Chapter- 2

Experimental

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2.1 Material procurement and comminution

As illustrated in the previous chapter, extensive research has been carried out to extract metallic aluminium from bulk aluminium dross by various Rotary Salt Furnaces (RSF) and Salt Free Technologies (SFT). These industrial pyrometallurgical routes have high efficiency in liberating aluminium from its dross. Since the larger particles are easily utilized for the liberation of metallic aluminium by pyrometallurgical operations, the main target shifted to the finer particles, with relatively reduced amount of metallic aluminium entrapped in the matrix of alumina. Therefore, the finer particles – 100 mesh particles were separated and stored in a container for further experiments. Borosil glassware was used in all experiments. It should be noted that all the glassware used were washed properly with Labolene soap solution and rinsed with distilled water to ensure the glassware was free of contamination. Figure 2.1 shows the aluminium dross powder.

Figure 2.1: Photograph of fine aluminium dross powder

Bulk white aluminium dross was procured from Deva Metal Powders Pvt. Ltd., Varanasi, India. As received dross bulk samples were crushed, ground and reduced in size using jaw crushers, (Shivam Industries, India). The sieving of the samples was carried out to separate larger particles from smaller particles. For the experiments, fine powdered white aluminium dross was used. It has been found that coarse particles obtained after crushing the bulk aluminium dross have relatively greater percentage of metallic aluminium, as compared to the finer particles. This is due to the agglomeration of aluminium particles with each other, resulting in the formation of the coarser particles. The exterior layer of oxide is generated easily on the finer particles, which means the overall metallic content is less as the oxide layer restricts finer particles to agglomerate and become coarser in size.

2.1.1. Characterization of aluminium dross

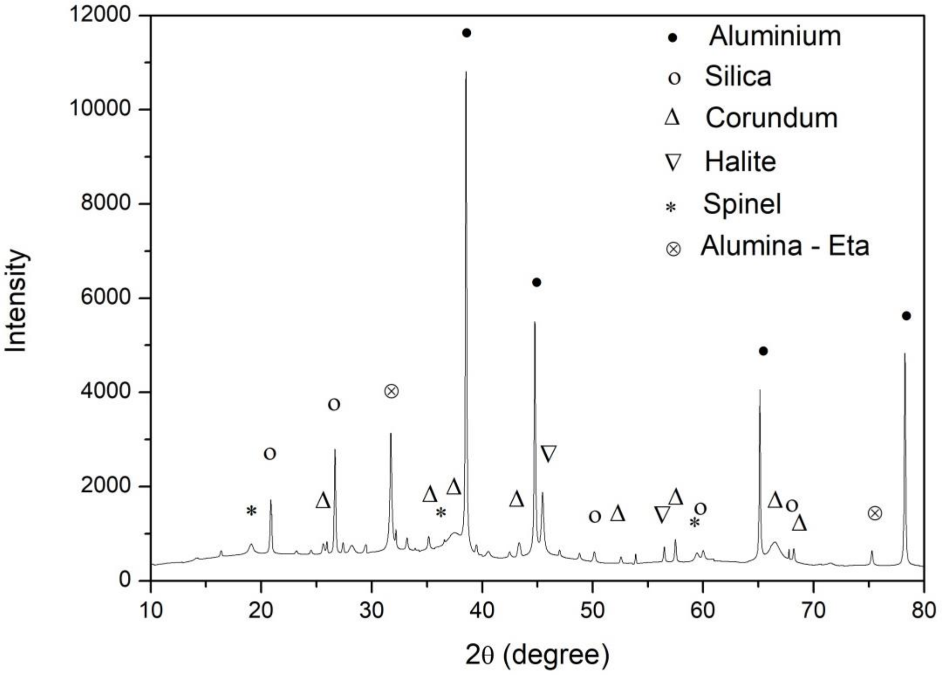


Figure 2.2: The X-ray diffraction pattern for white aluminium dross powder.

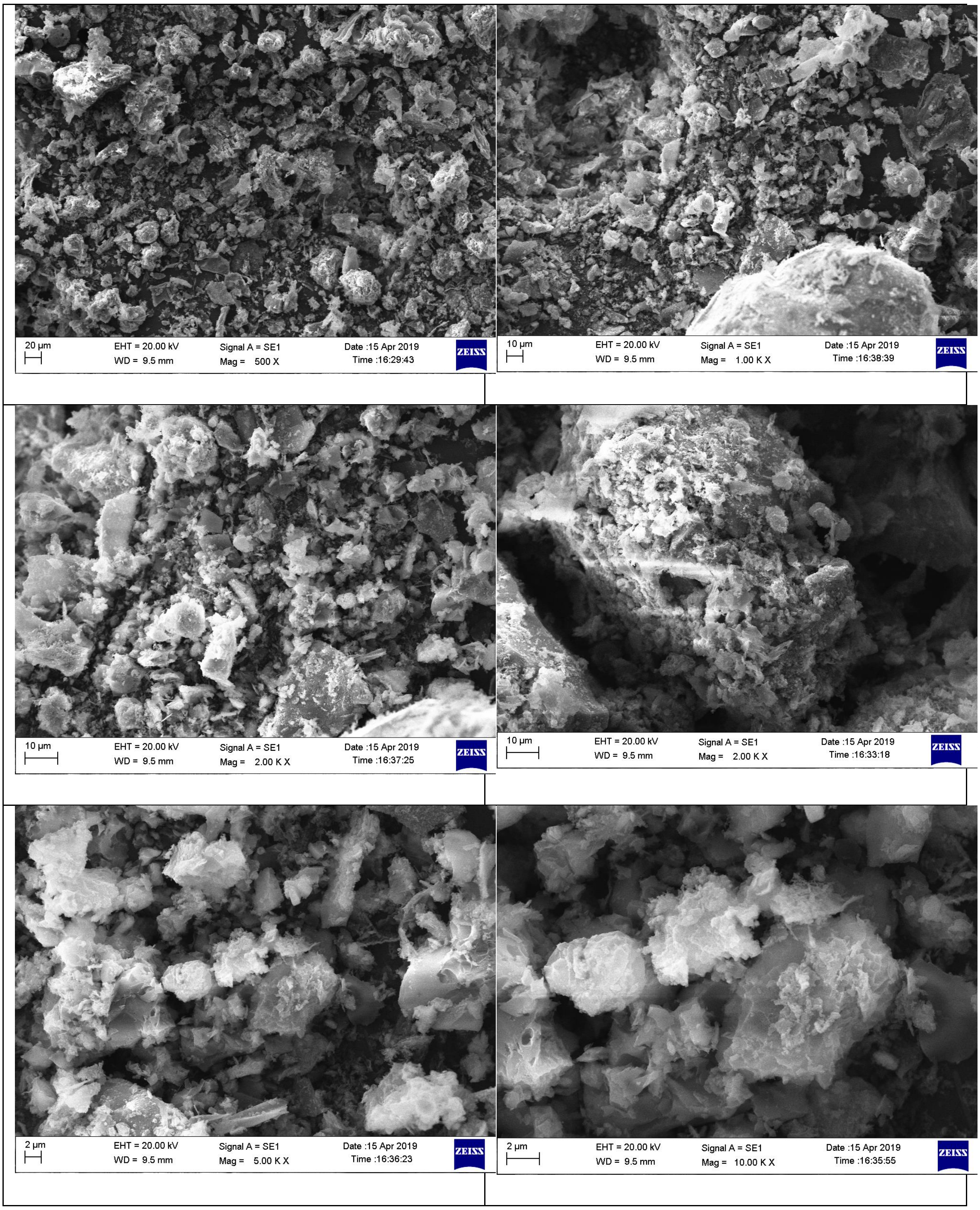
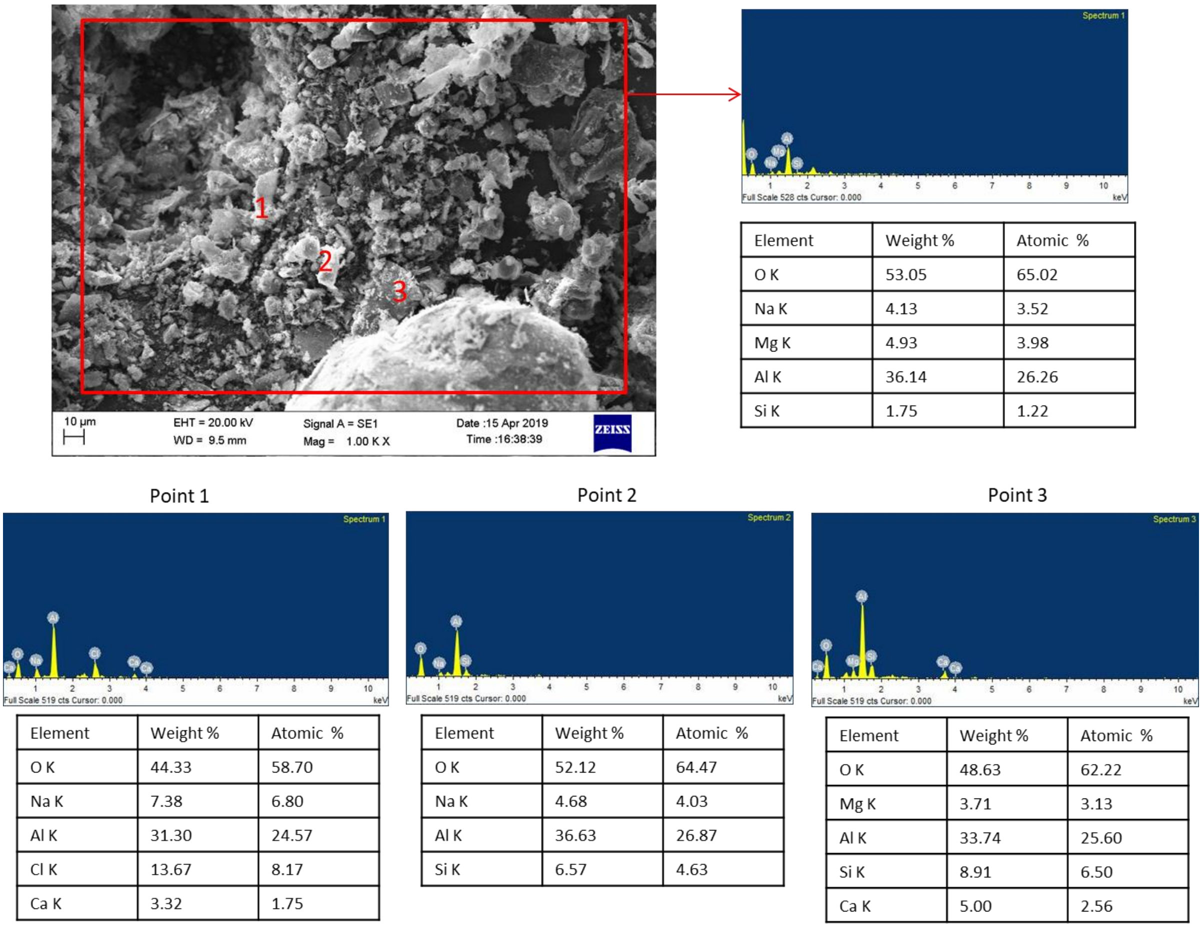


Figure 2.3: SEM images of white aluminium dross at magnification of 500x, 1000x, 2000x, 5000x and 10,000x



Element	Weight %	Atomic %
O K	53.05	65.02
Na K	4.13	3.52
Mg K	4.93	3.98
Al K	36.14	26.26
Si K	1.75	1.22

Point 1

Element	Weight %	Atomic %
O K	44.33	58.70
Na K	7.38	6.80
Al K	31.30	24.57
Cl K	13.67	8.17
Ca K	3.32	1.75

Point 2

Element	Weight %	Atomic %
O K	52.12	64.47
Na K	4.68	4.03
Al K	36.63	26.87
Si K	6.57	4.63

Point 3

Element	Weight %	Atomic %
O K	48.63	62.22
Mg K	3.71	3.13
Al K	33.74	25.60
Si K	8.91	6.50
Ca K	5.00	2.56

Figure 2.4: SEM-EDS of white aluminium dross

Table 2.1: The phases observed in the XRD pattern of aluminium dross

Phases identified	Amount of the phases
Aluminium	47.3 %
Corundum – Al_2O_3	17.3 %
η – Alumina	8.4 %
Silica	13.7 %
Halite	5.2 %
Spinel	8.1 %

Figure 2.2 and Table 2.1 illustrate the phases present in the dross and their amounts. It can be seen that the majority of the dross comprises of metallic aluminium, alumina, η-alumina with some amount of silica and lesser amounts of spinel and halite. The XRD pattern has been obtained for a 2θ range of 10°-80° and by observing the pattern, it can be seen that aluminium peaks have the highest intensity at around 38.5°, 44.8°, 65.1° and 78.3°, 2θ positions. The other peaks are of η-alumina (31.6°, 45.4°) and silica (20.9° and 26.6°).

A close examination of the elements shows that a wide variety of metals are present in the dross, in small quantities. Important elements identified are aluminium, silicon, oxygen with minor amounts of magnesium, sodium and calcium. The above SEM images illustrate the fine particles of aluminium dross with random morphology.

2.2 Synthesis of tamarugite from white aluminium dross powder

As described in the previous chapter, tamarugite has a chemical formula of $NaAl(SO_4)_2.6H_2O$ with sodium, aluminium and sulphate ions. In order to generate tamarugite from white aluminium dross, the powdered dross was leached with 3 M NaOH aqueous solution. The aqueous solution of sodium hydroxide is prepared and 50 mL of this solution is heated to 45 °C in a glass beaker of 250 mL volume. As the solution reaches the temperature, 4 g dross powder is charged. The formation of sodium aluminate takes place, as the addition of aluminium dross is done. The leaching process is carried out for around 45 minutes. The leached liquor was filtered and the solid residue was separated.

To supply sulphate ions into the product, an aqueous solution of 3 M sulphuric acid is prepared. The leached filtrate solution was mixed with 40 mL sulphuric acid using a burette with glass rod stirring. The solution mixture obtained after the reaction was heated to make the solution saturated.

The heated solution was transferred to the cold water bath. Just as the beaker containing the solution was placed in the water bath, the solidification of Tamarugite was observed. The beaker was placed in the water bath and kept in isolation for nearly 1 hour. The saturated solution completely solidified. No residual liquid was left in the beaker. The solid crop of tamarugite was scrapped out of the beaker using spatula and stored in desiccators. When the crystallization of tamarugite does not initiate and complete in 1 hour, the beaker containing the solution mixture should be left isolated for nearly 72 hours. Characterization was carried out using XRD and SEM – EDS. Figure 2.5 describes the experimental details of generating tamarugite.

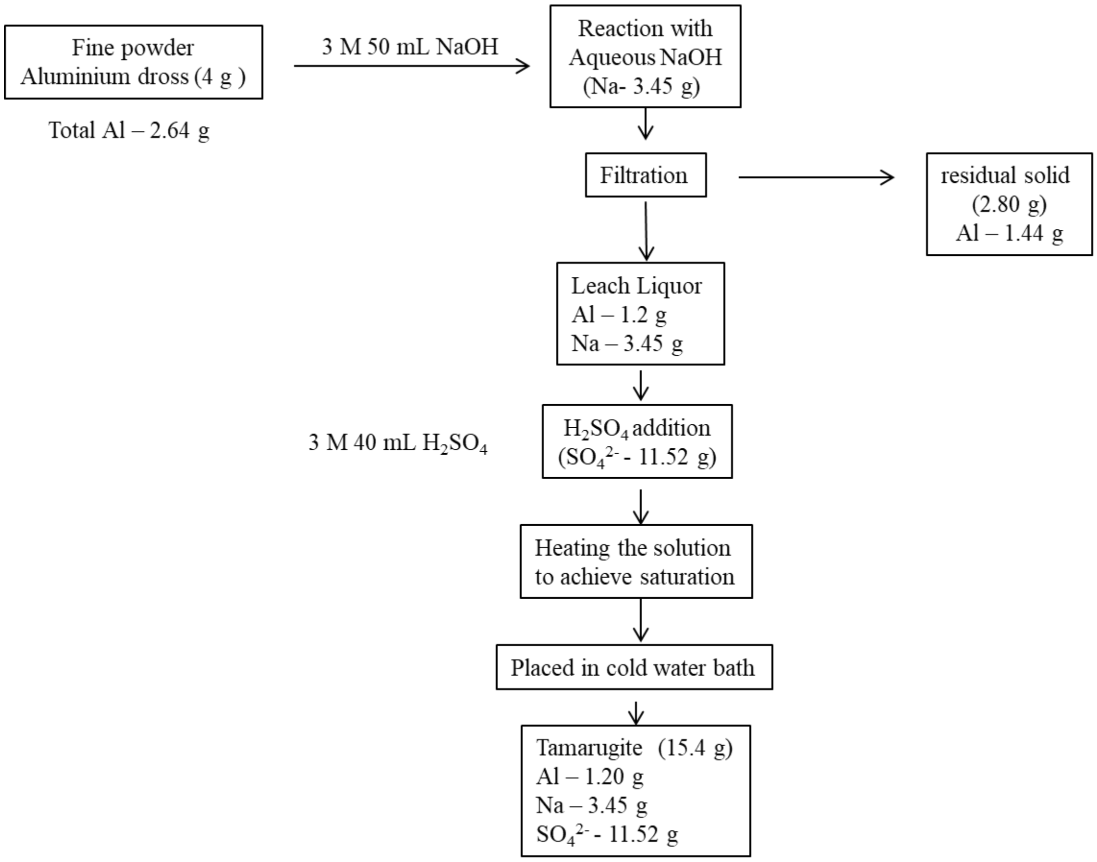


Figure 2.5: Flow sheet and material balance for the production of tamarugite

2.3 Synthesis of Tamarugite by organic solvent precipitation

To produce tamarugite using a different method, the leaching of white aluminium dross powder was done with 70 mL 50 % (v/v) sulphuric acid solution for nearly 4 hours. This was done to extract aluminium into the acidic medium. After the leaching, the solution was filtered to separate the residual solid associated to it. Complexometric titrations using EDTA-EBT have been employed to ascertain the leached amount of metallic aluminium. Aqueous solution of sodium hydroxide was prepared such that the molarity of sodium ions is exactly same as that of aluminium ions present in the leached liquor.

The addition of aq. NaOH solution is done to the leached filtrate solution. The solution mixture thus obtained is heated to make the solution saturated. This saturated solution is thermostated at 45 °C for nearly 4 hours.

Organic solvents (ethanol, propan-2-ol, acetonitrile and tert-butyl alcohol) are also maintained at 20 °C separately. A small amount of the saturated solution at 45 °C is taken using pipette and added to the organic solvent at 20 °C. This solution mixture is stirred at 400 rpm for nearly 10 minutes to ensure complete precipitation of Tamarugite.

It was observed that white precipitate of Tamarugite settled in all of the organic solvents used for the experiment. Tamarugite precipitated at the bottom of the beakers was removed from the solution mixture by decanting the organic solvent. It was observed that the Tamarugite precipitated (in all organic solvents) was soggy and wet; characterization of soggy samples was not advisable. The Tamarugite sample obtained in the previous method was not so soggy, it was hard mass. In order to make the Tamarugite samples dry and fit for characterization, the samples in the beaker were washed with Methanol. Required volume of methanol was added to the beaker to make a slurry containing Tamarugite.

The slurry was transferred to the centrifuge tubes previously washed with distilled water. These centrifuge tubes were placed in centrifugation machine (Remi R-4, Remi Electrotechnik Limited, Vasai, India). The centrifugation machine was operated at 7000 rpm for nearly 5 minutes. This process was repeated five times to ensure complete removal of sogginess. The dried samples were collected from the centrifuge tubes and stored in sealed vials. The characterization of the samples was carried out using XRD, SEM – EDS, TGA and DSC.

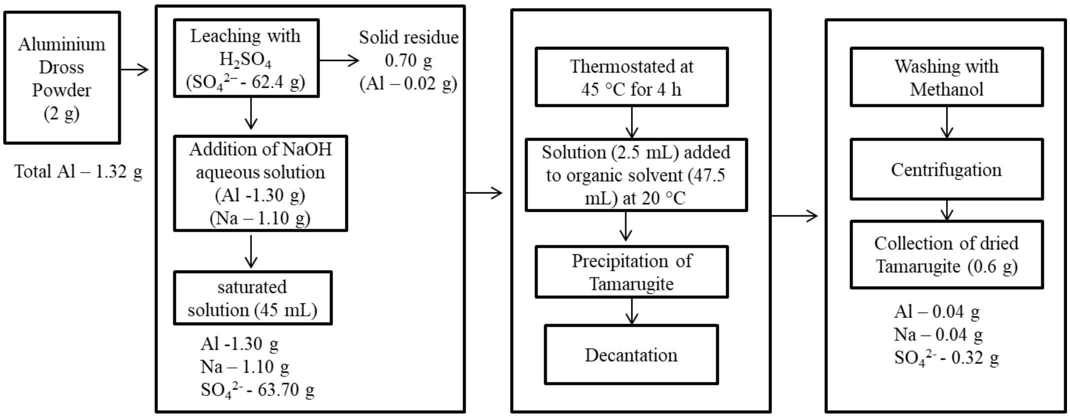


Figure 2.6: Flow sheet and material balance for synthesis of tamarugite using organic solvent precipitation

2.4 Application of tamarugite: Coagulation test

As mentioned earlier, the applications of tamarugite require more investigation and there is a great scope in this area of research. In order to study the application of Tamarugite in waste water treatment, colloidal solutions with soil were prepared. This test was a preliminary step to observe the coagulation tendency of tamarugite.

To one of the sample colloidal solution, tamarugite was added. The other sample colloidal solution was left pristine. It was observed that in the sample colloidal solution with tamarugite, the particles had completely settled down. The solution was clear and free from colloidal particles. The other sample colloidal solution was still the same. No settling was observed. With this preliminary test results, the jar test was conducted to study the coagulation tendency in greater depth.

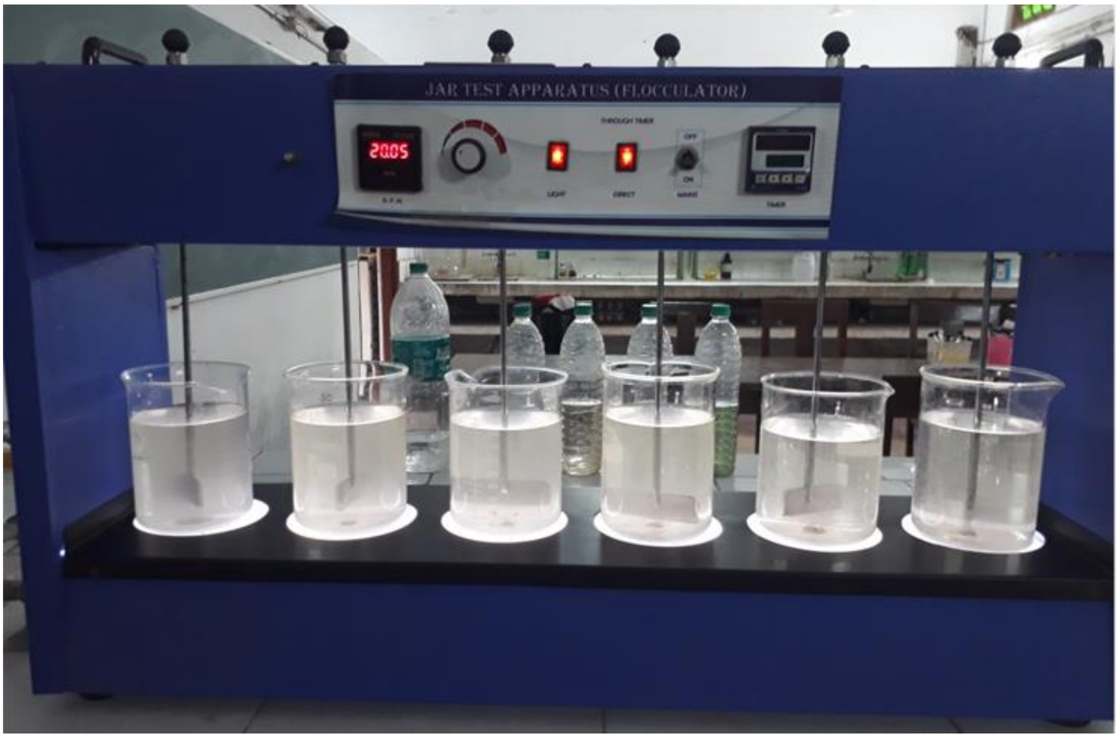


Figure 2.7: Flocculator apparatus used for the jar test

Raw water was collected from Assi Ghat, River Ganga, Varanasi. The characterization of the raw water was done using Nephalometer. The addition of coagulant solution was done to study the effect of coagulant on the colloidal particles and turbidity of the water. Coagulant solution was prepared at a concentration of 1 g/L for tamarugite (crystallized and organic solvent precipitated), commercial alum. Also Poly aluminium chloride was tested alongside these coagulants. The final turbidity of the water samples was determined again using the Nephalometer.

2.5 Production of potash alum from white aluminium dross powder

The production of another valuable product, potash alum, using white aluminium dross is described. This method required 3 M aqueous solution of KOH. The temperature of 50 mL freshly prepared solution is raised to 45 °C and maintained. The addition of dross (2 g) is done to the solution. As mentioned in the previous section, the dross is the source of metallic aluminium. After the addition of dross, the reaction was continued till 45 minutes. The leached solution was filtered using Whatman filter paper 41 and the residual solid was separated, leaving behind pale solution containing $KAl(OH)_4$. The next step was the introduction of sulphates to the solution. For this, 70 mL of freshly prepared 3 M sulphuric acid is used. Care is taken that the addition of sulphuric acid is done slowly with stirring. If sulphuric acid addition is done in haste, the rate of formation of $Al(OH)_3$ is altered and the other reactions do not take place properly. The end product may contain the residual acid and the experiment ends in a failure.

The resultant solution contained in the beaker is heated on the hot plate to attain saturation for various time periods (5 min.-15 min.). To determine the degree of saturation, a clean glass rod was dipped from time to time into the solution. If small crystals would form on the rod, the saturation was achieved.

To produce potash alum from the solution, the hot saturated solution was placed in cold water bath for nearly 20 to 24 hours. The crystallization of potash alum took place at the bottom of the beaker. This alum was characterized using XRD, SEM – EDS, TGA. Figure 2.7 describes the methodology of producing potash alum from aluminium dross.

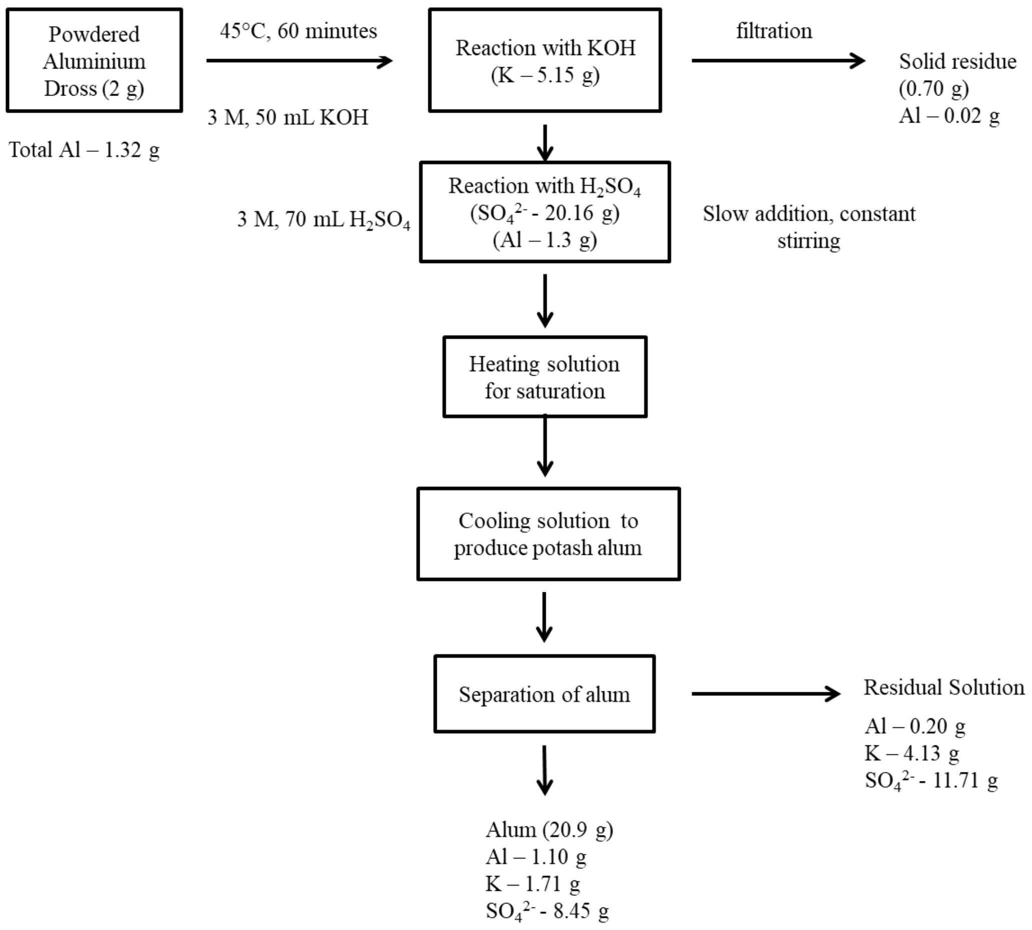


Figure 2.8: Flow sheet and material balance for production of potash alum

To understand the mass flow from white aluminium dross powder to leach solution (obtained after reaction with aqueous KOH solution) and to the potash alum formed in the end, EDTA – EBT back titrations were carried out. The details of complexometric titrations are described in the later sections.

2.6 Generation of hydrogen gas from white aluminium dross powder

As described by David and Kopac [76], the generation of hydrogen gas is an important utilization of aluminium dross. For their experiments, high energy ball milled samples were prepared with nearly 45 µm particle size. Regular water initiated the aluminium – water reaction to produce hydrogen gas. The present research work focused on the utilization of powdered dross to produce hydrogen. This was achieved using alkaline solutions.

In order to produce hydrogen gas using the aluminium – water reaction, aqueous alkaline solutions of sodium hydroxide and potassium hydroxides of different concentrations were prepared. These aqueous alkaline solutions were heated to temperatures at which the generation of hydrogen was to be studied; after the solutions attained the temperatures, fixed quantity of white aluminium dross powder was added.

The experiments were carried out using drilled rubber cork sealed with pipe especially fabricated for this process. Fig. 2.9 shows the rubber cork with pipe employed for the hydrogen evolution experiments and Fig. 2.10 shows the schematics for the generation of hydrogen gas.

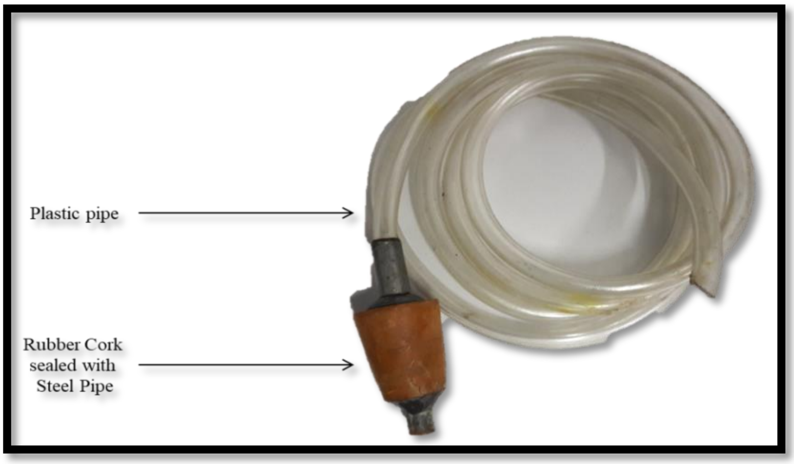


Figure 2.9: The gas collecting pipe: rubber cork with steel pipe attached to a long plastic pipe

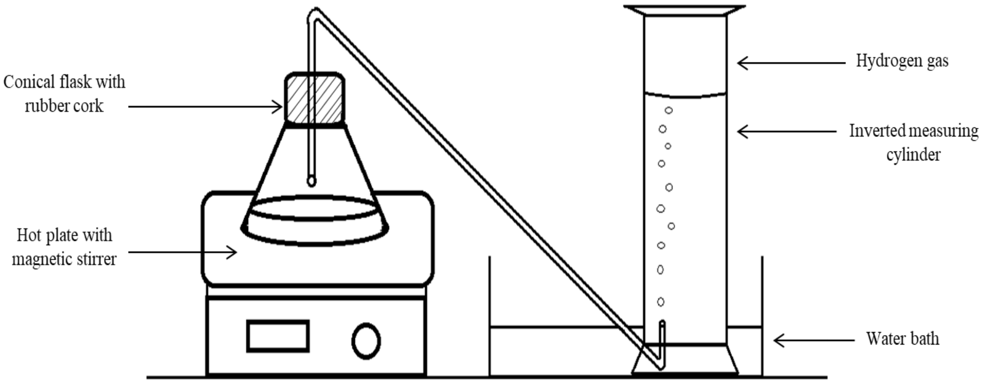


Figure 2.10: Schematic diagram describing the generation of hydrogen gas from aluminium dross

From figure 2.10, it can be seen that the aqueous alkaline solution is reacted with white aluminium dross powder in a conical flask after it reaches the required temperature. As soon as the powdered dross is introduced to the conical flask with alkaline solution, the rubber cork is attached to it. At this point, the stirring is also initiated in the solution to increase the reaction rate and hydrogen evolution. The rpm was nearly 400 rpm.

It is made sure that no gas is leaking out of the conical flask. As the reaction proceeds, the generation of hydrogen gas takes place and it fills the conical flask, eventually passing through the pipe to the inverted measuring cylinder. The water present in the cylinder gets displaced by the hydrogen gas and gets collected at the top of the cylinder. The amount of gas generated is measured by the reading obtained on the cylinder. This is possible due to the downward displacement of water. To account for the errors during the experiments, triplicates of experiments were carried out and the resultant average value was reported. The variation of parameters for the hydrogen evolution experiments have been shown in Table 2.1.

Table 2.2: The reaction parameters studied for the evolution of hydrogen

NaOH		**KOH**	
Concentration (M)	**Temperature (^{0}C)**	**Concentration (M)**	**Temperature (^{0}C)**
0.5	40 50 60	0.5	40 50 60
1	40 50 60	1	40 50 60
2	40 50 60	2	40 50 60

2.7 Production of alumina from the residual solid

The residual solid present in the leached solution after the aluminium – water reaction has been filtered using ash – less filter paper number 41 and collected for analysis. After the phase identification using X – ray diffraction analysis, the residual solid was heated in alumina crucible for nearly 4 hours at 900 °C in muffle furnace (Anil scientific, India). For heating in the furnace, ash – less filter paper was used.

Collecting the cooled samples of residual solid and analysing it again using the XRD, it was found that alumina had formed as the end product. Thus, the residual solid can be utilized for the generation of composite and other products, as alumina is an important industrial material.

2.8 Details of characterization techniques

X – Ray Diffraction analysis was done using Rigaku Tabletop MiniFlex 600; Dtex Ultra, with copper target Cu K_α = 1.54 Å. The 2θ range was usually 10° - 80°. Scanning Electron Microscopy – Energy Dispersive Spectrometer was carried out on Zeiss Evo-18 Research 2045, Oxford X-act INCA x-act.

Thermogravimetric analysis of potash alum was carried out on TGA – 50 Shimadzu Thermogravimetric Analyser. The gas flow rate of nitrogen was 50 mL per minute. The heating rate was around 10 °C per minute and platinum crucibles were used for the characterization. The range of temperature was 30 °C to 500 °C. Thermogravimetric analysis of Tamarugite was at temperature range of 30 °C to1000 °C.

ICP Continuous, Spectrometer model: optima 7000 was used for the determination of the amount of aluminium, sodium and potassium present in the tamarugite and potash alum samples. Aqueous solutions of the samples were prepared such that the ions were present in the detection range (in ppm) of the ICP-OES.

Proton NMR and Carbon NMR: Bruker ASCEND ^{TM} 500 NMR was used to determine the spectra for the organic solvents. Dimethyl sulphoxide was used as the solvent for the organic solvents to facilitate the characterization.

Gas chromatography with TCD, CS5800, Centurion Scientific, New Delhi was used for the characterization of the gas samples. Argon carrier was used during the experiments.

Jar Test – Flocculator: turbidity measurement was done using Nephalometer. The unit of turbidity is Nephalo Turbidity Unit (NTU). The Flocculator is the instrument shown in figure 2.7.

2.9. Determination of aluminium present in the solution by complexometric titrations

A simple method of determining the amount of aluminium leached in the solution is the complexometric titrations. As illustrated in the literature, the use of Ethylenediaminetetraacetic acid (EDTA) as a complexing agent is a must. In these titrations, sodium salt of EDTA is employed.

The most important aspect of these titrations is keeping the moles of EDTA salt greater than the expected moles of aluminium in the solution. Aluminium ions react with EDTA salts in a ratio of 1:1 and form complexes. After the reaction, the excess amount of EDTA is titrated against aqueous $ZnSO_4$ solution. The reaction between excess EDTA and zinc ions is also in the ratio of 1:1. The point of titration is determined when Eriochrome Black-T is used as an indicator.

To carry out the titrations, an estimate of moles of aluminium must be determined in the solution. With a fair estimation, excess moles of EDTA salt is added to distilled water to prepare an aqueous solution. A known amount of aluminium solution is added to the EDTA salt aqueous solution. This solution is allowed to settle, as the complexing reaction takes place. The pH of the solution mixture is determined using a digital pH meter. The value of the pH of the solution is so adjusted that it reaches close to 8. The temperature of the solution is maintained at room temperature.

After the adjustment of the pH, the addition of EBT indicator is done. The colour of the solution at this point turns blue. The solution is then subjected to titration with aqueous $ZnSO_4$ solution. During the transition, the colour changes from blue to violet to wine red in the end. The transition of the colour of the solution marks the end of the titration. The value of the $ZnSO_4$ solution required for the titration is noted from the reading on the burette and calculations are done to determine the moles of zinc consumed for the reactions. Subtracting the moles of zinc ions consumed for the complexometric titration from the total moles of EDTA salt used initially gives the moles of aluminium ions that actually formed complex with EDTA.

There are some important precautions for these titrations. The use of distilled water is a must. The presence of unwanted metal ions in the tap water can affect the value of $ZnSO_4$ consumed for the reaction. The pH of the solution must be adjusted before the addition of indicator and the titration; else the colour transition will not be very evident. To ensure the amount of $ZnSO_4$ consumed for the titrations, the reactions should be repeated. The initial assumption of aluminium ions in the solution affects the amount of $ZnSO_4$ used for the titrations.