

Chapter- 1

Introduction

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Aluminium is one of the most important elements in the service of mankind. Apart from being one of the most abundant elements available, aluminium has found its applications in many fields. With a global production of 64 million tons, aluminium is used in numerous fields, namely production of utensils, beverage cans and generation of sophisticated alloys. Aviation industry is heavily dependent on aluminium alloys that furnish the required mechanical properties, reducing the overall weight, thereby increasing the fuel efficiency.

Waste aluminium products and aluminium scraps are being generated every day in large quantities. This trend of scrap and waste generated has escalated in the recent years. This is purely due to the sheer rise in the overall production of aluminium from the primary aluminium production industries. The focus has now been shifting toward the secondary aluminium production industries that consume the waste aluminium products and scraps to extract metallic aluminium. This 'shift' is to mitigate the excessive generation of these waste products.

When compared to the primary production of aluminium, secondary aluminium production reaches nearly 60 % for the year 2003. This trend has emerged with the utilization of scraps, wastes and recycled aluminium. It has also been projected that the growth rate of secondary aluminium industry is nearly 2.4 % per year [1-2]. Similarly in Japan, the secondary aluminium ingot production has reached 1257.7×10^3 tons [3]. In 2010, the total amount of secondary aluminium reserves across the world was around 413 million tons [4]. A large segment of this reserve ends up in the landfill sites, which is definitely not the justified method of recycling aluminium waste products.

Utilization of aluminium scraps through powder metallurgy and severe plastic deformation (SPD) can be carried out on a larger scale, but still the problem of waste aluminium persists [5]. The only method of resolving this issue is focusing on the secondary aluminium production industries.

It is not only the growth of aluminium production (primary and secondary) and application that attracts the attention of the researchers; the growth in the generation of aluminium industrial waste is also alarming the research fraternity. The important steps during recycling are sorting the raw feed/scraps obtained from various sources, salt fluxing of the given feed to maintain the required composition and remelting of the feed. As understood from the above, the raw materials used are beverage cans, scraps of aluminium. Secondary smelters are used for the remelting of these feed products. The molten metal comes in contact with atmosphere, leading to the formation of semisolid aluminium oxide. During the tapping process, this semisolid oxide skin is removed [6].

Apart from the major constituent phases of metallic aluminium, aluminium oxides, the other phases present in the semisolid products are oxides like silica, periclase and spinel, etc. along with the salts added (NaCl and KCl) during the remelting of the feed. Aluminium carbide and nitride are also present in traces [6-8]. The presence of carbides and nitrides in the dross is due to their formation after aluminium dross is removed from the remelting furnace. Aluminium reacting with carbon present in traces leads to aluminium carbide, whereas the nitrogen present in the atmosphere reacts with aluminium to give aluminium nitride [6, 9].

Maintaining operation temperature during the melting is essential. It has been reported that refining of molten aluminium is not quite efficient below 973 K whereas above 1063 K, the tendency of hydrogen absorption increases. Optimizing the operation

temperature to around 1013 K ensures proper refining while avoiding any hydrogen absorption. Salt fluxing around this temperature serves the purpose of refining the molten aluminium [10].

The salt fluxes come into the picture as equimolar salts (like NaCl and KCl) are added into the melting furnace during the melting process to bring down the operation temperature and to form a protective layer over the molten metal. Trapped along with the salt fluxes remains the metallic aluminium and alumina.

One of the important industrial wastes produced during the processing of aluminium ingots is the aluminium dross. Smelter units present in aluminium production plants consume raw aluminium obtained for the previous processing unit and melt / re-melt it according to the requirement. Such melting processes are carried out in appropriate melting furnaces.

Aluminium dross is a heterogeneous mixture of aluminium entrapped in the matrix of alumina. The researchers have always been interested in extracting metallic values from aluminium dross and reusing the same into the mainstream applications. It is still quite unexplored as to how metallic aluminium gets liberated from this matrix of alumina when the temperature of the dross is raised to around 900 °C. The preliminary study of aluminium dross leads to the classification of dross into three categories: white aluminium dross, black aluminium dross and salt cakes, depending upon the composition of the metallic aluminium present in it.

White aluminium dross has nearly 80 % of metallic aluminium and the rest is alumina and salt fluxes, whereas the black dross may have nearly 50 % aluminium content. The rest of the composition may have dominance of alumina and salt fluxes. Salt cakes primarily comprise of salt fluxes; these cakes have relatively less amount of alumina

and metallic aluminium. These cakes are produced when aluminium dross are consumed as raw materials for the extraction of metallic aluminium from it. Salt cakes are also referred to as the Non-Metallic Product (NMP) left over post liberation of aluminium. The composition of white aluminium dross, black aluminium dross and salt cakes is described in Table 1.1.

Table 1.1: The classification and composition of aluminium dross

Components	White Dross	Black Dross	Salt cakes
Aluminium	15-80	20-85	<5
Alumina	7-50	30-50	30-50
Salt fluxes	3-10	20-60	20-80

The presence of other metallic elements is fairly possible and quite common in aluminium dross. It has been observed that magnesium, zinc and iron may be present in aluminium dross in small quantities. This is mainly due to the interference of the alloying elements present in the raw feed of scraps taken during the melting and remelting of aluminium. If the scraps fed into the melting furnace comprises of these elements, it definitely gets reflected in the dross produced post melting.

A complete analysis of material flow of white aluminium dross in Japan shows that the domestic production and consumption of dross is around 234×10^3 tons whereas nearly 215×10^3 tons of residual waste is generated after the extraction of aluminium from the dross. This residual waste is consumed in hydrogen production and the aluminium dross is steelmaking industries [3].

The research fraternity is focused on the extraction of aluminium from dross because the total quantity of aluminium dross produced is very large. Nearly 15-25 kg of white dross is produced per ton of aluminium, whereas around 80 kg black dross is produced per ton of secondary aluminium. Depending upon the process parameters, nearly 200-500 kg salt cakes can be produced per ton of aluminium.

Observing the trend in the UK, nearly 200,000 tons of industrial aluminium waste (white dross and salt cakes) has been produced [11]. In order to recycle this amount of dross, nearly 80 million Euros were spent. Similarly, the production of dross is around 5 million tons. Examining the growth of the primary and secondary aluminium industries, it can be clearly projected that the dross generation will also increase [12].

Variation of composition is clearly observed when considering the amount of aluminium in the waste aluminium dross. These variations are basically the consequences of operational schemes followed in the primary and secondary smelter plants. To produce aluminium through secondary production, the sorting of the raw material is essential and a necessary step prior to the smelting process [13]. For instance, it has been observed that larger amount of metallic aluminium is lost to the dross generated during the recycling of coated aluminium sheets, as compared to the uncoated sheets [14]. Hence, the selection of raw materials becomes a very important parameter for the recycling of waste aluminium products.

The chemical composition gets drastically altered when operation parameters like the depth of dross removal and the speed of dross removal are changed. With higher speed of dross removal, the continuous film of the semisolid oxide present over the surface of molten aluminium breaks, inviting the metallic aluminium to be skimmed along with the semisolid layer of dross. This eventually drops the efficiency of the removal of dross

and incurs loss of metallic aluminium, which ends up being entrapped in the dross. Increasing the depth for the removal also results in the increase in the aluminium content in the dross [15].

The particles of dross have a tendency of forming granules when the metallic aluminium content is above 53 %, whereas with lower aluminium content, the oxide formation is commonly observed [9]. The entrapment of liquid metallic aluminum in the semisolid state and the agglomeration of aluminium inside the oxide films are major issues that lead to the metal losses. To understand and analyze the physical properties inherent in the heterogeneous dross waste, these factors are important.

Archimedes' Principle and fully automated pycnometer can be used to determine the density of the dross. It has been found that compacted dross can have density nearly $2.396 - 2.528 \text{ tons/m}^3$, whereas the density of granular dross is around $0.828 - 1.118 \text{ tons/m}^3$. In case of higher aluminium content, the compacting leads to sharp increase in the density of the dross, accompanied with morphological changes [9,16].

The inherent aluminium content of the waste aluminium dross is determined by leaching a known quantity of the waste aluminium dross with 6 N HCl solution for a period of 2 hours. The vacuum filtration of the leached liquor leads to the separation of the residual solid, leading to the difference in the weight of the samples. The difference is the aluminium content in the dross [16]. An alternative model has also been proposed, according to which the free aluminium content is the function of the density of the pressed skull of the dross, the density of the non-metallic phases present in the dross and the volume fraction of the closed pores [17].

To study other physical attributes of waste aluminium dross, bricks are prepared. This leads to the examination of permeability, volume shrinkage and bulk density cold-crush

strength. These bricks are subjected to various experiments. The composition of the bricks is of 50-90 % aluminium dross, with 10-50 % bentonite (serves as a binder) and water. This composition of the brick is dried and sintered at temperatures ranging from 303 K to 723 K for 8-24 hours. When the particle size of the bricks is around 105 μm , around 15 % volume shrinkage has been observed whereas the peak bulk density is around 1.9 g/cm^3 . Sufficient cold crushing strength of the brick is recorded (nearly 940 KN/m^2). With these properties the bricks can be the alternatives of refractory brick, replacing medium fireclay refractories.

The resistance towards physical attacks dictates the permeability of the refractories. With increased permeability, the resistance towards chemical and physical attack reduces. With lower permeability, higher resistance to physical attacks like slag erosion, gas erosion and penetration of material is ensured [18]. Permeability is inversely proportional to the particle size, as 85 % permeability has been reported for 105 μm whereas around 70 % is achieved for 185 μm [19].

Owing to the large amount of total aluminium produced worldwide and understanding the growth of aluminium industry, it can be easily understood that the generation of aluminium dross shall increase in the coming years and so shall the overall loss of the metallic aluminium. Figure 1.1 shows the basic routes of recycling waste aluminium dross, illustrating the pyrometallurgical and hydrometallurgical processes.

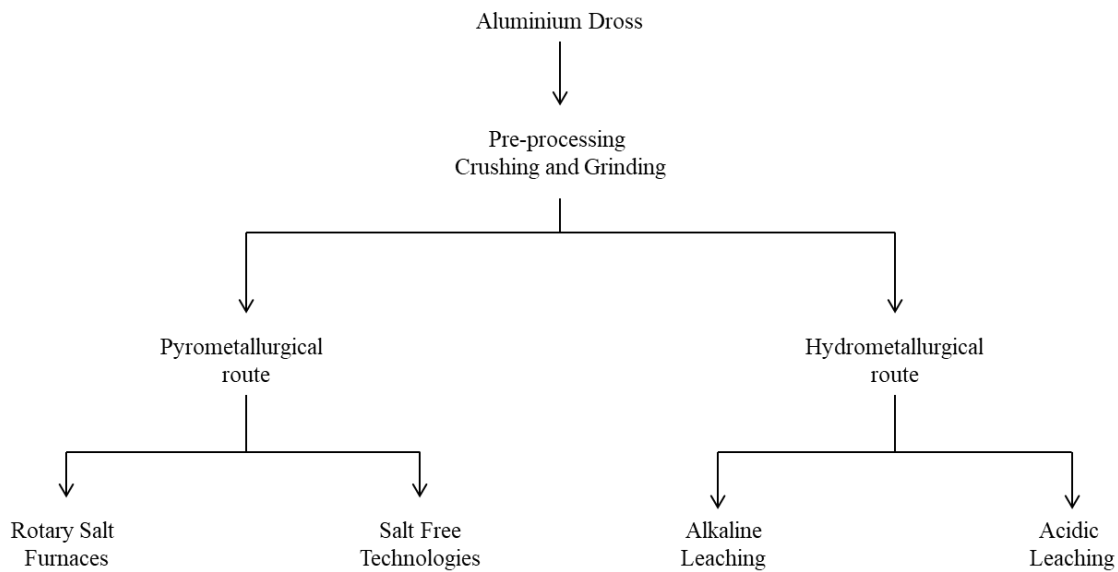


Figure 1.1: Various methods of recycling aluminium dross

1.1 Pre – processing of waste aluminium dross: an essential stage for its recycling

The essential initial steps for pre – processing aluminium dross are cooling the hot skimmed dross to the room temperature, crushing, grinding and reducing the particle size of the cold dross. The liberation of metallic aluminium from the hot dross obtained post skimming is possible if some mechanical agitation is provided. The solid residue obtained thereafter can be crushed, ground and sorted, as this will further lead to the separation of metallic aluminium from the powdered dross. Nearly 30 – 50 % metallic aluminium is left entrapped in the dross, even after the initial mechanical operations and physical separation [16, 20].

In order to cool the hot dross, special dross pans and cooling hoods are employed. In these processes, inert gases like Argon are purged at a high rate to initiate the cooling [21]. The cooling of the dross is carried out to decrease the oxide formation in the dross. When the hot dross (containing considerable amount of metallic aluminium) comes directly in the contact of the atmosphere, most of the aluminium gets oxidized. This is a

loss of metallic values that can be effectively extracted from dross. In order to combat this issue, the disturbances in the molten metal surfaces should be precisely controlled. These processes are efficient ways of cooling the hot dross and have been able to put an end to the age – old inefficient practices of spreading the dross on the shop floor to cool it.

The reduction in particle size by the crushing of the waste aluminium dross exposes the inherent heterogeneity clearly. It is observed that with larger particles, the amount of metallic aluminium content also increases, whereas it is lower in the smaller particles. This is mainly due to the higher viscosity of metallic aluminium. When the oxide content dominates the composition of the dross, brittle fracture is evident. On the other hand, ductile fracture can be seen where the agglomerates have greater metallic aluminium. Therefore, it can be understood that with greater particle size obtained after crushing, greater shall be the metallic content and lesser shall be the proportion of nitrides and carbides [22]. The larger particles (with greater metallic values) can be directly used for the metal extraction and the finer particles can be further processed to recycle the dross completely. Hot aqueous solutions, crystallization, drying and treatment with gases are other pre – processing operations to treat aluminium dross. The residual solid and metal oxide fraction obtained after the pre – processing operations can be used as a raw material for road paving, construction and mortar components [11,22].

Eddy current separators (ECS) have been employed to liberate the metallic aluminium from the dross. The eddy currents generated in the ECS units are used to efficiently separate non – ferrous metallic content from the powdered dross charged into it. The charged dross is transferred into it by conveyer belt and the eddy current rotor at the end of the unit separates the ferrous and the non-ferrous metal components from the dross

[23]. Metal recovery from both, white and black dross, has been achieved using the ECS technology. Downsizing the charged dross feed improves the separation of the particles. It is observed that particles in the mesh range 6 – 10 show extensive metal recovery in white dross in contrast to the particles of black dross [24]. A pre – processing technology that facilitates the metal recovery right from the beginning, the ECS technology is a good method for recycling dross.

1.2 Pyrometallurgical route for recycling of aluminium dross

Firstly, it is necessary to understand how aluminium dross comes into existence during the melting and remelting of aluminium wastes, scraps and ingots. Various chemical compounds like Al_2O_3 , Al_4C_3 , and AlN form due to the following reactions that take place [25]:



The researchers have tried to critically evaluate the importance of recycling all types of aluminium dross and liberate the metallic contents to bring back the lost aluminium into the mainstream applications. For that, the pyrometallurgical routes have been chosen by many industries. The conventional pyrometallurgical route comprises of utilizing rotary salt furnaces for the extraction of aluminium from dross. Rotary salt Furnaces (RSF) have the mechanism for the heating the charge feed and simultaneous rotation of the

furnace. The coupled action of heating the charged dross to a high temperature of 900 to 1000 °C and rotation of the molten aluminium dross takes care of the extraction from the entrapped alumina matrix of the dross.

To recycle and refine aluminium, use of good fluxing salts like mixtures of NaCl and KCl is necessary. During the melting and remelting operations, aluminium dross production increases as the amount of salt fluxes added for the refining increases [26]. It has been reported that a chain microstructure of aluminium oxide is evident with a high specific area, which facilitates the metal loss by entrapment.

The destruction of aluminium oxide net that entraps the metallic aluminium is initiated and controlled by molten flux [27]. When the furnace rotation is started, the interaction between salt fluxes and oxide layer gets enhanced. In the end, the oxide layer entrapping aluminium gets broken, leading to the agglomeration and merging of aluminium drops. The small agglomerated drops of aluminium sink into the aluminium bath. Other fluoride salts like MgF_2 , CaF_2 have also been used and found to be efficient in the extraction of aluminium.

Experimental evaluation illustrates the variation of aluminium liberation with variation in the composition of the fluxes used during the processing of dross. Combinations like AlF_3 -NaF- $BaCl_2$ have been used for the extraction of aluminium from the casting dross samples at temperatures around 1073 K [28]. Other salt fluxes include NaCl – KCl – KF, Na_3AlF_6 with chlorides and NaCl, KCl, and Cryolite [26, 29-32].

The coalescence of metallic aluminium drops is affected by layer at the interface of metal and salt flux. The exterior oxide layer on the surface can be dissolved by the interactions of salt flux. To break the oxide layer and attack the strong protective exterior, the initial stage is the generation of cracks in the layers. The second stage is the

penetration of salt into the crack generated. Interfacial tensions present in the metal surface, the viscosity and the density of the salt fluxes used for the process are the important factors for the metal extraction and the dissolution of oxide layer.

The recycling of waste aluminium dross with salt fluxes (halite etc.) is accomplished by following a holistic method. According to this method, the initial separation of metallic aluminium content is essential. This is followed by the leaching of the residual solid dross and salt slags to extract the salt fluxes from it. This solution containing the salt flux is subjected to crystallization to recycle and reuse them again. The non-metallic residue obtained after these operations should be provided with heat treatment. This process shows the way for recycling salt slags and dross that contain fluorides and chlorides. Aluminium entrapment in the slag matrix is dependent on the slag viscosity. The slag production increases and the metal recovery drops with the increase in the fine sized non-metallic content in the charge [31]. Calcium, cerium, lanthanum, lithium, magnesium and strontium are extracted by applying salt fluxes during the recycling of secondary aluminium dross. Salt fluxes with composition 45 mol% NaCl–45 mol% KCl–10 mol% AlCl₃ and 35 mol% NaCl–35 mol% KCl–30 mol% AlCl₃ are used [33]. The chlorination reactions are very crucial in the extraction of these elements from the molten aluminium metal.

The RSF were fantastic in their approach of liberating aluminium from the dross, but they required the fluxing of salts. This was required to bring down the operation temperature and further enhance the extraction process. Although the extraction of aluminium was achieved successfully, the generation of the Non-Metallic Product (NMP) after the processing was another issue. This mainly comprised of the salt cakes, as the salt fluxes added into the furnace were separated from the molten aluminium and discarded. This in turn meant that the salt cakes recycling unit was necessary. This was

an environmental problem as the dumping of the salt cakes into waste lands was not the viable option. The generation of the salt cakes was questioned, and it dawned to the research fraternity that the conventional RSF processing units could be modified to reduce the amount of salt cakes.

Therefore, in order to modify the existing pyrometallurgical approaches, the Salt-Free Technologies (SFT) was developed. These advanced technologies targeted the recycling of aluminium dross without consuming salt fluxes. Alcan, Alurec, Droscar, Drosrite, DC electric arc furnaces, Hydro – Quebec unit are based on the principle of no salt flux consumption. In these units, the heat energy was provided by the plasma arc technologies, DC electric arc torches and oxy – fuel heating units. Just like the conventional pyrometallurgical routes, these units also have the mechanism of rotating the furnaces. This ensures the complete liberation of the metallic aluminium from dross.

High operation temperatures in the range of 973-1073 K are reached with the plasma torch to avail the heat required to melt the charged dross in the rotary furnace of the Alcan dross treatment process. To reduce the oxidation of the metal, the furnace atmosphere is properly maintained. The electric arc is established when high voltage is applied. Better liberation of aluminium is achieved with the rotation of the furnace, ultimately producing the non-metallic residue at the end of the process [34-36].

The plasma arc reaches the temperature range of 4273-6273 K. For various classes of industrial dross: Mg-free aluminium dross, low-Mg aluminium dross, high-Mg aluminium dross, foundry aluminium dross and alloy dross of aluminium, the average process efficiency has been reported to be nearly 85 %. Salt fluxing can be reduced by a large margin and therefore salt cakes are not formed in this process [34, 37].

Direct current powered Hydro-Quebec DROSCAR graphite arc process is another pyrometallurgical process developed for the recycling of aluminium dross. The major sources of heat energy are the arc radiation and the conduction of the charge and the refractory lining. Consumable and non-consumable electrodes are used for the generation of arc. As the charge is melted in the furnace, the metallic aluminium is tapped and the residue is removed. Mechanical stirring, causing the agitation of the charged feed improves the energy efficiency of the furnace. It also counters the problem of formation of hot-spots during the furnace operation. To prevent the oxidation of molten aluminium, the purging of Argon gas is done [34, 38-39]. It has been reported that aluminium reacts with nitrogen beyond 1123 K and forms aluminium nitride. When aluminium nitride is brought in contact with water, the formation of ammonia takes place. To prevent this, the purging of Argon gas is done [40].

Similarly, DC electric arc process has been developed for the dross recycling and aluminium extraction. The dross feed is initially crushed and downsized before charging to the DC electric arc rotary furnace. The operation temperature reaches 973-1023 K. Various operational controls like rotation speed of the furnace, inert gas utilization during the process, time for retention and the refractory crushing material are crucial [41]. For both, granular and compacted dross feed, the rotation speed is optimized to nearly 4 rpm. It has been reported that around 75 % aluminium recovery can be achieved by this process. More than 1000 L/hr Argon gas is supplied for the efficient recovery of aluminium at 4 rpm. With lower gas flow rates, the recovery aluminium is fairly less and higher gas flow rates are favoured for the greater metal extraction. The retention time is optimized to nearly 10 minutes, as the metal extraction reaches around 80 %. Also it has been found that with the introduction of refractory bodies employed for crushing the charged dross, the extraction of aluminium increases by nearly 10 %.

The overall extraction of aluminium is averaged to nearly 70-80 %, when all of the above parameters are controlled [41].

Oxy-fuel purging is carried out in ALUREC process to extract aluminium from dross. The furnace is so designed that body of the furnace can be tilted. This ensured proper transfer of energy within the charged dross. In this process, the operation temperature has been reported to be 1273 K, as it sufficient to melt the charged dross completely [34].

ECOCENT process consumes hot dross as a charge feed into the furnace and the centrifugation of the furnace controls the extraction of aluminium. The charged dross is homogenised and aluminium is separated from the non-metallic oxide and other impurities during the centrifugation of the hot dross. To melt aluminium present in the dross, the heat energy is extracted from the hot dross charged in the furnace [34].

PyroGenesis DROSRITE process is another salt-free technology for the recycling of white and black dross. Tumbling of the hot dross feed is done for 15-30 minutes accompanied with Argon gas purging. Just like the ECOCENT process, no external heating is provided in this process. Adequate amount of oxygen is supplied to maintain the temperature in the range of 973-1073 K. The heterogeneous composition of the dross governs the liberation of aluminium from its oxide products, leading to the formation of droplets of aluminium. Around 60 % metal is recovered from white aluminium dross and 40 % is extracted from black dross. With minimum or no salt flux addition, this process imparts high energy efficiency in the extraction of aluminium from dross [34, 42].

Utilizing marine oil accompanied with oxygen as the source fuel, ALUR process helps in recovering metallic aluminium from dross. This process is quite influenced by the

ALUREC process, heating the charge to achieve melting and separation of metallic aluminium from its oxide. The power consumption for a furnace of 5 m³ is around 200-300 kWh per ton of dross. The gas released is primarily CO₂ and the residual solid is majorly non-metallic product. Salt cakes are not generated in this process; therefore this process is clubbed with Salt-free Technologies [43]. Salt cake processing unit employing electromagnetic and mechanic separators is present in IDALSA at Zaragoza. Equipped with oxy-combustion mechanism and 18 ton tilting rotary furnace, this process efficiently recycles salt cakes [25].

Simulation experiments to design the plasma arc furnace for recycling aluminium dross have shown that conduction of heat energy, convection of the gases with molten aluminium are important points to be examined to understand the performance of the furnace. The absolute calculations that describe the complete operation of the furnace is quite difficult [44].

Using stationary resistance furnace and laboratory scale rotary furnace, the recycling of black aluminium dross has been studied [45]. The chlorides present in the black dross are recovered when the pressure is reduced to 20 Pa, the recovery reaching as high as 95 %. Aluminium nitride present in the dross is also oxidized in the process. Small quantities of magnesium result in the formation of MgO.Al₂O₃, due to its association with alumina.

Similarly, the black dross is consumed for the generation of ladle fluxing agent [46]. The black dross is sintered at high temperature (1523 K) with calcium oxide to form different aluminate phases. To make the synthetic ladle flux compatible with the standard fluxes used in the industries, the CaO/Al₂O₃ ratio was fixed to nearly 0.94. To improve the sintering process and the quality of the end product, the black dross charge

needs to be heated at 1473 K for 6 hours at reduced pressure of 20 Pa. Even from the aluminium dross generated from alloys, the metal recovery is possible. It has been reported that for alloy A380, the metal extracted from the dross had density, chemistry and tensile properties similar to the parent alloy [47]. Electric furnace of 2.6 kW specifications was used for the experiment to recover the metal.

The major advantages of these SFT units are the reduction in the salt flux consumption and overall drop in the generation of salt cakes. This changed the impacts of pyrometallurgical route on the environment. The source of heat energy required to melt dross and extract aluminium from it was also advanced and it ensured relatively less pollution. The overall efficiency of the extraction of aluminium was also improved in many cases. Due to these advantages, many industries have readily accepted these new technologies.

The researchers working to improve the extraction of metallic aluminium dross have filed various patents in the field of Pyrometallurgy. Table 1.2 illustrates the patented technology and the inherent advances in the recycling of aluminium dross and other industrial wastes.

Table 1.2: Patented technologies for recycling aluminium dross by pyrometallurgical route

Patented Technology	Raw Materials	Resultant Products	Operational Features	References
Salt cake processing method and apparatus	Salt cakes, skim, dross	Salt flux and aluminum	Salt flux recycled by dissolving in water, evaporation and crystallization	[48]
Aluminum Dross Reclamation	Aluminum dross	Calcined aluminum oxide refractory	Pelletizing aluminum dross without free water and calcining the pellets at 982 °C	[49]
Recovery of non ferrous metals from dross	Aluminum dross	Metallic aluminum	Plasma torch in rotary furnace with dross, N ₂ and Ar gases purged, operation temperature 1000 °C	[34, 37, 40]
Recovery of aluminum from dross using the plasma torch	Aluminum dross, lime flux	Metallic aluminum and slag	Stationary furnace, DC plasma arc with inert gas environment to temperature above 1400 °C	[50]
Method and apparatus for treating aluminous metal skim material and by-products of said method	Aluminum dross skim	Metallic aluminum with foaming agent solid	Rotary container with peripheral gaps used to separate aluminum at temperature above 540 °C	[51]
Process for recovery of free aluminum from aluminum dross or aluminum scrap using plasma energy with oxygen second stage treatment	Aluminum dross and scrap	Metallic aluminum and Non Metallic Product (NMP)	Application of plasma torch with oxygen purging in the furnace	[52]
Salt based melting process	Aluminum scraps, skims with salt fluxes	Metallic aluminum and impurity metal chlorides	AC electrical resistance furnace and salt fluxing in the molten product	[53]
Process for using dross residue to produce refractory products	Aluminum dross with nitride and other	Refractory products	Mixing and calcining the raw materials in required proportions to produce the refractory	[54]

	metallic oxides		material at 1000 – 2300°C	
Process for preparing calcium aluminate from aluminum dross	Non metallic product and source of CaO	Calcium aluminate	NMP is blended with CaO and heated to 1093 to 1193°C	[55]
Process for the preparation of calcium aluminates from aluminum dross residues	Aluminum dross residues and CaO, CaF ₂	Sintered calcium aluminate	Aluminum dross mixed with CaO, CaF ₂ and sintered at 1250 to 1300 °C	[56]

The overall performance of Salt – Free Technologies (SFT) units is even better than the conventional Rotary Salt Furnaces (RSF). Processes like Alcan, ALUREC, ECOCENT and Drosrite have definitely redefined the extraction of metallic aluminium from the waste hazardous dross. The production of salt cakes (previously due to the RSF) also decreased with the advent of these processes.

1.3 Hydrometallurgical route for the recycling of aluminium dross

Waste aluminium dross processing is also carried out using hydrometallurgical route across the world. The metallic values present in the dross have been extracted into the leaching media (acidic or alkaline). Although the production of metallic aluminium is not possible through this method, but the aluminium leached into the leaching media can be converted into alumina and other valuable products, thereby bringing the aluminium back into the material cycle. Since aluminium has amphoteric nature, it can react with both acids and alkalis. This gives the advantage to all the hydrometallurgical researchers to subject aluminium dross to both the types of leaching media: acidic as well as alkaline. The tendency of reaction of aluminium with acids and alkalis depict the overall extraction of aluminium from the dross, apart from the experimental parameters governing the leaching operation.

The experiments of acidic leaching of aluminium dross are commonly performed using H_2SO_4 . The details of the experiments conducted by various researchers have been illustrated in Table 1.3.

It has been seen that aluminium leaching is possible at relatively high concentrations of sulphuric acid. This requires high amount of pure sulphuric acid to make the solution of the desired concentration, also the handling of the solution becomes a little difficult.

Table 1.3: Parameters of acidic leaching of waste aluminium dross

Raw material	Leaching medium	Concentration	Temperature K	Time hours.	Maximum value leached	References
White dross	H ₂ SO ₄	20 and 40 % (v/v)	363	1	Al ₂ O ₃ 95%	[57]
White dross	H ₂ SO ₄	15-40 % (v/v)	363	3	Al ₂ O ₃ 84%	[58]
White dross	H ₂ SO ₄	30-96 % (w/w)	373	1	Al and N 88.5 %	[59]
White dross	H ₂ SO ₄	5-12.5 %	433-513	5	Al 96%	[60]
Black dross	HCl	1-6 mol/L	373	4	Al ₂ O ₃ 71 %	[61]

Nearly 85 % alumina has been recovered from aluminium dross using sulphuric acid leaching with 2-5 µm sized aluminium dross fine powder [57]. To enhance the reactions involved in the process, the amount of water needs to be properly maintained at high acid concentrations. The leaching temperature is maintained at 363 K and the leaching period is 180 minutes. Washing the dross fines improves the leaching operation; the efficiency reaching up to 95 %, after removing the salts from the dross.

Addition of 10 % aqueous ammonia solution to the filtered leach solution generates the precipitates of aluminium hydroxide. This precipitated hydroxide product can be heat treated at high temperatures to generate various phases of alumina [58]. The formation of η-alumina has been reported, when aluminium hydroxide precipitate was heated to 1173 K, whereas at 1373 K, α-alumina had formed. The end product, η-alumina can be utilized for catalytic and adsorbing applications, as it is highly activated form of alumina. This method of extracting aluminium content from dross is another alternative of recycling dross, thereby generating valuable products.

Aluminium dross leaching with sulphuric acid produces aluminium sulphate leach solution. Using this leached solution, ammonium alum can be produced. This method is

possible when the leached liquor is allowed to react with solutions that provide the ammonium ions. This process was utilized to extract the metallic content from aluminium dross into the ammonium alum, generating yet another valuable product. The metallic aluminium content and aluminium carbide when react with sulphuric acid solution, get converted to aluminium sulphate, whereas aluminium nitride give aluminium sulphate and ammonium sulphate [59, 60]. At high acid concentrations, around 96 % extraction of aluminium has been reported.

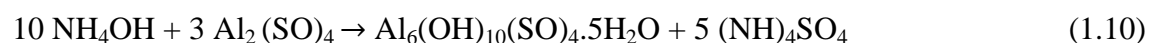
When aluminium dross reacts with sulphuric acid, following reactions take place [62]:



Aluminum nitride and water react to form ammonium hydroxide and aluminium hydroxide:



This ammonium hydroxide further reacts with aluminum sulfate present in the leach liquor to produce ammonium-aluminum alum [59]:



From the above reactions it can be seen that aluminium carbide and aluminium nitride can react with sulphuric acid to give ammonium-aluminum alum.

Just like sulphuric acid, hydrochloric acid solution also helps in the extraction of alumina from aluminium dross fine powder. It has been reported that as high as 71 % metal recovery is possible after hydrochloric acid leaching [61]. The pre-leaching

washing of the dross can be skipped for this leaching because hydrochloric acid is quite corrosive in nature. Heat treating the dry-gel obtained after the leaching produces phases like θ -alumina, a mixture of $(\alpha + \theta)$ -alumina and α -alumina at 1273 K, 1473 K and 1673 K. The synthetic alumina produced in the end is nearly 99.0 % pure, thus making it fit for applications of alumina.

Alkaline leaching is carried out primarily using sodium hydroxide. The generation of aluminate takes place when alkaline solutions are used. When sodium hydroxide is used, sodium aluminate is formed. This leaching would further result in the synthesis of various valuable important products. Table 1.4 describes the parameters for alkaline leaching of aluminium dross in various experiments.

Table 1.4 Alkaline leaching of aluminium dross

Raw material	Leaching medium and concentration of the medium	Maximum value leached	Temperature K	Time hrs.	References
Black dross	Distilled water	Na 80%, K 85%	363	1	[63]
Black dross	Aq. NaOH 180-280 g/L	Al 57.5%	433-533	2	[63]
Salt cakes	Distilled water	Cl 86-89% Na 54-58% K 37-43%	298 and 333	4	[64]
Salt cakes	Aq. NaOH 16% w/v	Al ₂ O ₃ - 42.9%	298 and 333	4	[64]
Black dross	Saturated Carbonated aq. solution	NaCl – 95% KCl – 95%	291	3	[65]
White and black dross	Aq. copper chloride solution 1 M	Aluminum oxychloride	298	1.5	[66]

Around 80 % and 85 % of sodium and potassium have been reported to be extracted from black dross after water leaching. Utilizing the dross for alkaline leaching operation showed that around 57 % aluminium can be extracted effectively [63]. Phases like α -Al₂O₃, MgAl₂O₄ (spinel), NaAl₁₁O₁₇ (diaoyudaoite) and CaAl₁₂O₁₉ are dominant in the solid residue obtained after the leaching.

To generate cement clinker, the addition and mixing of the raw materials like sand, bauxite, clay and limestone to the residual solid is done and a mixture is produced. This mixture is sintered at high temperatures of 1273 K and 1723 K [67]. It has also been reported that with 4 % substitutions of the solid residue in the cement clinker mixture increases calcium aluminate phase. Therefore, black dross can be used to produce cement clinker.

Around 1 to 2 M NaOH solutions have reported to be sufficient enough to produce hydroxide ions to extract aluminium from industrial waste aluminium by-products like dross and slags [8]. After leaching aluminium dross with NaOH aqueous solution followed by precipitating the leached liquor with 30 % H₂O₂ and calcination at 873 K results in the increase in the surface area of the end product [68]. This product has good catalytic and absorbing qualities; therefore it finds the applications in such areas of waste management.

To understand the kinetics involved in the recovery of alumina from aluminium dross, the fusing of NaOH and aluminium dross in ratio of 2:4 has been done at high temperatures (773-1023 K). This fused product has then been dissolved in distilled water [69]. The metallic content extracted in the leaching operation has been determined by EDTA complexometric titrations. The activation energy for the alumina has been found to be 6.452 kJ /mol. Avarami-Erofeev equation describes the kinetics of alumina recovery:

$$-\ln (1-\alpha) = (kt)^m \quad (1.11)$$

Here, t is time for fraction of reaction, k is specific reaction constant, α is reacting particle and $m = 3/2$.

Around 12 major metals with 19 different phases can be present in salt cakes, with overall 37 % aluminium [64]. Therefore, salt cakes are also great sources of valuable products. With aqueous leaching, recovery of around 89 %, 58 % and 43 % chloride, sodium and potassium ions can be achieved. Nearly 40 % extraction of metallic alumina has been reported after concentrated NaOH leaching. The decomposition of aluminium nitride can be effectively achieved when finely ground salt cakes are subjected to leaching with hot alkali.

The leaching and calcination operations of the salt slags obtained from secondary aluminium industries results in the efficient separation of the dissolvable salts and impurities. The residual solid is transformed into the oxides and hydroxides [70].

Majorly Al_2O_3 or $\text{Al}_2\text{O}_3\cdot\text{MgO}$ is obtained. Recovering salts from the leached liquor can be done by crystallizing by freezing and applying solvent/anti-solvent methods, using concentrated HCl to initiate precipitation [71]. Electrodialysis process can also be carried out for the same purpose [72]. Selective precipitation is observed when electrical forces are applied on the salt solution, driving the ions to be entrapped in the ion exchange membranes. After these operations, maximum extraction of salts is ensured, leaving behind small amount of aluminium and alumina.

Toxicity threats of the salt cakes have been determined by the toxicity characteristic leaching procedure [73]. Using two leaching liquors (1.14 % glacial acetic acid and NaOH solution mixture, pH 4.95 and 1.14 % glacial acetic acid, pH 2.88), the leaching of salt cakes have been done. The overall concentrations of the toxicity metals are lower than the specified limits.

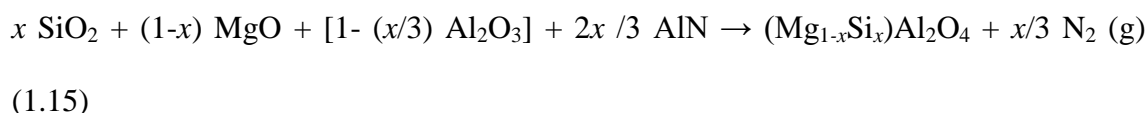
Reacting aluminium dross with saturated CO_2 water can be done to absorb the ammonia gas produced when aluminium nitride reacts with water [65]. During this process, salt extraction is coupled with ammonia absorption. It has been found that 95.6 % and 95.9 % of sodium and potassium salts can be extracted using this leaching medium. Supplying the CO_2 into the solution at 40 mL/ minute and maintaining pressure of 1 MPa provides the conditions for saturation and proper extraction. This reduces the loss of ammonia into the surroundings as it gets converted to NH_4HCO_3 as illustrated in the following reactions:





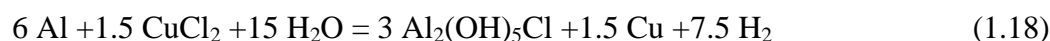
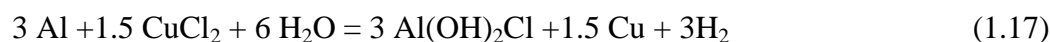
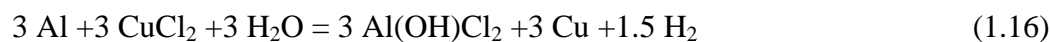
As can be seen from the above, aluminium nitride can be decomposed into a variety of products, including $\text{Al}(\text{OH})_3$ when reacted with various acidic and alkaline solutions. With aqueous solutions of hydrochloric acid and sodium hydroxide, the formation of $\text{Al}(\text{OH})_3$ is much more favored, as compared to the use of deionized water for the same purpose [74]. This is possible when the reaction of aluminium nitride generates amorphous aluminium oxy-hydroxide AlOOH . This amorphous product can be transformed to its crystalline form $\text{Al}(\text{OH})_3$ in a heating period of 16 hours [75]. Therefore, it can be clearly understood that AlOOH , $\text{Al}(\text{OH})_3$ and Al_2O_3 are the major phases that get produced after the hydrolysis. Aluminium oxy-hydroxide finds its application in paper industry [76].

The fractional amount of magnesium that is found in some of the alloy dross, after hydrolysis and combining with alumina, can produce spinel. This material is well known for its structural refractory properties. Under the presence of silica, magnesium oxide and alumina, the partial oxidation of aluminium nitride can be understood from the following reaction [77]:



Just like leaching with acids and alkalis, leaching with other reagents like copper chloride can also produce some valuable products, like aluminium oxychloride [66]. This product finds its utility in waste-water treatment plants and paper industries. It can also be used as a refractory material. Both white and black dross can be reacted with 1

M copper chloride solution to generate Al(OH)Cl_2 , $\text{Al(OH)}_2\text{Cl}$ and $\text{Al}_2(\text{OH})_5\text{Cl}$ as illustrated in the equations as under:



Additional amount of hydrochloric acid can be added to maintain the forward direction of the reactions involved in the process. Similarly, the utilization of secondary dross can be done by employing a process similar to Bayer Process [78]. Leaching of the secondary dross with 10 % sodium hydroxide solution, fixing $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 = 2$, leads to the formation of sodium aluminate. With the addition of CO_2 , the alkalinity of the solution gets altered and the aluminate becomes unstable. This leads to the production of aluminium hydroxide. The following reactions describe the decomposition of aluminate and formation of aluminium hydroxide.



Many processes have been patented by various researchers in the field of hydrometallurgical routes for recycling aluminium dross. The alkaline as well as the acidic leaching operations have been described by them. Nearly 15-25 kg of white dross is produced per ton of aluminium, whereas around 80 kg black dross is produced per ton of secondary aluminium. Depending upon the process parameters, nearly 200-500 kg salt cakes can be produced per ton of aluminium.

Table 1.5 shows the important patents filed for extracting aluminium content from aluminium dross and the related aluminium waste products generated in the industries.

Table 1.5: Patents for the recycling of aluminium dross by hydrometallurgical route

Patented Technology	Raw Materials	Resultant Products	Operational Features	References
Aluminum sulfate manufacture from aluminum dross	Aluminum dross tailings and concentrated solution of H_2SO_4	Aluminum sulfate	aluminum dross leached with 30 to 99 wt.% concentration acid	[79]
Process for recycling waste aluminum dross	Aluminum dross and alkaline solution	Aluminum hydroxide and metallic aluminum	Larger particles subjected to remelting, finer particles leached in 10-20 wt.% NaOH solutions	[80]
Process for production of sulfates	Aluminum oxide by-product waste and sulfuric acid	Aluminum sulfate solution, binary salt aluminum ammonium sulfate	Waste oxide is leached with sulfuric acid	[62]
Recovery of products from Non-Metallic Products derived from aluminum dross	Non Metallic Products obtained from aluminum dross	Aluminum hydroxide, magnesium hydroxide and spinel	Various acids used to leach NMP, pH of the solution increased to precipitate products	[81]
Method of recycling aluminum dross	Aluminum dross, NaOH, $Ca(OH)_2$, $Na_2B_4O_7$, H_2SO_4 , HNO_3 , HCl, Al_2O_3 and SiO_2	Fired inorganic, ceramic product containing Al_2O_3 and SiO_2	Slurries of aluminum dross with Al_2O_3 , SiO_2 , alkaline and acidic materials and heating the slurries to 980-1926°C	[82]

1.4 Generation of valuable products from aluminium dross

A new horizon of recycling of dross has been explored by many researchers in the present scenario. The main target is to recycle dross completely and produce valuable chemical compounds. The synthesis of zeolites, refractory materials, composites, important industrial chemicals and other products from aluminium dross has been the focus of the researchers.

1.4.1 Refractories

Production of high alumina refractory bricks is done by using magnesium oxide with aluminium dross as a raw material. Taking the raw materials in proper proportion and mixing their finely ground particles with phenolic resin homogenizes the brick mass. This mixture mass is stored for 24 hours in plastic bag. Pouring the mixture brick mass to metallic mold is done, after which these molds are subjected to hydraulic pressing operation with a pressure of 200 MPa. This pressed product is dried at 110°C and then sintered at 1400 °C. This finally generates sintered High Alumina Refractory Bricks [83].

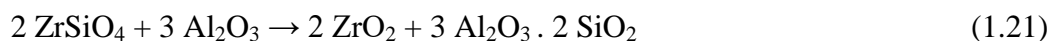
The formation of $MgAl_2O_4$ spinel is observed in the HAR bricks along with $CaAl_4O_7$, which is actually acting as a bridge holding the alumina and magnesium spinel together. The refractoriness of the bricks is attained from the magnesium spinel. The heat resistance of the bricks is achieved due to the macro-pores present in the bricks. Other important properties attained from the high temperature sintering operation are: improved bulk density, higher compressive strength and mechanical properties. Comparing the properties of the HAR bricks thus synthesized with the existing LZ-65 type refractory bricks, it has been found that the compressive strength of HAR bricks is higher than its counterpart [83]. Similarly, $(Mg, Si)Al_2O_4$ Spinel alongside $MgAl_2O_4$

have been generated from aluminium dross [77]. Water washed dross is heated in temperature range of 1500 - 1625°C in a furnace with induction coils in a carbon capsule. The end product has both the types of spinel and has refractory properties.

1.4.2 Composites

Mullite/zirconia composite can be generated from aluminium dross, which is a metal matrix composite (MMC). The raw feed of dross needs to be properly crushed, downsized and screened to remove the coarser fraction of the dross from finer fraction. The decrease in the size of dross particles ensures greater homogeneity in the raw material. This is followed by water washing to remove the dissolvable impurities from the dross. The ball milling of the fine particles can be done to further reduce the size of the particles. To the matrix of finely ball milled aluminium dross powder, - 10 µm sized zircon powder is added such that the stoichiometry of the product is achieved. This mixture is ball milled again in presence of acetone. The ball milled mixture is subjected to uniaxial pressing at a pressure of 100 MPa to produce pellets which are sintered at 1500°C to form the required mullite/zirconia refractory composite [84].

With the drop in the particle size of the raw materials, the porosity of the composite produced also decreases. When the raw materials of the required particle size are used, greater binding of the resultant phases is observed, which increases the homogeneity. The properties of the resultant composite are low thermal expansion, high strength at elevated temperatures and improvement in fracture toughness [84]. Similarly, ZrSiO₄ and α-Al₂O₃ can be used to produce mullite refractories above 1372 K, as illustrated in the following equation:



The formation of mullite is completed when the matrix is seeded with mullite and nucleation and growth of the product take place [85]. It has been found that alumina rich mullite can impart derogatory mechanical properties at elevated operation temperatures. To avoid this, step annealing operation can be done to make mullite composite relatively free from alumina [86]. Also the use of Indian bauxite can be done for mullite production [87].

Employing the Rheocasting Process, composite A356 has been produced using aluminium dross as reinforcement raw material. The dross is washed and pre-heated before adding it to the molten metal to achieve the composition of the composite. It has been observed that the tensile and wear properties are dependent on the particle size of the dross, when the volume fraction of aluminium dross is kept constant [88].

1.4.3 Cement and concrete products

Lightweight expanded clay aggregates (LECA) can be successfully produced from the non-metallic product obtained from aluminium dross. Ball milling high carbonate clay with aluminium dross to achieve particle size of nearly 54 μm can produce a plastic mass, to which 20-22 % water is added. This plastic mass is sintered at 1170 °C to generate LECA. Properties like expansion, density and porosity are affected by the composition of the raw input and the sintering temperature. Due to the emission of the gases produced at high sintering conditions, the pore size of the LECA increases [89]. Similarly, calcined alumina and refractory clay can be produced from aluminium dross. Addition of other raw materials along with aluminium dross and water and ball milling of the mixture can be done to generate a wide range of refractories: low cement castable refractory, ultra-low cement castable refractory and self-flowing castable refractory [90]. The amount of dross added into the mixture is limited to around 5 %.

Refractory phases like corundum, spinel and quartz are present in the NMP of the dross. Utilizing this NMP and the dross for the synthesis of concrete blocks is another method of recycling these waste products [91]. Binders, clay, cement and aggregate fines are mixed to the dross, keeping the dross at 20-30% of the mixture. It has been found that with the increase in the dross addition, the resistance to acid attack also increases. calcium silicate, quartz, portlandite, corundum and mullite are the major phases present in the concrete produced from aluminium dross [92].

High pressure concrete bricks can be prepared from secondary aluminium dross [93]. Stabilization and hydrolysis of Desulphurization slag was done, followed by stabilization and hydrolysis of aluminium dross using the same solution, because of its high pH. The residual secondary aluminium dross was mixed with other raw materials like cement and additives, compressed at high pressure, cured to form the high pressure concrete bricks. Also, use of Portland cement, fly ash and silica fume with aluminium dross can also result in the production of concrete bricks [94]. It has been reported that around 5 % dross with 10% of both fly ash and silica fume provides sufficient strength.

Alumina from aluminium dross can be employed for the manufacturing cement. The metallic content of the aluminium dross can be removed to a great extent by milling and screening. This metallic aluminium can be utilized and the black dross thus generated can be used again for the cement production in closed circuit. Raw materials like lime, silica, iron oxide are used with the dross to produce cement clinker [95]. It has also been reported that with aluminium sludge, slag and alumina can be used to produce calcium aluminate cement mixtures that meet the international standard specifications. The use of aluminium slag and dross is justified because these materials are rich source of Al_2O_3 [96]. The temperature of firing the mixture has been reported to be around 1350°C to 1550°C. The major phases present in the cement mixture are calcium aluminate CA,

calcium dialuminate CA_2 and calcium hexaluminate CA_6 . CA and CA_2 are important and desirable phases that should dominate the cement mixtures.

Sonochemical process has been used to produce Calcium Aluminate phases CA and CA_2 . For this, the alumina and calcium oxide are mixed in required proportion and slurries are prepared. These slurries are subjected to an ultrasonic bath for 60 minutes, after which the slurries are heated at $1200\text{ }^\circ\text{C}$ to generate the cement mixture [97]. A lot can still be done, in order to improve the end products.

1.4.4. Aluminium alloys

To produce Al-Si alloy and Brown Fused Alumina from aluminium dross, the dross was subjected to different operation steps. For Al-Si alloy, the raw materials (gangue, petroleum coke and sulfite liquor) along with aluminium dross were charged to Submerged Arc Furnace, which was the chief processing unit for this product. The operating temperature was $2250\text{ }^\circ\text{C}$ to maintain an environment thermodynamically favorable for the alloy production. Electric arc furnace was employed to produce brown fused alumina. In this case, the raw materials included bauxite, scrap iron and coke powder along with aluminium dross. To complete the process of brown fused alumina production, the impurities present in the charge needed to be vaporized. For this, the temperature of the operation was as high as $2030\text{ }^\circ\text{C}$ [98].

Utilization of salt slags for silicon aluminium masteralloy is another method of consuming this industrial waste to form a valuable product. Palletisation of the salt slag with adequate amount of quartz is done. The quartz maintains the amount of silicon in the final masteralloy. The operation temperature for this carbothermic reduction process is around 2000°C . For this purpose, AC electric arc furnace is employed [99].

1.4.5 Zeolites and other miscellaneous products

Reaction of isopropyl alcohol with aluminium dross can produce aluminum isopropoxide. Catalysts like HgI_2 , I_2 , HgCl_2 or FeCl_3 are used to make the reactions feasible. Additional system of vacuum distillation is required for this process. It has been observed that as high as 97 % pure aluminum isopropoxide can be prepared by this method using aluminium dross as a source of aluminium. This process can simply cut down 10 % production costs of the commercial process if the use of aluminium dross is considered [100].

Just like aluminum isopropoxide, aluminum Sec-butoxide can also be prepared using the chemical reactions involving Sec-Butyl Alcohol (SBA) and aluminium dross. Under the presence of catalysts, the production of aluminum Sec-butoxide can be done. It has been reported that the activation energy for the process is 40.9 kJ per mol [101].

Important materials like ion exchangers can also be produced using aluminium dross as a raw material. Layered Double Hydrates are a class of materials that are ion exchangers designed to extract Cr(VI), B, As(III) and Se(IV) ions. Powdered aluminium dross is leached with NaOH and HCl with constant stirring. The metal ions desired in the product LDH (Ca^{2+} , Mg^{2+} and Zn^{2+}) are added to the liquor obtained after the leaching leading to the generation of LDH. To complete the LDH formation, the crystallization of the product is essential; this is done by the addition of NH_4Cl to the solution. The LDH products function properly and are successful in extracting anions [102].

Zeolites like $\text{AlPO}_4\text{-5}$ are generated from aluminium dross after dissolving it in phosphoric acid. Tri-ethylamine (TEA) is added to the solution and additional water is added such that $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : \text{TEA} : \text{H}_2\text{O} = 1:1:1:40$ (molar ratio) is achieved. This mixture is heating in an autoclave at 453 K [103]. Variation of molarity of the raw

materials used for the synthesis of the zeolite leads to the change in the phases as TEA is a structure directing agent. The formation of $\text{AlPO}_4\text{-34}$ has been observed which is quite undesirable while $\text{AlPO}_4\text{-5}$ is the required end product. Gases like ammonia, dipropylamine and benzene can be adsorbed using these zeolites [104].

Leaching of aluminium dross with NaOH and subsequent addition of $\text{Al}(\text{OH})_3$, HNO_3 and NH_4OH solutions leads to the precipitation. This product is reacted with H_3PO_4 solution to form aluminophosphates. These micro porous aluminophosphates are designed to adsorb various ions [105].

Utilizing silicon sludge and aluminium dross, the production of X-zeolites ($\text{Na}_{86}\text{Al}_{86}\text{Si}_{106}\text{O}_{384}\cdot x\text{H}_2\text{O}$) has been studied [106]. The dissolution of silicon sludge and aluminium dross in NaOH was done separately and the solutions thus obtained were mixed later. The solution mixture was agitated and heated at 363 K and to complete the crystallization of the zeolite, the mixture was heated for 8 hours, without agitation.

Saline slags are modified to function as adsorbing materials after treatment with aqueous solutions of NaOH, H_2SO_4 and HNO_3 of varying compositions (0 – 2 mol/dm³). The centrifugation of the slurries is done followed by drying at 60°C. It has been observed that the modified saline slag samples are adsorbing ions like Cu (II), Pb (II) and Cd (II) from their respective solutions successfully [107]. High surface alumina can be produced from aluminium dross tailing by high pressure leaching with NaOH under high pressure followed by H_2O_2 precipitation. The end product, high surface alumina is quite applicable as a catalytic-grade material [108-110].

Table 1.6: Valuable products generated using aluminium dross

Raw Materials	Product	Procedure applied	References
White and black dross	High alumina refractory brick	Mixing with binders, compacting at 200 MPa, sintering at 1530°C	[83]
Non Metallic Product and black dross	Concrete blocks	aggregates or additives for manufacturing concrete	[91]
Non Metallic product	Lightweight expanded clay aggregates	Green aggregates ball milled with high carbonate clay, sintering at 1270 °C	[89]
Black dross	Low cement castables, Ultra low cement castables	Ball milling and mixing in planetary mixer with water	[90]
White dross	Mullite-zirconia composites	Ball milling, mixing with zirconia, uniaxial pressing and sintering at 1500 °C	[84]
White dross	Discontinuously reinforced aluminum based composites	Ball milled and vacuum filtered to use as reinforcement in Rheocasting process of A356 alloy	[88]
White dross	Aluminum isopropoxide	Chemical reaction of dross and isopropyl alcohol under presence of catalysts, followed by purification and vacuum distillation	[100]
White dross	aluminum sec-butoxide	Dissolution of dross in sec-butyl alcohol	[101]
White dross	AlPO ₄ -5 and CrAPO-5	Treatment with various solutions like NaOH, Al(OH) ₃ , HNO ₃ , NH ₄ OH and H ₃ PO ₄	[105]
White dross	AlPO ₄ -5	Mixing of tri-ethylamine with phosphoric acid, aluminum dross in water and heated at 823 K	[103, 104]

White dross from alloys	Various layered double hydroxides	Leaching in HCl and NaOH, co-precipitation with metal chloride solutions	[102]
White and black dross	Cement pre-mixes, aluminum metal	Milling, screening, treatment in DC furnace	[95]
White dross	Calcium aluminate cement	Sintering and briquetting at 1250-1500 °C	[111]
White dross	Concrete blocks	Water, binder, Portland cement, fine aggregates and dross mixed in proportion	[92]
White dross	Al-Si alloys and Brown Fused Alumina	Treatment in submerged arc furnace and electric arc furnace	[98]
White dross	Structural refractory materials containing spinel	Water washed, heated at 1500-1650°C in carbon capsules with induction coils	[77]
Black dross	High pressure concrete bricks	Aluminum dross mixed with cement and additives, high pressure formed, cured and stabilized	[93]
White dross	X-zeolites	Silicon sludge, aluminum dross dissolved in NaOH separately, mixed and crystallized at 363 K for 8 hours	[106]
Saline Slags	Saline Slags with adsorbent properties	Treating with NaOH, HNO ₃ and H ₂ SO ₄ for 24 hours, centrifuged and dried	[107]
White dross tailings	high surface alumina	Leached in high pressure with NaOH and precipitated with 30% hydrogen peroxide	[108-110]
Saline Slag	Silicon aluminum masteralloy	Pelletized with quartz, carbothermic reduction at 2000°C	[99]

1.5 Environmental impacts of aluminium dross

Considering the large amount of aluminium dross produced all around the globe, it is very important to develop proper recycling methods to counter this problem. It is a bitter truth that presently, in many countries, proper recycling methods have not been developed. Due to this, the aluminium dross generated in the industries are transported away and landfilled. Understanding the fact that landfilling is never an alternative for the recycling of dross is very necessary.

When such hazardous industrial wastes are landfilled, the soil around the landfilled pit gets degraded and it consumes land resource, which is altogether scarce. The leaching tendency of aluminium dross when it comes in contact with ground water is explained by many researchers. It is well understood that if dross remains in contact with ground water, it will produce harmful gases like ammonia and hydrogen and it can also pollute the water resources and atmosphere [112]. The pH of the water can change and the soil contamination is also possible due to the leaching of heavy metals from dross and other waste products.

Aluminum nitride finds its application in ceramic industry, as it is used as high thermal conductive refractories [113], but when dross containing aluminum nitride comes in contact with water, nitride gets decomposed and ammonia gas is released. The effluents produced in the tertiary aluminum treatment industries that recycle aluminum dross contain chemical species like Na^+ , Ca^{2+} , Mg^{2+} , K^+ , and N-NH_3 [114]. Heavy metal precipitation results when these effluents are disposed into aquatic bodies. Moreover, ammonia oxidation declines in the reducing conditions at the bottom of water bodies, leading to unionized accumulation of ammonia (NH_3), which is highly toxic to aquatic organisms. The contamination of soil and groundwater is also evident in the proximity

of these tertiary aluminum treatment plants [114]. The pH of the groundwater drops down to 4 due to the action of bacteria that break down ammonia, which is highly unfavorable and the disposal of non-metallic products (NMP) in the soil increases the percentage of aluminum in the form of $\text{Al}(\text{OH})_3$.

During the processing of aluminium scraps for the melting and remelting operations, the generation of Polychlorinated Dibenzo – p – Dioxins and furans (PCDD and PCDF) take place that are toxic chemicals harming the life cycle of many organisms that come in contact with them. Such harmful chemicals are produced during the aluminium dross generation and a lot of these chemicals get associated with it. The salt fluxes (NaCl and KCl) inherent within the dross are leachable and alter the ionic balance of the soil.

It has been found that a large variety of toxic chemicals exist around the secondary aluminium smelter plants. Polychlorinated dibenzo-p-dioxins and furans (PCDD/DF) and Polybrominated dibenzo-p-dioxins and furans (PBDD/DF) are a few of these hazardous chemicals. These chemicals come into existence because of the incomplete combustion of raw materials and organic compounds associated with the raw materials [115]. In order to combat the problem of these toxic chemicals, the pretreatment of the aluminium alloy scraps is essential. The leachable salts contaminate the water resources and disturb the land resource where aluminium dross waste ends up being landfilled [116, 117].

Keeping the environmental impacts created by the improper waste disposal procedure followed by many industries, an immediate need of developing proper methods and viable alternatives to pyrometallurgical and hydrometallurgical routes is felt. Advancing technologies to enhance the metal recovery and complete waste utilization are being developed.

1.6 Production of gases using aluminium dross

Various gases are produced when aluminium dross comes in contact with water. The primary gas produced is hydrogen [76, 118-119] with lesser amounts of ammonia and methane [120]. Table 1.7 shows the technologies for the production of gases.

Table 1.7: Industrial technology for the utilization of aluminium dross for gaseous products

Patented Technology	Raw Materials	Characteristic Features	Gaseous products	References
Aluminum dross processing	Aluminum dross tailings	Decomposition of Al_4C_3 and AlN in presence of metal hydroxide solution	H_2 , NH_3 , CH_4	[118]
Processing of aluminum slag	Aluminum slag	Leaching of slag with neutral, acidic and basic solutions	Recovery of salts and H_2 , NH_3 , CH_4	[119]
Method for treatment of aluminum dross oxides	Aluminum dross	Digestion of raw feed in water to expose aluminum	Dissolution of salts and H_2 , NH_3 , CH_4	[120]

Aluminium metal for the purpose of metal-water reaction is quite expensive, while using the waste products containing fair amount of aluminium can be a good alternative. Use of aluminium dross is the way suggested for this purpose. Around 1.2 litre of hydrogen can be successfully produced with 1 gram of pure aluminium.



Making the water alkaline by adding NaOH and KOH can lead to the formation of aluminium oxy-hydroxide that can be employed for synthesis of refractory materials or calcium aluminate cement [121].

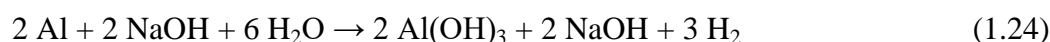


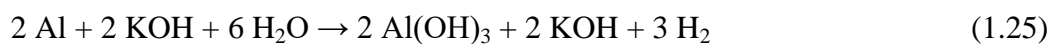
Some other methods to produce hydrogen using aluminium-water reaction include the catalysis reactions using precursors of $\text{Al}(\text{NO}_3)_3$ / NaOH . These precursor materials enhance the production of aluminium hydroxide, which is catalyzed to produce hydrogen. The molar ratio of $\text{Al}(\text{NO}_3)_3$: NaOH is maintained at 1:5 [122]. Reaction for the formation of aluminium hydroxide is shown in eq. (6.6):



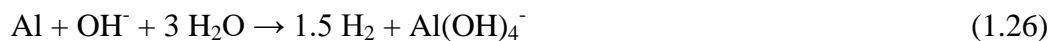
Enhancing the rate of the reaction for the hydrogen production can be done by many methods. One of the methods would be to provide thermal shock treatment to the fine particles to season these particles for precise reaction. Cycles of heating and cooling the fines would pile up thermal shock in these particles. Similarly, the application of inorganic salt mixtures like NaCl , KCl and NaNO_3 for the activation of the aluminium powder leads to the enhanced hydrogen production. This is assisted with an increase in temperature of the reaction. To the aluminium pellets, the additions of alkali materials like NaOH and CaO elevates the aluminium-water reaction thereby increasing the hydrogen production [123].

The production of hydrogen is not a reaction that can continue for a substantial amount of time. The major hurdle in these reactions is the presence of aluminium oxide layer at the surface of aluminium. This can be done by renewing the surface of aluminium continuously, so that aluminium always remains in contact with water to produce hydrogen. Fine particles of aluminium dross when subjected to reaction with water can give hydrogen [76]. Ball milling the dross fines can produce particles as fine as $45 \mu\text{m}$. Bringing NaOH and KOH into the water-aluminium dross system, leads to enhanced reactions.





The activation energy of the reactions are found to be 68.4 kJ mol^{-1} :



$$\Delta H = - 415.6 \text{ kJ}, \Delta G = - 437.1 \text{ kJ} \text{ and } K_a = 3.78 \times 10^{76}$$

It can be possible that due to the presence of other metals like Zn, Ni and Mg in the dross, the hydrogen production yield can be enhanced [76].



The other gases formed when water comes in contact with aluminium dross are ammonia and methane.



The generation of toxic gases is greater in case of salt cakes as the aluminium present in them is very less [121, 124].

1.9 Objectives and scope of present work

The main objective of the present research is to generate valuable products from aluminium dross and recycle it to ensure complete waste management. Developing newer methods to recycle aluminium dross covers the overall aspects of this present work.

In the present research, new methods of recycling of aluminium dross are illustrated. The synthesis of Tamarugite is described in the first and second method using hydrometallurgical route of recycling. Tamarugite has been obtained in two methods and it opens a fresh horizon for research. Tamarugite is a relatively rare mineral found in natural environment where sodium, aluminium and sulphate ions are abundant. With the chemical formula $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, Tamarugite has been identified in alum caves and various geological sites. The application of Tamarugite as a coagulant is also described. The characterization of the products has been carried out and further analysed.

Potash alum generation from aluminium dross is described in the third method. Potassium aluminium sulphate, commonly known as potash alum, is one of the most important chemical compounds used for waste water treatment and coagulation purposes. The chemical formula of potash alum is $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. These products are discussed in greater detail in the subsequent chapters.

The production of hydrogen gas by the reaction of aluminium and water in presence of sodium hydroxide and potassium hydroxide, which can be treated as a fuel for other operations is the last method. It is anticipated that with these methods, the research fraternity can work on this issue with greater insight.