

PREFACE

Aluminium is one of the most important metals employed by mankind. The applications of aluminium range in a vast multitude. The wide utility of aluminium has governed the overall production of aluminium. With the increase in the amount of primary and secondary aluminium produced from primary and secondary aluminium industries, the generation of aluminium wastes has also increased in the present scenario. Among the industrial wastes of aluminium industries, aluminium dross is one of the most important, as it usually contains metallic values that can be recovered.

Aluminium dross is a waste product generated in the aluminium industries. It primarily comprises of metallic aluminium, alumina and salt fluxes. This has attracted the attention of the researchers and new methods of recycling aluminium dross have been developed. There are mainly three types of aluminium dross:

1. *White aluminium dross* (contains higher metallic aluminium content)
2. *Black aluminium dross* (contains lesser metallic aluminium and has higher oxide)
3. *Salt cakes* (minimum metallic aluminium and higher salt fluxes).

The industrial methods of recycling aluminium dross involve the extraction of metallic aluminium from aluminium dross. This is achieved by the pyrometallurgical method of recycling, where aluminium dross is heated with or without salt flux at high temperatures in a rotary furnace. This leads to the separation of metallic aluminium from the matrix of aluminium oxide. Salt flux may be added to bring down the operation temperature and form a protective layer for prevention of further oxidation of the metallic aluminium.

The hydrometallurgical method of recycling aluminium dross involves the leaching of aluminium dross with various media: acidic or alkaline. Many researchers have studied the properties of acidic and alkaline leaching of aluminium dross. This involves the introduction of the raw feed into the aqueous solution at the reaction temperature and allowing it to leach

for a specific period of time. This leads to the extraction of metallic content into the aqueous solution.

Another approach to recycle aluminium dross has been to utilize it as a raw material for the preparation of valuable products. Generation of various industrially and commercially important materials have been produced, like zeolites, composites, refractories and aluminium derivative chemicals. Cement, clinker and concrete products have also been produced using aluminium dross as a raw material. Some researchers have used it as a raw material for making composites.

Another aspect that draws attention is the liberation of gases when aluminium dross comes in contact with water. It has been reported in literature that hydrogen, ammonia and methane can be generated when aluminium dross reacts with water. Moreover, the leaching tendency of aluminium dross makes its disposal very crucial. The heavy metals present in trace amounts can leach out into the soil, thereby disturbing the balance of the pH value of the soil and contaminate the groundwater. This is one of the most important reasons why the recycling of aluminium dross becomes very important.

In the research work embodied herein, the recycling of white aluminium dross is described. The bulk white aluminium dross has been procured from Deva Metals Pvt. Ltd., Varanasi, India. The received dross has been crushed and ground using jaw crushers and ball mills to reduce the particle size.

The primary route recycling aluminium dross has been in hydrometallurgical method. A wide variety of products have been generated using white aluminium dross as a raw material.

As mentioned earlier, the liberation of hydrogen takes place when aluminium dross comes in contact with water. However, the aluminium-water reaction does not take place when distilled water is used. It has been found in literature that slightly alkaline solution leads to

the metal-water reaction. This fact has been exploited and the solution has been made alkaline.

The generation of hydrogen has been studied in with varying the concentration of the solution, temperature of the reaction and the alkali itself. Sodium hydroxide and potassium hydroxide have been used for the experiments. The amount of gas produced has been determined after an interval of every 15 minutes. The gas has been measured by using an inverted measuring cylinder by downward displacement of water.

It has been found that increasing the molarity of the solution increases the cumulative amount of gas released. At lower reaction temperature (40 °C) and lower concentrations (0.5 M), the amount of gas liberated is higher in NaOH solutions, vis-à-vis KOH solutions. At higher concentrations (2 M) and higher reaction temperature (60 °C), nearly 1200 mL of gas can be produced using 1 g of aluminium dross in NaOH and KOH aqueous solutions. The purity of the gas has been confirmed by gas chromatography and it has been found that 96 % of the gas is hydrogen and rest is nitrogen.

The leaching of aluminium dross using potassium hydroxide aqueous solutions has also led to the extraction of metallic aluminium into the leach liquor. The formation of potassium aluminate takes place in the leach liquor. The aluminium content in the leach liquor has been utilized by producing potash alum from it. This is done by adding the required stoichiometric amount of sulphuric acid slowly, drop-wise into the leach liquor. Constant stirring of the solution is done with glass rod.

This solution mixture is then saturated by heating for nearly 15 minutes. The saturated solution mixture is then transferred into a cold water bath. The crystallization of potash alum is allowed to take place. The solution is left undisturbed for nearly 24 hours. The crystals of potash alum are separated from the solution and are washed using ethanol solution to protect

it from contamination. These crystals have been characterized using XRD and SEM-EDS and it has been found that it is of good quality.

It can be seen that after leaching and addition of sulphuric acid into the leach liquor, a series of chemical reactions take place and resultant product is quite valuable. The utilization of aluminium dross to produce potash alum is one of the methods of recycling it and simultaneously generating an important industrial product. Potash alum finds its applications in leather tanning, as mordant, as an astringent and in cosmetic industries. The most important application of potash alum is in the water treatment plants, as a coagulant.

Similarly, the leaching experiments have been carried out using NaOH aqueous solutions. The formation of sodium aluminate in the solutions takes place. The addition of sulphuric acid into the leach liquor produces tamarugite, $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, which is a relatively rare mineral. It has been isolated by various geologists across the world in alum caves and volcanic sites. Along with tamarugite, the presence of other phases, like sodium hydrogen sulphate and trisodium hydrogen bisulphate, is also confirmed. This has been done by subjecting the resultant crystallized product to characterization using XRD and SEM-EDS techniques.

After the addition of sulphuric acid into the solution to produce a solution mixture, the saturation has been carried out by heating. This resulted in reduction of the overall amount of the solution. The heated solution mixture has been transferred to cold water bath. It has been observed that the crystallization of tamarugite takes place almost readily.

This mineral, tamarugite, has not been deeply explored and its applications have not been described much. Therefore, tamarugite has been used for the coagulation experiments. This was done because the presence of aluminium sulphate in tamarugite benefits the coagulation. The preliminary coagulation tests showed that tamarugite is a good coagulant. It readily assists in the coagulation of colloidal particles of the water to settle at the bottom of the

container. The confirmation Jar tests have been carried out using a Flocculator apparatus. Raw water samples have been collected from the River Ganga (Assi Ghat) and used for the experiments.

It has been observed that using tamarugite as a coagulant, the colloidal particles did settle at the end of the experiments. The performance of tamarugite has been compared with that of commercial alum, a common coagulant used for the purpose. It has been found that tamarugite performs well and commercial alum is slightly better coagulant than tamarugite. The performance of tamarugite depends on its quality. After variation of processing steps, it was observed that other phases (sodium hydrogen sulphate and trisodium hydrogen bisulphate) have been present in all cases.

To prepare a pure tamarugite product, the leaching experiments have been done using sulphuric acid first. This led to the production of aluminium sulphate in the solution. The amount of sodium required for the production of tamarugite has been supplied by the addition of sodium hydroxide solution to the leach liquor. This resulted in the supply of aluminium, sodium and sulphate ions into the solution mixture. However, the readily crystallization of tamarugite is not observed in this case.

A different method of generating tamarugite has been explored to solve this anomaly. The use of organic solvents to precipitate out the solutes has been a common method of producing drugs in pharmaceutical industries. The same analogy has been employed to eject tamarugite from the aqueous phase and precipitate it.

Four organic solvents, Ethanol, Acetonitrile, Propan-2-ol and Tert-Butyl-Alcohol, have been used for the purpose. These organic solvents have dielectric constants lesser than water and have good solubility in water. These organic solvents have been maintained at lower temperature while saturated solution mixture containing aluminium, sodium and sulphate ions have been thermostated at 45 °C for 4 hours.

When a small amount of solution mixture is added to the organic solvents, the precipitation of tamarugite is observed. The organic solvent is agitated for around 10 minutes to complete the process. The process is repeated for every organic solvent. It has been observed upon characterization of every sample precipitated that all of them contained tamarugite as the major phase.

Applying the resultant tamarugite for the coagulation, the Jar Tests have been repeated with raw water procured from the River Ganga (Assi Ghat). This time, the comparison has been made between Commercial alum, Poly Aluminium Chloride (PAC), tamarugite (crystallized) and tamarugite (organic solvent precipitated). The determination of pH values of water samples have also been done to study the effect of coagulant addition in water.

It has been found that although PAC is the best coagulant among these coagulants, the drop in pH values of water samples was very drastic. This meant that the maintenance of pH of water required further processing. The drops in pH of water samples have been very less for Commercial alum, tamarugite (crystallization) and tamarugite (organic solvent precipitation). Among the three coagulants, tamarugite (organic solvent precipitation) has performed on par with commercial alum, while tamarugite (crystallization) slightly lagged in coagulation. Even if PAC is the best coagulant among the coagulants tested, the advantage of tamarugite lies in the stability of pH of water.

The utilization of the solid residue obtained after the leaching of white aluminium dross is essential for its complete recycling. One of the methods is to employ it as a raw material for the production of composites. It can also be subjected to second step leaching, to extract the remaining metallic values from it.

The major phases identified are Bayerite and Nordstrandite along with some amount of Silica. These are mainly aluminium hydroxide phases and can be employed for the production of alumina. In order to prepare alumina from the residual solid, heating of the

collected residual samples is carried out at 900 °C for 4 hours in a muffle furnace. This leads to the transformation of residual solid into white powdered alumina. This alumina can be employed in the production of Al-Al₂O₃ composites, or used as a raw material for the generation of refractories.

In chapter 1, the **Introduction** of aluminium dross is described. An industrial waste generated in large quantities in aluminium plants is illustrated. The conventional pyrometallurgical and hydrometallurgical recycling and newer trends of utilization are described. Some introductory remarks about the products described in the later chapters are also given.

Chapter 2 is the **Materials and Methods**, wherein the methodology and processes are described. Details about every valuable product, its process flow sheet, its raw materials and the aqueous solutions required for the synthesis of the products are provided. This chapter bridges the introduction to the results and key findings of the research work.

Chapter 3, 4, 5 and 6 illustrate the **Results and Discussion** of the research conducted. The synthesis of valuable products, **tamarugite, potash alum, hydrogen, and alumina** using aluminium dross as a raw material are described in this chapter. Just as the previous chapter, section-wise division has been done for every product. Sectional conclusion is also provided for improved clarity.

Chapter 7 comprises of the **Conclusions** of the research. In this chapter, the key findings of each chapter and major conclusions of every recycling method illustrated are summarized. It builds a complete holistic inference of the research.

Chapter 8 provides the **Scope for future work** in this field. Many aspects of the work described herein can be further investigated and a lot many different valuable products can be generated using aluminium dross. These aspects are described in this chapter.

The References follow the chapters and a list of publications is provided in the end.