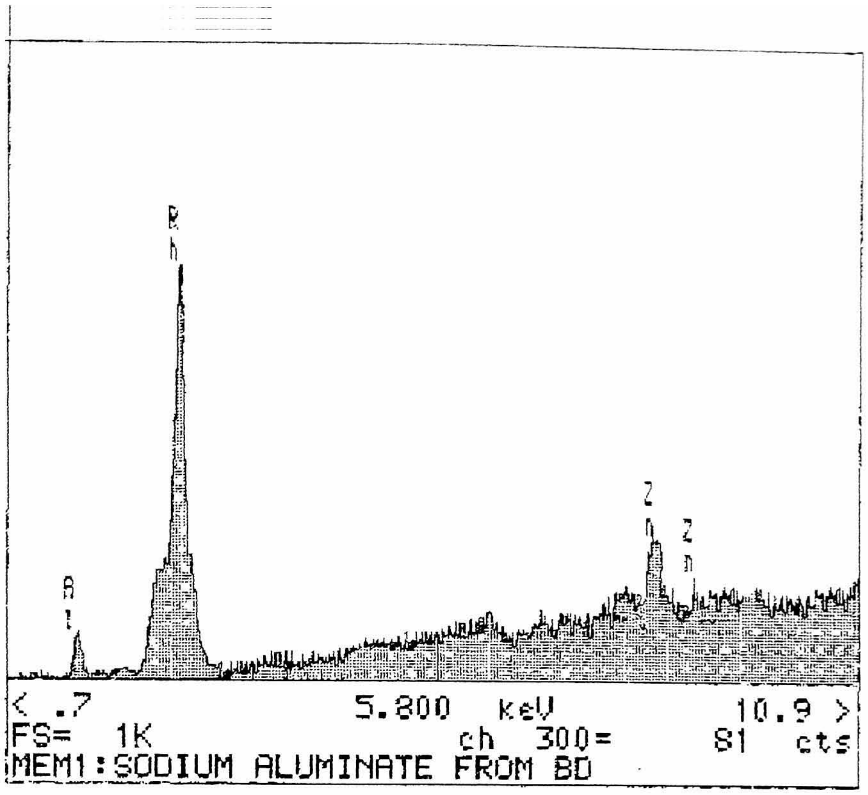


**Figure-4.38. XRF spectrum of sodium aluminate produced from bulk amount of black dross and 4M sodium hydroxide.**

## 4.4.9. Analysis of black dross residue after leaching with (4M) sodium hydroxide

After leaching black dross sample with sodium hydroxide, the dry mass weight of the residue was found to be higher (268g) than the initial weight (250g). The dross residue was analysed. The XRF spectrum (Figure 4.39) of the dross residue sample shows the presence of: Cr, Cu, Fe, Mn, Ti, Si and Zn.

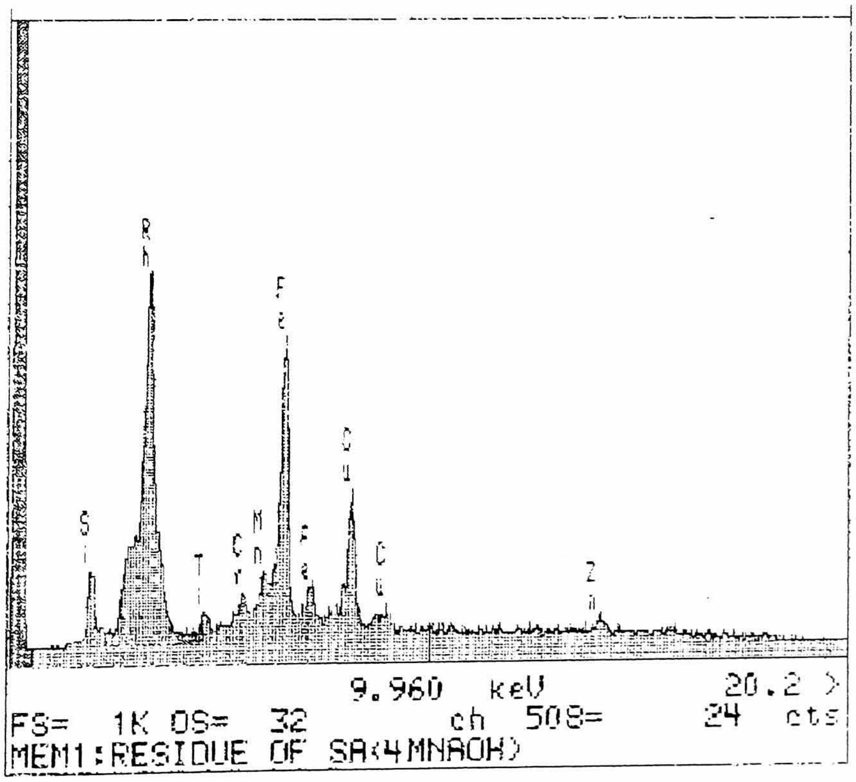


**Figure-4.39. XRF spectrum of washed black dross residue after treatment with 4M sodium hydroxide**

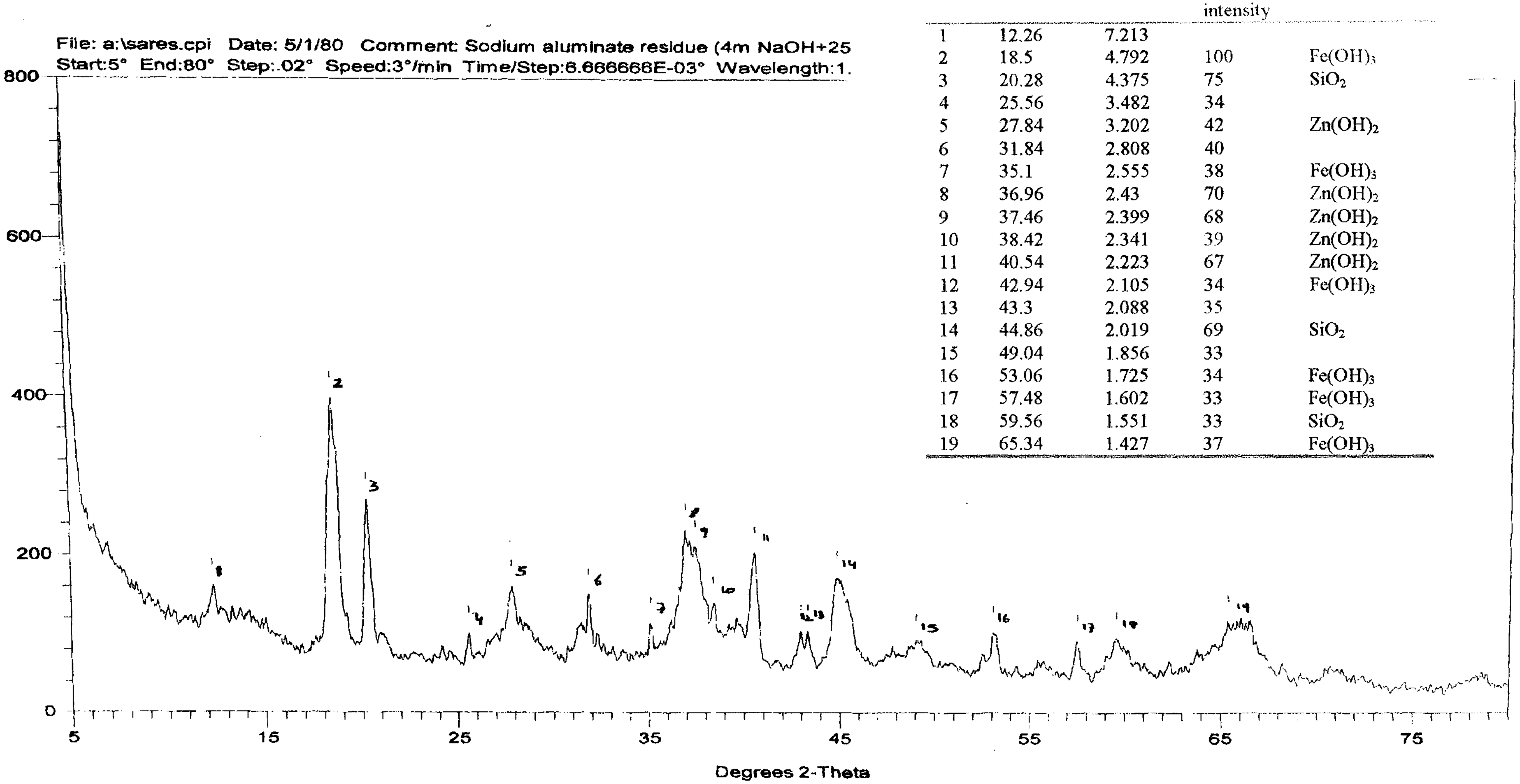
The XRD result (Figure-4.40) of the dross residue shows presence of iron hydroxide [$Fe(OH)_3$], zinc hydroxide [$Zn(OH)_2$] and silica ($SiO_2$). The dross residue was leached with de-ionised water at room temperature and at $100^0$C, and 2M HCl at $100^0$C. The results are summarised in Table-4.7.

**Table-4.7. Analysis of black dross residue**

| Leaching media and Temp | De-ionised water at room temp | De-ionised water at $100^0$C | 2M HCl at $100^0$C | Env Agency (Lower threshold)[10] |
|---|---|---|---|---|
| Weight (g) | 2.5 | 2.5 | 2.5 | - |
| Vol of leaching media (ml) | 100 | 100 | 100 | - |
| Time (h) | 3 | 3 | 3 | - |
| Residue after leaching (g) | 2.49 | 2.33 | 0.96 | - |
| Conc of elements (mg/kg) | | | | |
| Cr | 13.6 | 3.2 | 680 | 600 |
| Cu | 1.2 | 0.8 | 2800 | 130 |
| Fe | 5.2 | 2.4 | 14160 | N/A |
| Mn | 1.2 | 1.2 | 2000 | N/A |
| Ti | 0.2 | 0.2 | 5000 | N/A |
| Zn | 1.2 | 1.2 | 1400 | 300 |

N/A= Not Applicable

It can be seen that the compounds in the dross residue are not very soluble in water even at raised temperature. The amount of heavy metals leached out in water does not exceed the Environment Agency's lower threshold value limit. The residue was later leached with 2M HCl at raised temperature and it was found that almost 60% is dissolved in this reagent. The results in Table-4.7 show that iron dominates the residue after the aluminium has been leached out by sodium hydroxide. Copper, manganese, titanium and zinc are also present. The XRF and XRD spectra (Figure-4.41 and 4.42) of the dross residue after treatment with 2M HCl show that the undissolved residue is silica ($SiO_2$).



**XRD data of Washed black dross residue after treated with 4M NaOH**

| No | Angle(°) | D space | Relative intensity | Peak identity |
|---|---|---|---|---|
| 1 | 12.26 | 7.213 | | |
| 2 | 18.5 | 4.792 | 100 | $Fe(OH)_3$ |
| 3 | 20.28 | 4.375 | 75 | $SiO_2$ |
| 4 | 25.56 | 3.482 | 34 | |
| 5 | 27.84 | 3.202 | 42 | $Zn(OH)_2$ |
| 6 | 31.84 | 2.808 | 40 | |
| 7 | 35.1 | 2.555 | 38 | $Fe(OH)_3$ |
| 8 | 36.96 | 2.43 | 70 | $Zn(OH)_2$ |
| 9 | 37.46 | 2.399 | 68 | $Zn(OH)_2$ |
| 10 | 38.42 | 2.341 | 39 | $Zn(OH)_2$ |
| 11 | 40.54 | 2.223 | 67 | $Zn(OH)_2$ |
| 12 | 42.94 | 2.105 | 34 | $Fe(OH)_3$ |
| 13 | 43.3 | 2.088 | 35 | |
| 14 | 44.86 | 2.019 | 69 | $SiO_2$ |
| 15 | 49.04 | 1.856 | 33 | |
| 16 | 53.06 | 1.725 | 34 | $Fe(OH)_3$ |
| 17 | 57.48 | 1.602 | 33 | $Fe(OH)_3$ |
| 18 | 59.56 | 1.551 | 33 | $SiO_2$ |
| 19 | 65.34 | 1.427 | 37 | $Fe(OH)_3$ |

Figure-4.40. XRD spectrum of washed black dross residue after treated with 4M hydroxide and 2M HCl at 100$^0$C.

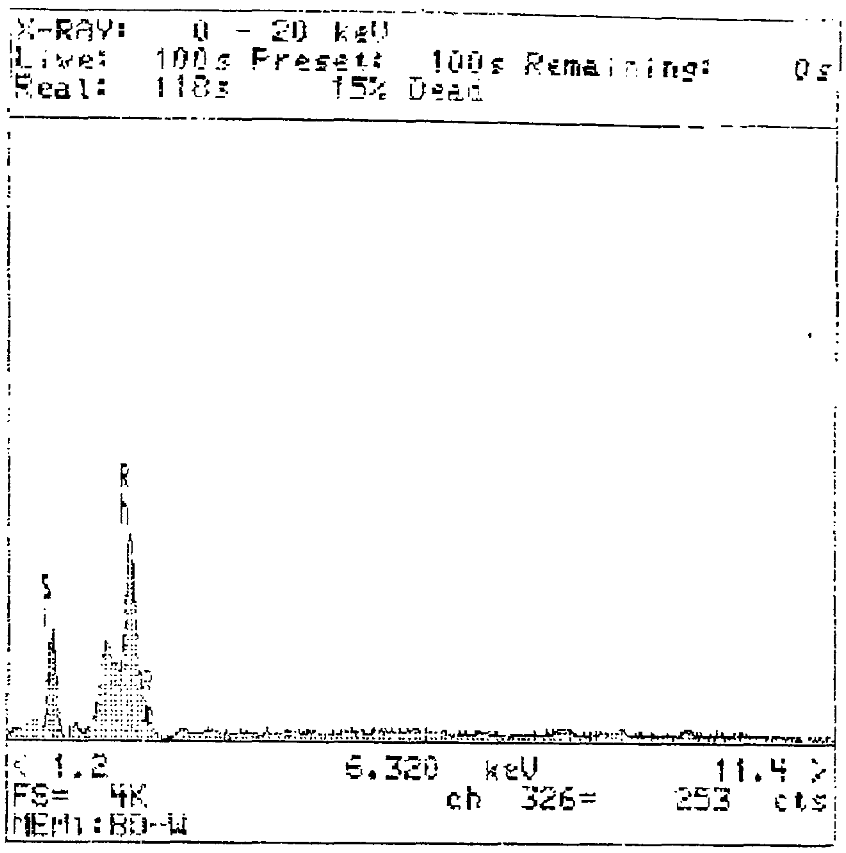
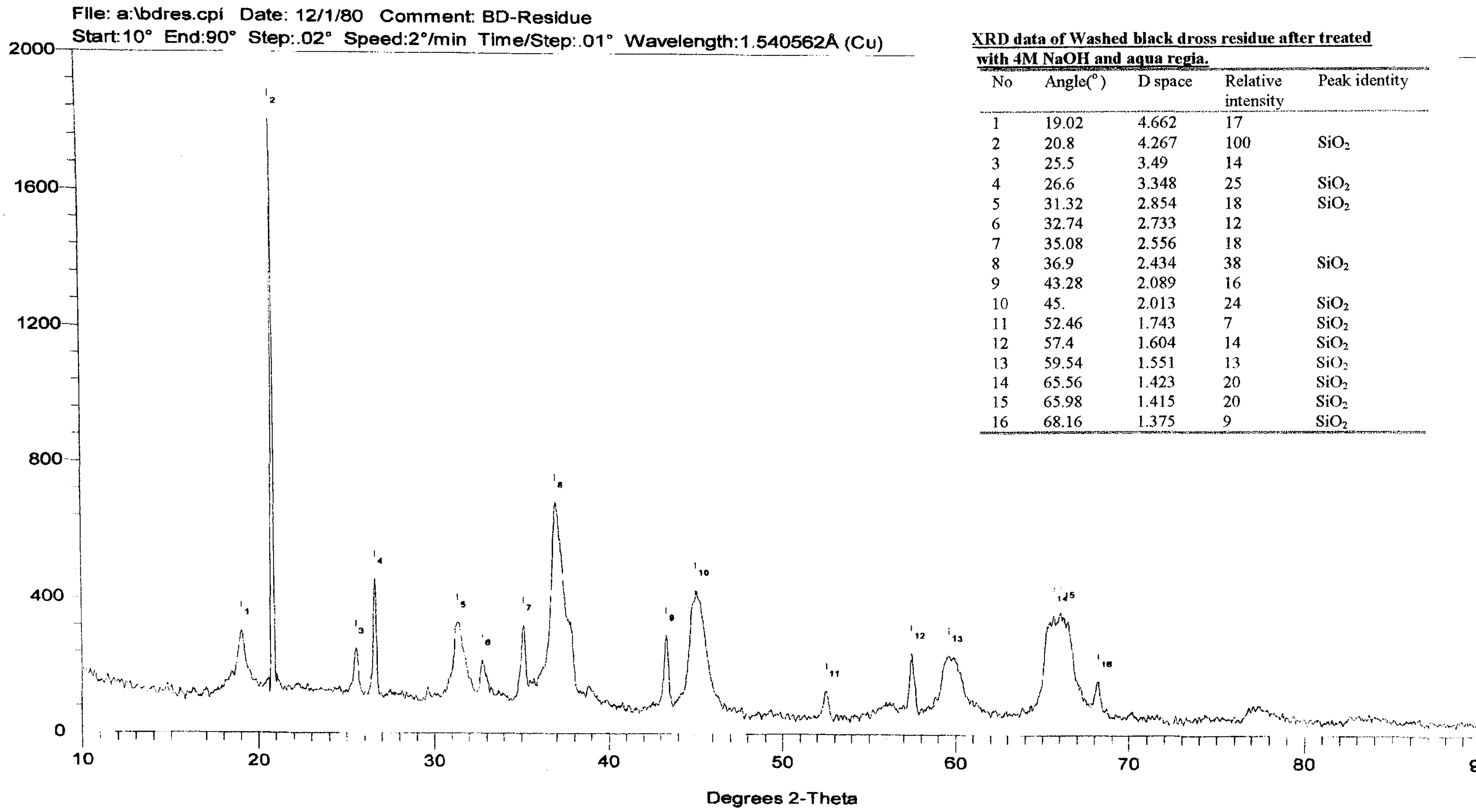


**Figure-4.41. XRD spectrum of washed black dross residue after treated with 4M sodium hydroxide and 2M HCl.**

The aim of this project is to reclaim the valuable aluminium from the black dross tailings. The experimental work has shown that aluminium can be successfully recovered from dross by preparing a selection of added value chemicals and the purity of the chemicals are >95%. After aluminium has been reclaimed, the dross sample is left with mainly iron and considerable amount of copper, manganese, titanium and zinc, which are found to be relatively insoluble in water, and therefore, is safe to landfill. The disadvantage of landfilling will be economical rather than environmental.

Leaching of black dross with sodium hydroxide leads to the production of hydroxides of various metals (Cr, Cu, Fe, Mn, Ti and Zn), which increases the final weight of the black dross residue. As a parallel study to the work presented in this study, research was carried out[11] in CER at Brunel University on the uses of this dross residue as a soil conditioner, in brick and concrete production, in road surfacing.



**XRD data of Washed black dross residue after treated with 4M NaOH and aqua regia.**

| No | Angle(°) | D space | Relative intensity | Peak identity |
|---|---|---|---|---|
| 1 | 19.02 | 4.662 | 17 | |
| 2 | 20.8 | 4.267 | 100 | $SiO_2$ |
| 3 | 25.5 | 3.49 | 14 | |
| 4 | 26.6 | 3.348 | 25 | $SiO_2$ |
| 5 | 31.32 | 2.854 | 18 | $SiO_2$ |
| 6 | 32.74 | 2.733 | 12 | |
| 7 | 35.08 | 2.556 | 18 | |
| 8 | 36.9 | 2.434 | 38 | $SiO_2$ |
| 9 | 43.28 | 2.089 | 16 | |
| 10 | 45. | 2.013 | 24 | $SiO_2$ |
| 11 | 52.46 | 1.743 | 7 | $SiO_2$ |
| 12 | 57.4 | 1.604 | 14 | $SiO_2$ |
| 13 | 59.54 | 1.551 | 13 | $SiO_2$ |
| 14 | 65.56 | 1.423 | 20 | $SiO_2$ |
| 15 | 65.98 | 1.415 | 20 | $SiO_2$ |
| 16 | 68.16 | 1.375 | 9 | $SiO_2$ |

**Figure-4.42. XRD spectrum of washed black dross residue after treated with 4M sodium hydroxide and aqua regia.**

## 4.9. ECONOMIC ASSESSMENT OF ALUMINIUM RECLAMATION

### 4.9.1. Production of Sodium aluminate

The commercial product is available as either a liquid containing about 22% by weight of sodium aluminate (£350 per ton) or as a solid product (£1000 per ton)[12] which is essentially anhydrous. In this current research work a good quality sodium aluminate was produced by simply dissolving washed black dross in sodium hydroxide at atmospheric boiling point. The process is similar to the Bayer process. Figure 4.42 presents a pie chart of alumina refining (through Bayer process) cash cost based in year 2002. This chart is based on research work by AME Mineral Economics[13], which is a global firm of independent economists in the metal and mineral industries with offices in Australia and North America. AME specialises in all the market and financial aspects of the aluminium, coal, copper, gold, iron ore, steel, lead, zinc, nickel and titanium mineral industries. Figure 4.42 is based on 51 refineries representing around 96% of current world alumina production. As the process of production sodium aluminate in this current work is similar to the Bayer process, the economical calculation is carried out based on the Figure 4.42.

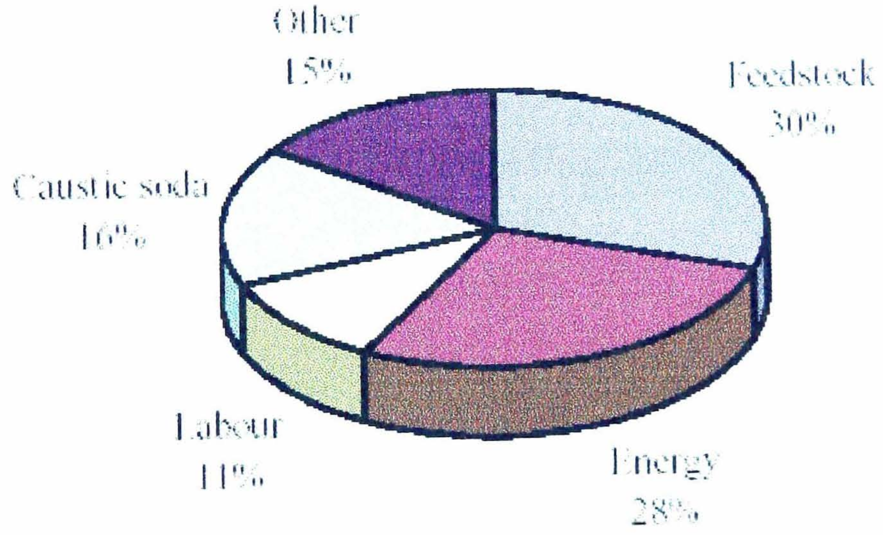


Figure-4.42. Elements of alumina refining cash costs[13] in 2002

30% of the costs are feedstock costs. These feedstock costs can be eliminated by using the dross in place of aluminium ore. The process using dross as the feedstock is essentially the same as the process for aluminium ore; therefore, the labour energy and other costs will remain the same for both processes (based on 1 kg sodium aluminate production). To produce an equivalent quantity of sodium aluminate, the dross process requires sodium hydroxide in the same quantities as for the aluminium ore. Therefore, the production costs for producing sodium aluminate from dross would be 30% lower than for producing sodium aluminate using aluminium ore. Table 4.8 presents the cost of individual items to produce sodium aluminate (solid) from aluminium ore and aluminium dross. It can be seen that production of sodium aluminate from dross is clearly profitable.

**Table-4.8. Cost of individual items to produce sodium aluminate**

| Item | Cost from Ore | Cost from Dross |
|---|---|---|
| Labour | 11p / kg (of $NaAlO_2$) | 11p / kg (of $NaAlO_2$) |
| NaOH | 16p / kg (of $NaAlO_2$) | 16p / kg (of $NaAlO_2$) |
| Energy | 28p / kg (of $NaAlO_2$) | 28p / kg (of $NaAlO_2$) |
| Feedstock | 30p/ kg (of $NaAlO_2$) | 0p |
| Other costs | 15p / kg (of $NaAlO_2$) | 15p / kg (of $NaAlO_2$) |
| Total | 100p / kg | 70p / kg |

### 4.9.2. Production of aluminium hydroxide from dross.

Due to the low concentration of aluminium in the dross, hydrogen peroxide was added to precipitate out aluminium hydroxide from the sodium aluminate solution.

**Table-4.9. Cost of individual elements to produce aluminium hydroxide**

| Item | Cost from Ore | Cost from Dross |
|---|---|---|
| Labour | 4p / kg (of $Al(OH)_3$) | 4p / kg (of $Al(OH)_3$) |
| NaOH | 6p / kg (of $Al(OH)_3$) | 0p ($NaAlO_2$ sol from BD) |
| Energy | 10p / kg (of $Al(OH)_3$) | 10p / kg (of $Al(OH)_3$) |
| Feedstock | 11p/ kg (of $Al(OH)_3$) | 176p$H_2O_2$/kg(of $Al(OH)_3$) |
| Other costs | 5p / kg (of $Al(OH)_3$) | 5p / kg (of $Al(OH)_3$) |
| Total | 36p / kg | 195p / kg |

Table 4.9 shows the cost of individual items to produce on kg aluminium hydroxide using black dross and aluminium ore through Bayer process. It can be seen that the cost of the hydrogen peroxide is very high which means the production of aluminium hydroxide from black dross is very expensive as well. However, there are other materials that could be used to produce aluminium hydroxide from sodium aluminate

(extracted from black dross), such as carbon dioxide, ammonium carbonate, ammonium bicarbonate, sulphuric acid etc. Hydrogen peroxide was chosen in order to prevent external contamination. Besides, price of sodium aluminate is more expensive in markets than aluminium hydroxide. The research work in this project has successfully produced very good quality sodium aluminate from black dross, which is also economically viable. There is scope for further research into using other compounds for producing aluminium hydroxide from black dross and making economically profitable.

## 4.10. SUMMARY

Black dross tailings, an aluminium waste product, has been landfilled every year costing millions of pounds of landfill tax to the aluminium smelters. Currently no viable methods are available to reclaim the valuable aluminium from the dross. The current research has shown that aluminium can be reclaimed from black dross tailings through producing aluminium compounds. Good quality sodium aluminate, aluminium hydroxide, aluminium oxide, aluminium sulphate, aluminium nitrate, aluminium chloride and aluminium carboxylates have been produced. After producing a bulk amount of sodium aluminate, the black dross residue was found to be greater than the original black dross. As the dross was treated with sodium hydroxide the residue contains different hydroxides, such as iron and zinc. Future research has been undertaken to reclaim the other elements from the black dross tailings and also the uses of the residue in road construction. The economical analysis has shown that the production of sodium aluminate is economically viable. However, aluminium hydroxide which was produced from sodium aluminate solution is not economically viable as the reducing agent hydrogen peroxide is very expensive. Other compounds can be used to produce aluminium hydroxide which could be more economically viable. This leads to an extended scope for future research work.

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# CHAPTER FIVE
# CONCLUSIONS

Dross is the inevitable waste product generated by the world-wide primary and secondary aluminium industries. Around 3.5 million tonnes of white dross and 0.85 million tonnes of black dross are produced per year world-wide. Half of the white dross and all of the black dross are currently landfilled because there is no commercially viable method to reclaim the valuable aluminium and the other elements. This is causing industries a huge economical loss through enourmous landfill tax and loss of aluminium. The practice of landfilling is also causing pollution in the environment as the dross contains a number of harmful elements.

As black dross contains maximum of 15 wt% of aluminium and the fact that the sodium chloride used in the smelting process makes up 50 wt% of the dross; the treatment of this black dross is complex. White dross, on the other hand, contains higher amount (40 wt%) of aluminium, a greater percentage of which is reasonably pure aluminium oxide

The focus of this research therefore, is on the development of methods to recover value from black dross, and divert this waste away from landfill disposal. The objectives of the research described in this thesis are:

(i)Characterisation and composition;
(ii)Purification by leaching out impurity phases with specific leach reagents;
(iii)Size fractionation to determine the relationship between size and impurity level;
(iv)Leachability studies to simulate landfill conditions;
(v)Dissolution of solid phases by digestion or leaching to give aluminium-containing solutions;
(vi)Purification of aluminium containing solutions to remove other metal impurities;
(vii)Recovery of commercially useful aluminium compounds from the aluminium-containing solutions;
(viii)Economic assessment of the developed technology;

Considering each of these objectives in turn, the output from the research is now described;

### *(i) Characterisation and composition*

Aluminium dross composition was found to be a mixture of various elements. Half of the dross (by mass) is a mixture of sodium and potassium chloride. Once the dross was washed thoroughly with water, the remaining residue was found to be mainly alumina with other main impurities: silica, iron oxide and copper oxide. Other trace amounts of metallic oxides were also observed.

### *(ii). Recovery of salt by counter-current leaching process*

A counter-current leaching process with water was designed to achieve salt recovery by spontaneous crystallisation from supersaturated solutions. The process was shown to be economically viable and there is no need of heating, and also reduced water consumption.

### *(iii) Dissolution of solid phases by digestion or leaching to give aluminium - containing solution and purification of aluminium containing solutions to remove other metal impurities*

Leaching of washed black dross was carried out in both acidic and alkaline media. Total dissolution of black dross could not be achieved under either condition at any temperature as silica is not very soluble within the conditions used. Most of aluminium can be dissolved in sodium hydroxide solution at elevated temperature with trace amount of impurities.

### *(iv) Size fractionating to determine the relationship between size and impurity level*

Analysis of the different particle size fractions of black dross shows that the aluminium content is higher in the larger particle sizes and sodium concentration increases with decreasing particle size. The coarse particles consist of pure aluminium metal covered with aluminium oxide layer. The fine particles are mainly salts and other impurities. Therefore, significant aluminium can be recovered (concentrated) by crushing black dross into reasonable particle size using crushers. Although by this method the presence of the salt cannot be avoided as it will be in every particle size distribution, its presence will be much less in the coarse fractions.

### (v). Leachability studies to simulate landfill conditions

An investigation was carried out on the leaching behaviour of the black dross under landfill conditions to identify any adverse environmental effects due to landfilling black dross. Leachability studies were carried with soil components, water, and with leach media to model the following conditions: humic acid-containing systems, acid rain (pH 2.5), and acetic acid solutions (pH 5). Up to 60 wt% of the dross was leached out in all media with the production of the saline solution providing the major impact. Only small amounts of aluminium were leached out by these solutions. Four different possible fates of aluminium were observed under the simulated environmental conditions used: (a) aluminium cations bound on the clay surface by ionic exchange (making available for plant uptake) (b) in the presence of humic acid aluminium ions form soluble Al-humic complex (aluminium mobility) (c) in the presence of humic acid and soil components aluminium ions are bound on the both surfaces through ligand exchange, forming complex bridges (not available for plant uptake) (d) in the presence of acid rain (pH 2.5) and acetic acid (pH 5.0) aluminium precipitates as nitrate, sulphate and acetate salts (making available for plants uptake) and these precipitates can be washed away reaching to aquifer, causing toxic effects to the aquatic organisms.

No leachability behaviour was detected once black dross was washed and salt has been removed. Washed black dross is not significantly soluble in any of the leach media. Therefore, landfilling washed black dross can minimise both environmental (no harmful elements leach out) and economical (reduction of mass weight by half as the salt been removed) problems.

### (vi). Recovery of commercially useful aluminium compounds from the aluminium-containing solutions

The primary product of the sodium hydroxide leaching of the recovered metal oxide is a sodium aluminate solution that can be used to crystallise out the sodium aluminate phase or as the raw material for the production of other aluminium chemicals. The production of aluminium hydroxide from sodium aluminate solution can be carried out by different methods most of which lead to the gelatinous precipitate that is difficult to filter, handle and dissolved. The novel method involves the slow addition of 30% hydrogen peroxide to sodium aluminate solution at ambient temperature to produce the crystalline modification, gibbsite. The product in this form is easy to filter handle, and dissolved in acid media for the preparation of aluminium salts. Using the aluminium hydroxide (gibbsite) as a raw material other aluminium salts were prepared. The compounds are: alumina, aluminium chloride, aluminium nitrate, aluminium sulphate, aluminium formate and aluminium acetate. All these compounds are >95% pure.

Apart from sodium aluminate, other aluminium salts can not be prepared straight from black dross just by dissolving it in the appropriate acidic media as the level of impurities are found too high. Unwashed black dross contains a large amount of NaCl and KCl salts and therefore, the products are saturated with these salts. The washed black dross is also not very suitable as it contains different metallic oxides, which are easily dissolved in the different acids at higher temperature.

### *(vii). Economic assessment of the developed technology*

Preliminary calculations on the data obtained after treating 1 kg of black dross showed that the technology developed to recycle black dross to sodium aluminate is economically viable. Aluminium hydroxide which was produced from sodium aluminate solution, showed to be not economically viable as the reducing agent hydrogen peroxide is very expensive. However, the price of sodium aluminate solution and solid is more expensive than aluminium hydroxide. The research work in this project has successfully produced very good quality sodium aluminate from black dross, which is also economically viable.

Figure-5.1 summarises the developments reported in this thesis. It represents a flow sheet of the methodology developed for:

(i) reduction of black dross by weight, by recovery of to 50% of salt

(ii) 100% recycle of the salt component of the dross

(iii) reclamation of aluminium by >98% and

(iv) preparation of aluminium compounds with >95% purity.

In summary for the first time it is reported that from a low grade alumnium waste, black dross, commercially viable chemicals have been prepared, the use of reagent minimised through recycle and the diversion of millions of tonnes of furnace residue from landfill can be achieved.

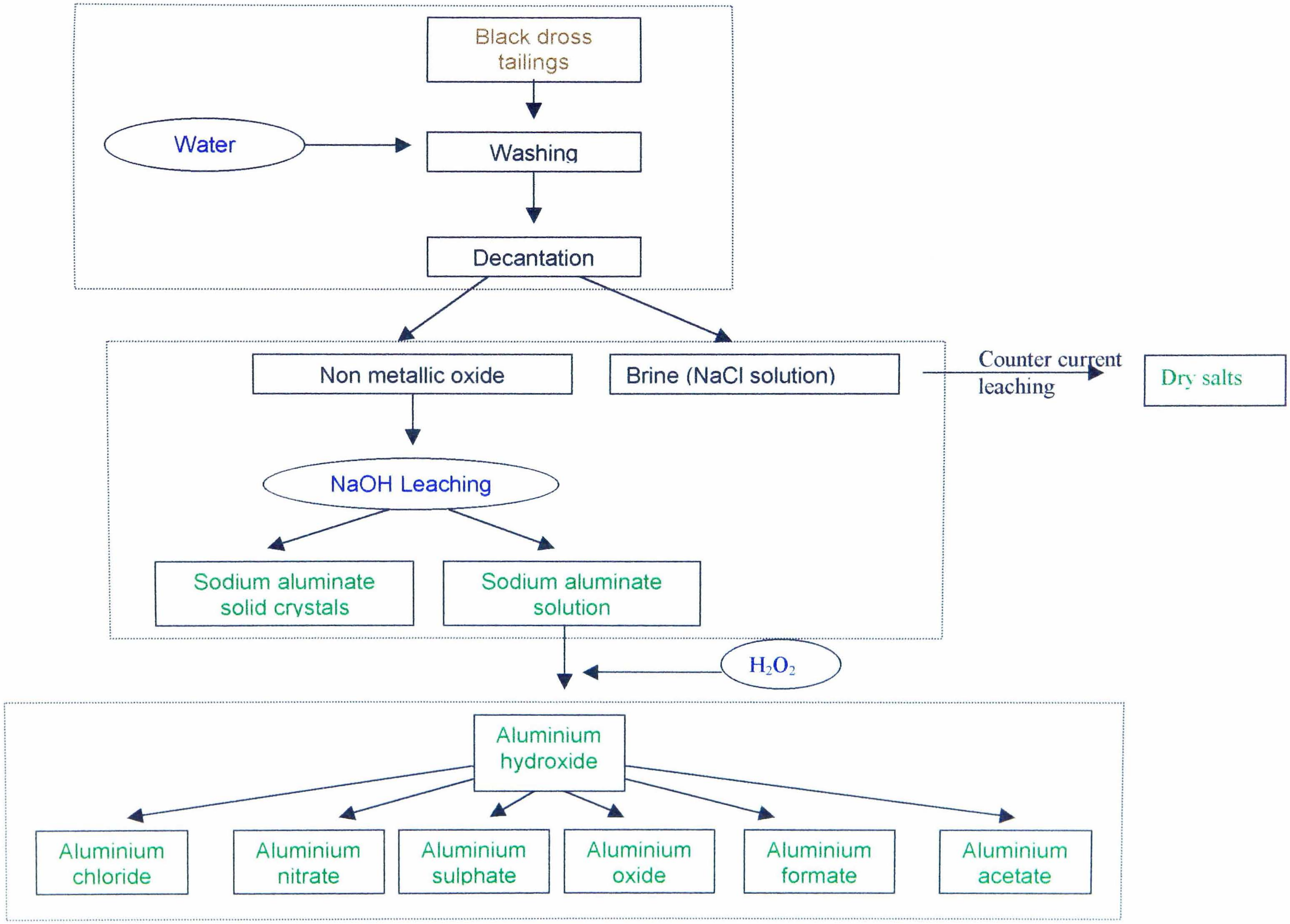

**Figure-5.1. Overall methodology for the recycling of black dross**