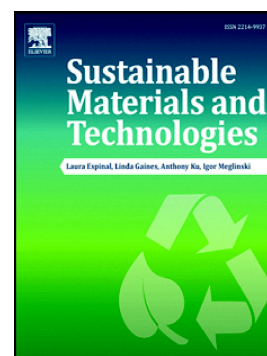


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Comprehensive utilization of bauxite residue for simultaneous recovery of base metals and critical elements

Himanshu Tanvar, Brajendra Mishra

Material Science and Engineering, Worcester Polytechnic Institute, Worcester, MA 01609, USA

Abstract

The growing stockpiles of bauxite residue and associated environmental hazards require a sophisticated recycling system for complete utilization and value recovery. The current application is limited as a raw material for building and construction applications. Considering the association of multiple elements (Fe, Al, Si, Ca, Ti, V, S) within bauxite residue, metal extraction is of prime interest with respect to the economic value of the final product. The following study presents a hydrometallurgy-based process flowsheet for the sustainable recovery of base metals and critical elements within bauxite residue. Major elements present in bauxite residue are recovered as materials for industrial application, including high purity magnetite, alumina, titania, silica, and calcium carbonate. Trace elements are recovered in the liquid stream generated after the recovery of base metals.

1. Introduction

Aluminum (Al) is the second most widely used metal globally and is primarily produced from bauxite ore. Despite the high recycling rate of scrap Al, more than 60 % is produced from bauxite through the Bayer and Hall-Héroult process (Habashi, 2016). The worldwide primary production of Al metal during 2021 was approx. 65.2 million tons, with 37.0 million tons alone from China (Bray, 2021). The global reserves of bauxite ore are estimated between 55 to 75 billion tons and are sufficient to meet the world demand well into the future (Bray, 2021). Production of alumina through the Bayer process results in producing a large quantity of caustic waste called bauxite residue or red mud. Approx. 1 – 1.5 tons of bauxite residue is generated per ton of alumina, and the annual waste generation is over 150 million tons, with a total of 3 – 4 billion tons accumulated by 2022 around the globe (Agrawal and Dhawan, 2021a; Anawati and Azimi, 2019; Evans, 2016).

Bauxite residue is characterized by fine particle size (80% passing 10 microns), high alkalinity (pH 10 – 12) and moisture (30 – 60 %) content (Khairul et al., 2019). The amount of moisture in

bauxite residue is determined by the solid-liquid separation process of individual Bayer refinery and impacts the storage conditions and requirements. The primary technology in Bayer refineries for solid-liquid separation is counter-current decantation which results in red mud slurry with more than 40 % solid content. Disposal, handling, and storage of such highly corrosive, low solid content slurry is expensive and requires a large land area (approx. 1 km² every 5 years for a 1 Mt/year alumina plant), generating potential health and environmental hazards (Ruyters et al., 2011; Tsakiridis et al., 2004). However, in recent years many Bayer refineries have adopted filter press technology to consolidate bauxite residue as high solid content residue (more than 70 % solid), resulting in dry storage (Healy, 2022). Dry storage has several advantages over traditional practice, including easy handling of residue, low land area required for storage and low maintenance cost of the storage facility. However, high alkalinity and salinity are the main chemical limitations to plant growth and rehabilitation of bauxite residue storage lands, which leaves storage area un-vegetated and causes environmental problems (Di Carlo et al., 2020). Less than 4 % of the bauxite residue is utilized globally as an additive in the building and construction industries. The rest is stockpiled near the bauxite processing plant and presents an alarming waste disposal situation (Evans, 2016). Bauxite residue consists of mixed phases of iron (Fe, 5 – 60 %), Al (5 – 30 %), titanium (Ti, 1 – 15 %), calcium (Ca, 2 – 14 %), silicon (Si, 5 – 50 %), and sodium (Na, 1 – 15 %) along with scandium (Sc, 0.001 – 0.012 %), gallium (Ga, 0.001 – 0.011 %) and vanadium (V, 0.03 – 0.23 %), as critical elements (Evans, 2016; Khairul et al., 2019; Ujaczki et al., 2018). Depending on the geographic location of the alumina refinery, bauxite used, and processing parameters, the mineralogy of bauxite residue varies drastically (Borra et al., 2016a; Mishra and Gesta, 2017; Swain et al., 2020). The presence of different elements including Fe, Ti, Al, Sc and V in the bauxite residue makes it a potentially lucrative source for metal extraction. Several research articles have been published investigating the extraction potential of valuable metals from bauxite residue; however, industrial-scale processing is still limited (Agrawal and Dhawan, 2021a; Ujaczki et al., 2018). The complex association of different elements, physical and chemical characteristics makes the extraction process expensive and challenging.

Basic metallurgical operations, including hydro and pyrometallurgical processes, are successful in recovering target elements from bauxite residue (Archambo and Kawatra, 2020a). Pyrometallurgical operations are mainly concerned with the recovery of Fe as pig iron or

magnetite concentrate (Borra et al., 2015a; Cardenia et al., 2018; Mishra et al., 2002). Smelting processes (Romelt process and EAF smelting) for recovery of metallic Fe are found successful on a pilot scale (Balomenos et al., 2012; Balomnenos et al., 2016). However, economic uncertainty due to high energy consumption is the limiting factor for industrial-scale applications (Anawati and Azimi, 2020; Archambo and Kawatra, 2020b). Furthermore, it results in the generation of poor-quality slag composed of Ca, Na, Al, Ti and Sc. There is very little information on slag processing for value recovery and is limited to the sulfation baking and leaching based route to dissolve Sc and Ti (Anawati and Azimi, 2020; Borra et al., 2015a).

Considering high selectivity, pure product, low capital and energy requirement, hydrometallurgical processes have been advancing progressively and adopted commercially in extractive metallurgy and recycling industries (Habashi, 2005). The selection of reagents and processing conditions is critical in hydrometallurgical operations to achieve high recovery. Hydrometallurgy-based studies are mainly concerned with the recovery of Sc and Ga from bauxite residue (Ding et al., 2022; Reid et al., 2017; Ujaczki et al., 2019). However, the low concentration of Sc, Ga and a high fraction of impurities (Fe, Al, Si, Ti, Na, Ca) demands high acid dosage during leaching and results in multi-element dissolution making downstream separation complicated and expensive (Aksil et al., 2017). These processes are concerned with the dissolution of elemental species, however, isolation and recovery of different elements from solution is limited (Agrawal and Dhawan, 2021b; Agrawal and Dhawan, 2021c; Borra et al., 2015b). Few literature works are concerned with recycling a high quantity of waste generated; therefore, scaleup efforts and industrial-scale processing are questionable for sustainable process development. Economically feasible, near-zero waste production hydrometallurgical flowsheet to recover both major (Fe, Al, Ca, Si, Ti) and minor (Sc, V) elements from bauxite residue is still lacking in the literature.

The following work presents a hydrometallurgical flowsheet using different lixivants to selectively dissolve and recover metallic values at various stages of treatment. Hydrochloric acid (HCl), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), and sulfuric acid (H_2SO_4) are utilized as chemical reagents for dissolution of (Al, Si, Ca), (Fe, V), and (Ti, Sc), respectively. Whereas precipitation from solution, photochemical reduction and hydrolysis are adopted to recover the dissolved species selectively. Furthermore, an effort is made to utilize the waste solution generated during the

process. Solution recycling shows positive results in terms of regeneration of chemical lixiviant and additional value recovery for closed loop recycling process. A comprehensive flowsheet and material balance are presented to recover high purity magnetite, titania, alumina, calcium carbonate, and silica from bauxite residue. Focus is also made on the recovery of critical elements, including Sc and V in the proposed flowsheet. The present work is one of the few studies focused on recovering high purity magnetite, alumina and titania from bauxite residue using a hydrometallurgy-based process and results in simultaneous recovery of critical elements. Based on the experimental work, theoretical and economic analysis, the proposed process is economically feasible, results in near-zero waste discharge, and presents an excellent opportunity for industrial scale processing of bauxite residue.

2. Experimental section

2.1. Sample information and chemicals

The bauxite residue sample used in this study was procured from an alumina refinery (Rio Tinto Alcan) located in Quebec City, Canada. The bulk sample was collected from the dried section of the bauxite residue pond, dried in a laboratory oven at 110 °C for 12 h to remove residual moisture and further sieved below 250 microns to remove large impurities (wood chips and pebbles). The bulk sample consists of Fe (21.4 wt.%), Al (10.2 wt.%), Na (6.9 wt.%), Ca (2.3 wt.%), Si (5.0 wt.%), and Ti (3.1 wt.%). The concentration of trace metals of significant interest, including Sc and V, was 0.0016 % and 0.1074 %, respectively. The major phases determined from X-ray analysis consist of hematite (Fe_2O_3), boehmite ($\text{Al}(\text{OOH})$), gibbsite ($\text{Al}(\text{OH})_3$), sodium aluminosilicate ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2(\text{H}_2\text{O})_2$), calcium carbonate (CaCO_3), quartz (SiO_2), and anatase (TiO_2).

2.2. Experimental procedure

The simplified process flowsheet followed in this study is shown in Fig. 1. Bauxite residue was subjected to a multistage leaching and precipitation route for selective recovery of different metallic oxides at different stages of treatment.

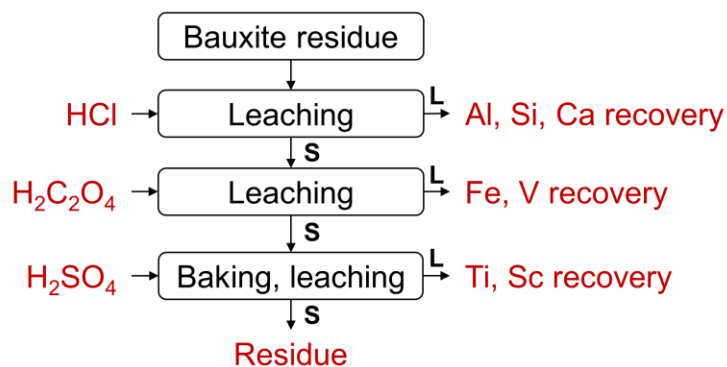


Fig. 1. Simplified processing flowsheet followed in this study.

2.2.1. Bauxite residue neutralization

Bauxite residue was neutralized by leaching with 1 M HCl in a 1000 mL Pyrex beaker at the following leaching conditions: 800 rpm stirring speed, 40 °C temperature, 130 g/L pulp density, 15 min. time. The following operating condition was based on our previous work and resulted in maximum removal of alkali fraction while retaining other elements (Fe, Ti, Sc, V) in the residue (Tanvar and Mishra, 2021). The neutralized slurry was filtered to obtain neutralized bauxite residue and leach solution. The leach solution was subjected to polymerization and aging to recover dissolved Si and Al values. Solution aging was performed by adjusting the solution pH to 3 and keeping the solution ideal for 1 to 3 days to initiate polymerization. At the end of the aging period, polymerized silica was filtered to obtain pH 3 precipitate and respective solution using vacuum filtration. The pH of the solution was subsequently increased to 6.5 – 7 to precipitate aluminum hydroxide (pH 6 precipitate). Aluminum hydroxide precipitate was recovered after filtration and further calcined at 1000 °C for 1 h in a muffle furnace to obtain alumina (Al₂O₃). The solution after Al precipitation was subjected to carbonation to recover Ca precipitate. Carbonation experiments were carried out in a 2000 mL Erlenmeyer flask equipped with a gas dispenser. Pure CO₂ gas (> 98%) was passed through the solution at a flow rate of 200 mL per minute at atmospheric pressure for 30 min at pH 10. The carbonated slurry was filtered to obtain calcium carbonate precipitate and solution. Ammonium hydroxide solution was added to the solution under magnetic stirring to increase the pH of the solution to the desired value. All the solid products at different stages of precipitation were separated by vacuum filtration setup and dried in a laboratory oven at 98 °C for 24 h before characterization.

2.2.2. Leaching with oxalic acid and photochemical reduction

Neutralized bauxite residue was leached with 2 M oxalic acid in a 1000 mL three-necked flat bottom Pyrex flask using a magnetic stirrer at the following conditions: 900 rpm stirring speed, 95 °C temperature, 100 g/L pulp density, 2.5 h time. One end of the flask was connected to a reflux condenser, while the other two ends were used to measure slurry temperature and add samples. The leached slurry was filtered using vacuum filtration setup to obtain ferric oxalate solution and residue.

The leach solution was subjected to ultraviolet (UV) light exposure for photochemical reduction of Fe (III) to Fe (II) and precipitation of ferrous oxalate. Precipitation experiments were carried out in a Pyrex crystallization dish using a UV lamp of 100 W power. UV lamp emitting UV A and B (280 – 400 nm) irradiations was fixed on the top to irradiate the solution. UV exposure was performed for 6 h using 500 mL leach liquor under continuous stirring at 150 rpm. Optimized conditions for leaching with oxalic acid and photochemical reduction were selected based on our previous work (Tanvar and Mishra 2021). The ferrous oxalate precipitate was collected after filtration of reacted slurry and further dried in a laboratory oven at 98°C for 24 h. The filtered solution obtained after precipitation was utilized for the next cycle of leaching with oxalic acid. The desired amount of oxalic acid was added to the solution to adjust the concentration at 2 M before leaching. The leach solution recycling was carried out nine times, and different residues, solutions and precipitates were collected and analyzed.

2.2.3. Ferrous oxalate decomposition

The ferrous oxalate precipitate collected after photochemical reduction of ferric oxalate leach liquor was subjected to thermal decomposition to produce magnetite. Decomposition experiments were performed in a tube furnace (MTI OTF-1200X) under an inert atmosphere to prevent oxidation of Fe(II) to Fe(III). Ferrous oxalate samples were heated to desired temperature (300 – 500 °C) with a heating rate of 9 °C/min, followed by decomposition for 1 h under a continuous flow of nitrogen gas (50 ml/min). The sample was cooled down to room temperature in a nitrogen atmosphere before taking out of the furnace to prevent oxidation.

2.2.4. Sulfation baking and Ti hydrolysis

After leaching with oxalic acid, the resulting residue was subjected to sulfation baking using sulfuric acid to recover Ti and Sc. The solid samples were thoroughly mixed with the desired

amount of sulfuric acid (1.3 mL/g) to form a paste which was further transferred into a ceramic boat and heated in a tubular furnace at different temperatures (150 – 400 °C) for 2 h. The sulfated sample was pulverized using a mortar pestle and subsequently leached in 0.5 M sulfuric acid at 65 °C for 90 min. Leaching experiments were carried out 500 mL Pyrex beaker using a magnetic stirrer at 800 rpm stirring speed. The leach residue and leach liquor were separated using a vacuum filter, followed by thermal hydrolysis of leach liquor to recover Ti precipitate. Hydrolysis experiments were carried out by boiling the solution to 100 °C for 4 h in a 1000 mL Pyrex flask connected to a condenser.

2.3. Analytical techniques

The chemical analysis of the samples was carried out using Inductively Coupled Plasma – Optical Emission Spectroscopy and Mass Spectroscopy (ICP – OES (PerkinElmer Optima 8000), MS (PerkinElmer NEXION350x)). ICP-OES was used to analyze major elements, while ICP-MS for trace elements. Solid samples were fused with borate flux at 1000 °C for 1 h, dissolved in 25 % nitric acid solution, diluted, and further analyzed with ICP – OES and MS. In contrast, the liquid samples were analyzed after dilution with 2 % nitric acid. Mineral phases present in the solid samples at different stages were determined using an X-ray diffractometer (XRD; PANalytical Empyrean). The diffraction data were measured using a Cr – K α radiation in the 2 – theta range of 10 to 80°, with a scanning rate of 2 °/min and a step size of 0.02°. Thermodynamic information and standard Gibbs free energy of different reactions were determined using the Reaction module in FactSage 8.0 and HSC Chemistry 5.1 software.

3. Results and discussion

3.1. Bauxite residue neutralization and recovery of Al, Si, and Ca

Direct leaching of bauxite residue in acid solution requires an additional reagent because a part of it is consumed to neutralize the alkali left behind from the Bayer process. Neutralizing bauxite residue with HCl reduces the acid demand during the second stage of leaching with oxalic acid. Oxalic acid is relatively more expensive than HCl; therefore, neutralization with HCl reduces the overall reagent cost. Based on the preliminary oxalic leaching experiments, it was found that the oxalic acid consumption in the Fe leaching process is reduced by 32 % after neutralization of bauxite residue with HCl and product purity was enhanced significantly. Therefore, bauxite

residue was neutralized with HCl before leaching with oxalic acid. Carbonation of bauxite residue slurry is reported to reduce the pH to a neutral range (6-7) during continuous purging with CO₂; however, the presence of unreacted sodalite and hydroxide buffers the pH of bauxite residue to an average value of 10 – 11 after CO₂ bubbling is stopped (Rivera et al., 2017). Carbonation is only efficient for removing freely available alkali and cannot dissociate the sodium aluminosilicate structure resulting in only 10-12 % Na removal. Therefore, leaching with mild HCl was adopted to neutralize and dissociate sodium aluminum silicate (sodalite, Na₈Al₆Si₆O₂₄(OH)₂) phase and reduce the Na, Ca content below 1 %. The underlying chemical reactions of Na, Ca, Al, Fe, Si and Ti oxides with HCl, along with the respective Gibbs free energy at 40 °C, are shown in Eq. (1-6). A high negative value of Gibbs free energy for dissolution of Na, Ca, and Al shows a high thermodynamic tendency to attain equilibrium in a short duration of time. Whereas the less negative value of Gibbs free energy for Fe shows that the reaction is thermodynamically favorable, however requires a high temperature and longer duration to reach equilibrium (Majima et al., 1985). Furthermore, positive values of Gibbs free energy for Ti and Si show that the reaction is not favored thermodynamically. The HCl leaching experiments were conducted for a short duration (15 min) at 40 °C to dissolve the maximum fraction of alkali and retain Fe, Ti, Sc and V in the residue for subsequent recovery.

The chemical composition of bauxite residue neutralized solid, and leach solution at optimized conditions (1 M HCl, 15 min, 40 °C, 130 g/L pulp density) based on our previous work is shown in Table 1 (Tanvar and Mishra, 2021). The HCl leaching resulted in the dissolution of 93.1 % Na, 92.7 % Ca, 59.3 % Si, and 39.1 % Al. Whereas dissolution of Fe, Ti, Sc and V was less than 5 %. The pH of bauxite residue slurry dropped from 11 to 3 after neutralization. The XRD spectrum of neutralized residue presented in Fig. 2 (a) shows that the peaks corresponding to sodalite (2 theta = 20.8°, 52.39°) and calcite phase (2 theta = 44.4°) dissociated after HCl wash. The XRD analysis shows that HCl wash predominantly dissociated sodalite and calcium carbonate phases resulting in the dissolution of corresponding Na, Al, Si, and Ca values. The reaction of gibbsite and hematite with HCl is thermodynamically favored with negative value of Gibbs free energy; however, based on XRD analysis, both phases are evident in neutralized samples showing limited dissolution due to kinetic limitations. Since the HCl leaching was performed for 15 min, the sodalite and calcite phase reacted spontaneously, consuming most of

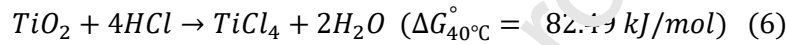
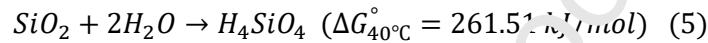
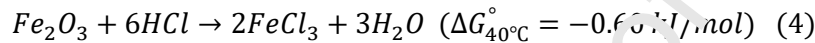
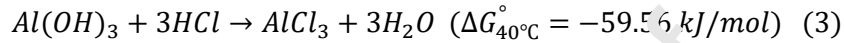
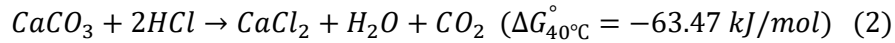
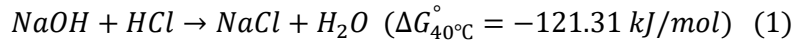
the free acid. In contrast, gibbsite and hematite did not react as sufficient time, temperature and acid were not provided for dissolution.

The solution obtained after HCl leaching (pH 2.7) mainly consists of 2882.82 ppm Ca, 8711.04 ppm Na, 3517.02 ppm Si, and 5309.20 ppm Al as dissolved species and was further processed for recovery of these elements. As per the standard E-pH diagram of the Al, Si, Na, Ca-O-H system, Al can be selectively precipitated as Al hydroxide in the neutral pH range (6-7). However, the dissolved silica forms a polymeric structure with monomers of $\text{Si}(\text{OH})_4$ branched together to form polysilicic acid and caused a gelatinous solution. Direct increase of pH to 6 causes silica to polymerize and results in poor recovery and purity of Al product. Therefore, silica needs to be separated before Al recovery is attempted to obtain a high purity product. The sol-gel method is widely applied to produce silica, ceramic and glass materials. The process involves dissolution of sodium silicate precursor in mineral acid (H_2SO_4 , HCl) followed by hydrolysis and aging to produce silica gel which is further dried and calcined to produce aluminosilicate geopolymer (Hench and West, 1990). The sol-gel method proceeds through a polymerization mechanism where the dissolved species of Si and Al form polymeric bonds of Si-O-Si and Si-O-Al and forms a long-chain polymeric gel in an acidic solution (Dimas et al., 2009; Giannopoulou and Panias, 2010). Silicic acid exists as isolated molecules in the form of monosilicic acid ($\text{Si}(\text{OH})_4$) and as linked molecules called polysilicic acid. As a function of time, polymerization degree reduces, and polymers decompose into short-chain species, which are stable and relatively easy to filter. The transformation of long-chain polymeric species to monomeric species and respective filtration ability is highly dependent on the pH of the solution, aging time, ionic strength, and other dissolved species (Dietzel, 2000).

Table 1. Chemical composition of bauxite residue, neutralized solid and HCl leach liquor.

Sample	Quantity	Unit	Ca	Si	Ti	Na	Fe	Al	Sc	V
Bauxite residue	130 g	%	2.31	5.01	3.67	6.98	21.44	10.21	0.0016	0.11
HCl residue	87.8 g	%	0.25	3.02	5.25	0.71	31.61	9.20	0.0022	0.15

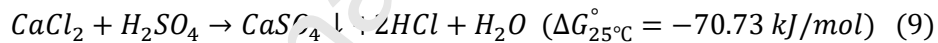
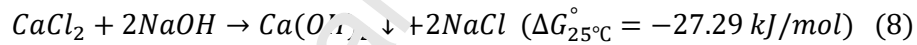
HCl solution	1000 mL	ppm	2882.8 2	3517.0 2	47.7 1	8711.0 4	197.2 3	5309.2 0	0.06	8.2 9
Dissolution value (%)			92.68	59.25	1.30	93.12	0.33	39.09	4.59	3.5 1



The silica gelation method was applied to the HCl leach liquor to precipitate and separate silica, followed by recovery of Al and Ca. The pH of the solution was adjusted to approx. 3 followed by aging for polymerization of silica. It was observed that after aging for 1 day the concentration of Si in Al precipitate was 2.02 % and decreased to 0.06 % after 3 days. The pH 6 precipitate obtained from 3-day aged solution yielded Al precipitate with minor impurities (< 0.5 %) of Ca, Si and Na. The pH 3 precipitate is mainly composed of Si (25 – 30 %) along with Na (~ 2.5 %) and Al (7 – 9 %). Association of Al in the Si-O-Al polymeric chain results in coprecipitation and loss of Al values. More than 99 % Si was precipitated at pH 3 condition along with 21.4 % of dissolved Al. Furthermore, Al was completely precipitated at pH 6 while retaining Ca and Na in the solution. The XRD spectrum and chemical analysis of pH 3 (silica) and calcined pH 6 precipitate are shown in Fig. 2 (b). pH 3 precipitate shows a characteristic broad peak of amorphous silica at a 2-theta value of approx. 25°, whereas calcined pH 6 precipitate shows peaks corresponding to alumina (Al₂O₃).

The solution obtained after Si and Al separation consist of approx. 2799.09 ppm Ca and 8634.11 ppm Na as the major elements. Recovery of Ca was attempted through three routes: precipitation as sulfate, hydroxide, and carbonate. The chemical reaction and respective Gibbs free energy for the reactions are shown in Eq. (7-9). The addition of sulfuric acid to the solution resulted in the precipitation of calcium sulfate, while the addition of NaOH generated calcium hydroxide precipitate. Precipitation in the form of carbonate using CO₂ gas was found efficient, with a high

thermodynamic tendency and faster reaction rate at moderate pH conditions. The CO_2 gas reacts with water to form carbonic acid (H_2CO_3), further dissociating to $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$ at $\text{pK}_{a1} = 6.35$, $\text{pK}_{a2} = 10.2$ respectively at 25°C (Marin Rivera and Van Gerven, 2020). The carbonate and bicarbonate ions react with dissolved species to form carbonate salts. Furthermore, the carbonation process has an additional advantage of carbon sequestration and will help reduce greenhouse gas emissions with a carbonation capacity of 17 kg CO_2 per ton of bauxite residue. The XRD spectrum of Ca precipitate obtained after sulfation, carbonation, and hydroxyl precipitation shows the presence of calcium sulfate, carbonate, and hydroxide, respectively, as shown in Fig. 2 (c). Almost all the Ca was recovered as calcium carbonate after 30 min carbonation, and the filtered solution consists of Na (8510.1 ppm) as the only dissolved species in the form of chloride. The solution pH was approx. 7 and can be processed through a desalination unit to separate NaCl and reuse water for acid neutralization. The leaching of bauxite residue with mild HCl provides the dual advantage of neutralization and recovery of value-added side products, including aluminosilicate geopolymer, ceramic grade alumina, and high purity calcium carbonate.



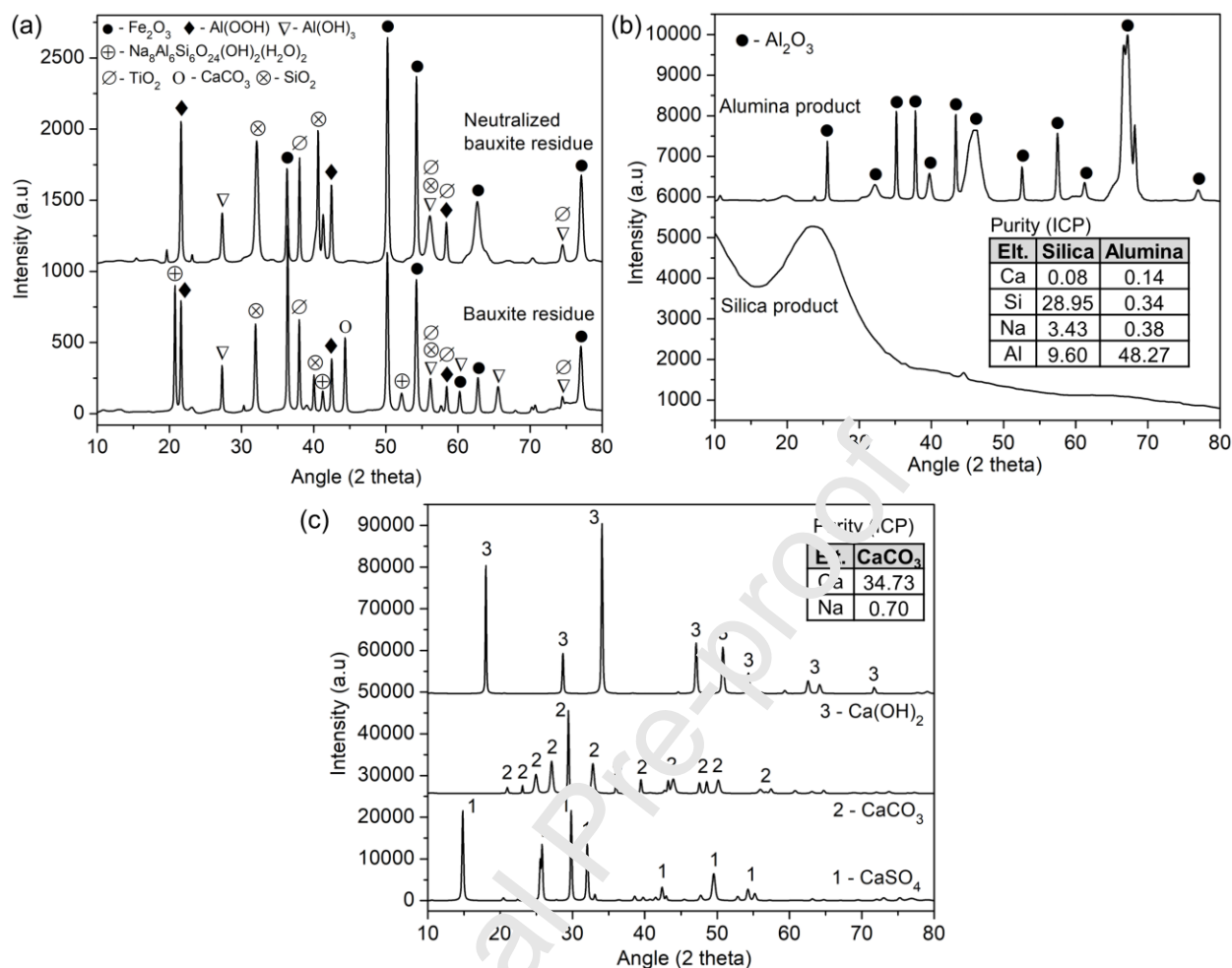


Fig. 2. (a) XRD spectrum of bauxite residue and neutralized solid, (b) XRD spectrum of pH 3 (silica) and calcined pH 6 precipitate, (c) XRD spectrum of different Ca precipitate.

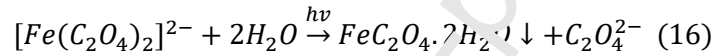
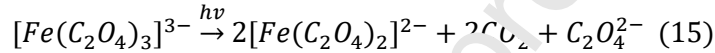
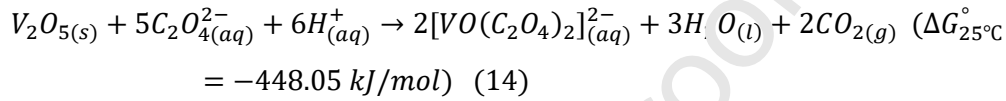
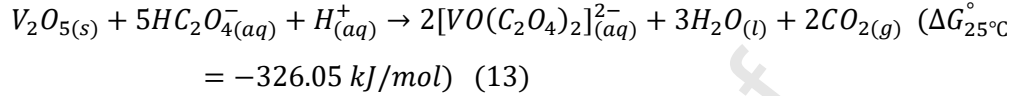
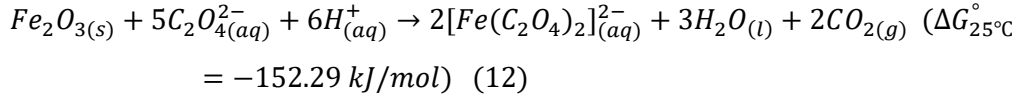
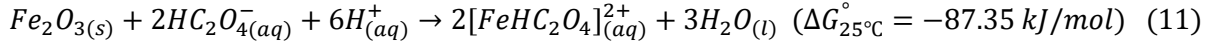
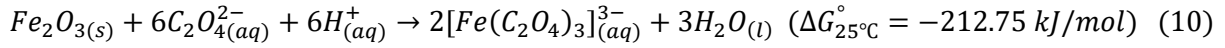
3.2. Fe leaching and precipitation

The neutralized bauxite residue was further leached with oxalic acid to dissolve Fe as ferric oxalate, followed by photochemical reduction of leach liquor to precipitate ferrous oxalate and subsequent decomposition to magnetite. Oxalic acid is an organic acid with a high affinity towards Fe and V due to its chelating ability and stability (Taxiarchou et al., 1997). Oxalic acid dissociated into HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$ at $\text{pH} < 4$ and $\text{pH} > 4$, respectively, and forms a coordination bond with metal ions (such as Fe^{3+} , V^{5+}), resulting in dissolution. The Fe leaching mechanism follows both reductive and non-reductive reaction pathways at different operating conditions, as per the chemical reactions shown in Eq. (10) – (12). The non-reductive reaction pathway involves adsorption of oxalate ion onto the solid particle and desorption of surface ferric ion

complex into the solution and possesses high activation energy. Non-reductive dissolution results in the formation of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ (Eq. (10)) and $[\text{FeHC}_2\text{O}_4]^{2+}$ (Eq. (11)) at high (> 4) and low pH (< 2), respectively. On the other hand, reductive dissolution is favored at lower temperatures and results in the formation of $[\text{Fe}(\text{C}_2\text{O}_4)_2]^{2-}$ complex (Eq. (12)). The reductive mechanism involves generation of ferrous ions via electron transfer from adsorbed complex to surface ferric ion and is a slow process. Based on our previous work and literature findings, the activation energy for dissolution of hematite using oxalic acid was determined as 100 – 150 kJ/mol in the temperature range of 65 to 95 °C following a non-reductive dissolution mechanism (Lee et al., 2006; Salmimies et al., 2012; Tanvar and Mishra, 2021). Both reductive and non-reductive pathways are thermodynamically favored at 25 °C; however, the slower kinetics requires a longer leaching duration; therefore, high-temperature dissolution is preferred to accelerate the kinetics. Furthermore, non-reductive dissolution can be advantageous over reductive dissolution, considering the stability of leach liquor. In reductive dissolution, Fe (II) oxalate can be precipitated from the solution as hydrated ferrous oxalate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) during leaching, thereby decreasing yield. Whereas the non-reductive dissolution results in a stable ferric oxalate solution, which can be further reduced to precipitate ferrous oxalate for clean separation.

On the other hand, V_2O_5 reacts with dissolved oxalic acid species (HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$) through a reductive reaction mechanism to form soluble VO^{2+} complex in the solution as per Eq. (13) and (14). The V species in the leach solution exists as $\text{VO}(\text{C}_2\text{O}_4)_2^{2-}$ with a stable π - π conjugated system between the O-C-O bond of $\text{C}_2\text{O}_4^{2-}$ and V=O bond of VO^{2+} (Hu and Zhang, 2021; Li et al., 2021). Photochemical reaction using UV light was performed to reduce ferric oxalate in the leach solution to ferrous oxalate while retaining V(IV) in the solution. Ferric oxalate ($[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$) is a photochemically active complex and induces a ligand to metal charge transfer under UV irradiation resulting in the formation of $[\text{Fe}(\text{C}_2\text{O}_4)_2]^{2-}$, CO_2 and $\text{C}_2\text{O}_4^{2-}$ ions in the solution as per Eq. (15). $[\text{Fe}(\text{C}_2\text{O}_4)_2]^{2-}$ is further hydrolyzed in the solution according to the reaction shown in Eq. (16) and results in the precipitation of ferrous oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). On the other hand, the thermodynamically stable V(IV) oxalate species in the solution remains dissolved and does not precipitate with Fe(II) oxalate. During the photochemical reduction process, electron transfer from ligand (oxalate) to metal (Fe^{3+}) generates a $\text{C}_2\text{O}_4^{\bullet -}$ free radical anion in the solution, which is extremely unstable and undergoes spontaneous dissociation into CO_2 and $\text{CO}_2^{\bullet -}$. The $\text{CO}_2^{\bullet -}$ anion can further reduce another Fe^{3+}

ion or combine with another CO_2^{2-} anion to form $\text{C}_2\text{O}_4^{2-}$ ion in the solution (Mangiante et al., 2017). Reduced ferrous ion is precipitated, while oxalate ion regenerated remains dissolved.



The leaching experiments were conducted using 2 M oxalic acid solution at 95 °C for 2.5 h and 100 g/L pulp density. The photochemical reduction was performed for 6 h using a 100 W UV lamp. Leaching resulted in the dissolution of approximately 82.4 % Fe, 77.9 % V, 16.9 % Sc, 4.2 % Ti, 12.7 % Si, and 48.5 % Al. Furthermore, after photochemical reduction, more than 99 % of the Fe in the solution was recovered as ferrous oxalate precipitate. In our previous work, leaching with oxalic acid and photochemical reduction process was optimized and thoroughly investigated to recover ferrous oxalate from bauxite residue (Tanvar and Mishra, 2021). The present work focuses on the regeneration of oxalic acid in the leaching circuit with the utilization of waste liquor generated after Fe precipitation. Regeneration of oxalic acid and utilization of waste solution will bolster the recycling process with reduced acid consumption and minimal waste generation. The solution after Fe precipitation was further recycled for the subsequent leaching to utilize the regenerated oxalate ion during reduction. It was found that after one cycle of solution recycling, the leaching of Fe was enhanced from 82.4 % to 90.6 % under the same conditions, while the dissolution of other elements remained the same (approx. 50.3 % Al, 4.7 % Ti, 7.4 % Si).

The dissolution value and extraction yield (precipitation efficiency) at different leaching – precipitation cycles are shown in Fig. 3 (a) and (b). During the solution recirculation

experiments, oxalic acid was found to crystallize out of the reduced solution, depicting that the solution contains an excess of oxalic acid beyond its solubility limit at room temperature (90 g/L). Therefore, after four cycles, no oxalic acid was added to utilize the excess oxalic acid in the solution. It is important to mention that no fresh oxalic acid was added to leaching during cycle number 5 and 9; therefore, the dissolution values obtained are due to regenerated oxalic acid in the solution. Results indicate that approx. 56.3 % of Fe was leached at the fifth cycle and 76.1 % at the ninth cycle without adding any oxalic acid.

The chemical analysis of solution after photochemical reduction at different leaching – precipitation cycles is shown in Fig. 3 (c). The precipitation efficiency of Fe decreased from 99.1 % to 95.7 % after the fifth cycle, and Fe concentration in the solution increased from 220.3 ppm in the first cycle to 1266.1 ppm in the ninth cycle. The increase in the concentration of other ions (mainly Al) in the solution limits the photochemical reduction capacity of Fe. However, the decrease in extraction ratio is very low ($< 4\%$) and does not affect the recovery process to a greater extent providing consistent product purity with reduced acid demand. The Al leaching was found consistent throughout the leaching cycles with approx. 45 – 50 % Al dissolution and was collectively recovered in the solution after ferrous oxalate precipitation. The concentration of Al was increased from 3595.5 ppm during the first cycle to approx. 15113.2 ppm at the end of the ninth cycle. The dissolved Al can be further recovered through pH adjustment and an ion exchange process for additional alumina recovery. The concentration of V increased from 58.4 ppm during the first cycle to 120.1 ppm during the second cycle and further saturated in the solution at approx. 141.8 ppm after the fourth cycle. The solution after nine cycles consists of 659.0 ppm Ca, 108.1 ppm Si, 1579.4 ppm Ti, 332.5 ppm Na, 1266.1 ppm Fe, 173.4 ppm V and 15113.2 ppm Al.

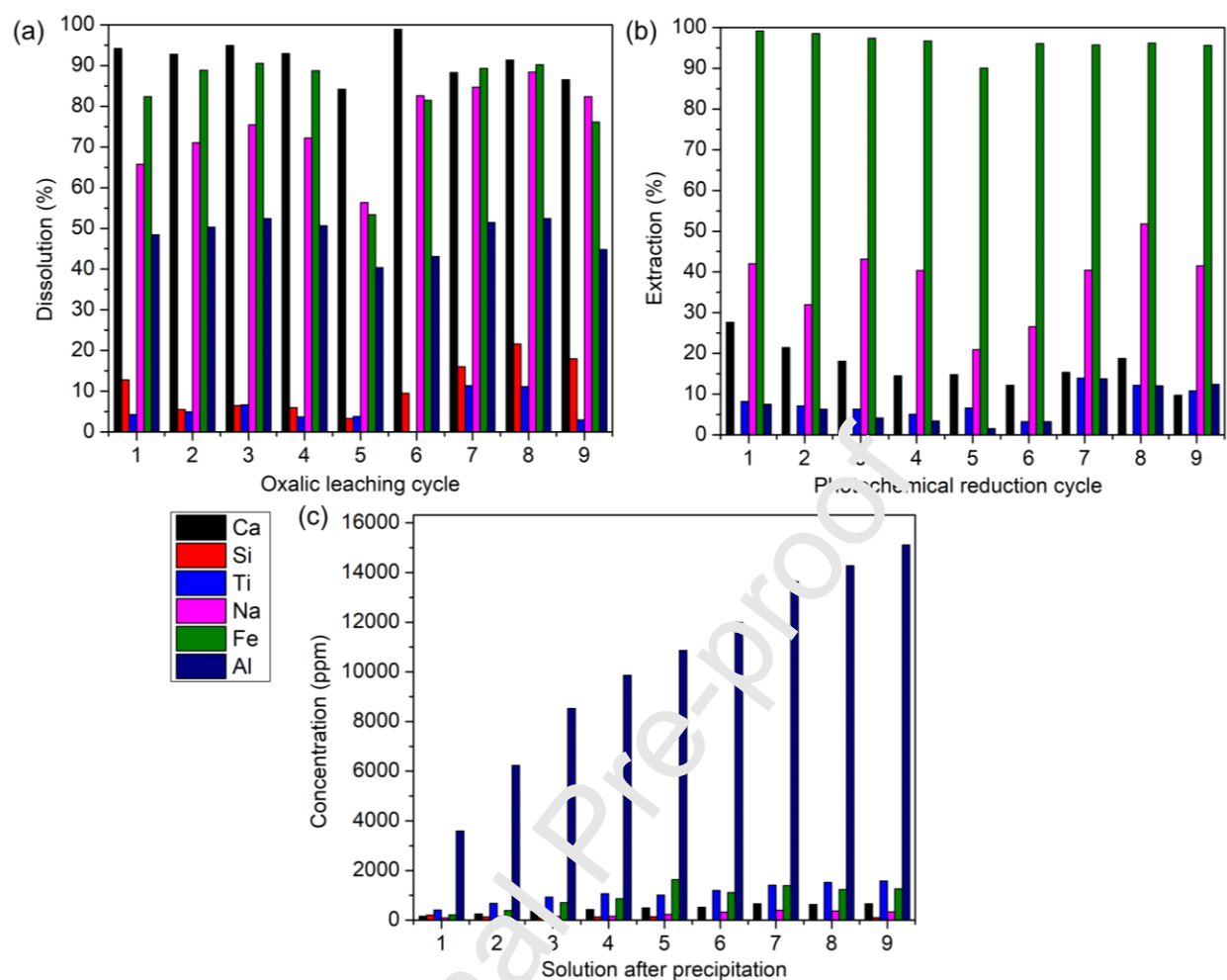


Fig. 3. (a) Dissolution value during leaching with oxalic acid, (b) Fe precipitation efficiency, (c) Solution concentration after precipitation.

The chemical composition and XRD spectra of oxalic acid leaching residue and ferrous oxalate precipitate at different leaching – precipitation cycles are shown in Fig. 4 (a - d). The residue at different cycles consists of approx. 11 – 14 % Ti, 10 – 12 % Al, 4 – 6 % Si and 8 – 10 % Fe as major elements. XRD spectra show the presence of boehmite, anatase and rutile as the major phases. Peaks corresponding to hematite and gibbsite were not identified in the residue, reflecting complete dissociation during leaching. The chemical analysis of ferrous oxalate precipitate indicates consistent purity throughout the solution recycling experiments with less than 1 % of Na, Ca, and Al impurities. The XRD spectrum of precipitate confirms the presence of orthorhombic crystals of ferrous oxalate.

The photochemical reduction was found successful in selective recovery of high purity ferrous oxalate and regenerating oxalic acid in the process further utilized with solution reuse. Based on the calculations, oxalic acid demand was decreased up to 30 % during each cycle of solution recycling and is significant. Consistent product purity and residue composition throughout the nine cycles presents a great potential to reuse solution providing reduced acid demand, minimal waste generation and a high recovery rate. Furthermore, the isolation and recovery of Ti in the residue and V in the solution after Fe precipitation presents future scope for the recovery of these critical elements.

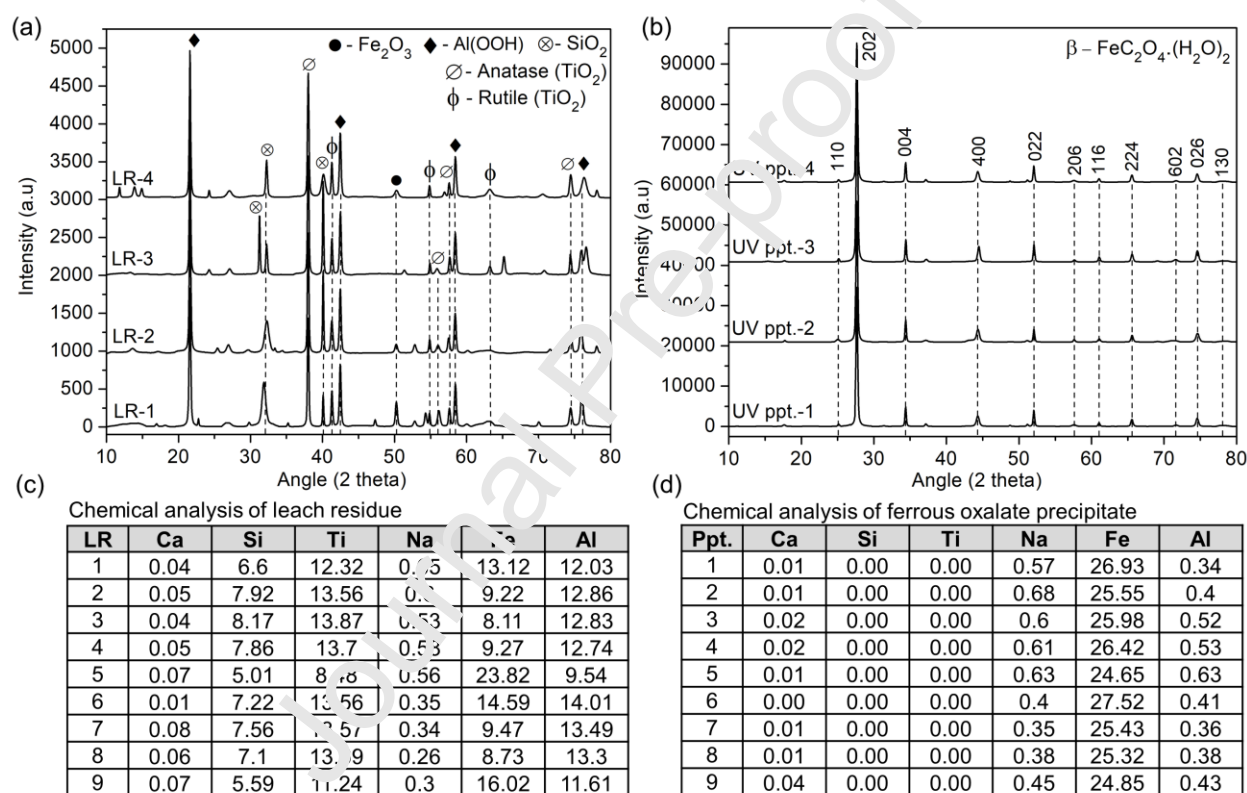


Fig. 4. XRD spectrum of (a) leaching residue and (b) ferrous oxalate precipitate, Chemical analysis of (a) leaching residue and (b) ferrous oxalate obtained at different solution recycling experiments.

3.3. Ferrous oxalate to magnetite decomposition

The ferrous oxalate obtained after photochemical reduction was decomposed in an inert atmosphere to produce magnetite. A low oxygen atmosphere was maintained using a continuous

flow of N_2 in the tube furnace to restrict the oxidation of Fe^{+2} to Fe^{+3} . The thermogravimetric analysis of ferrous oxalate precipitate in the temperature range of 25 – 600 °C under 8 °C /min heating rate and nitrogen atmosphere is shown in Fig. 5. Dehydration and loss of water of crystallization from $FeC_2O_4 \cdot 2H_2O$ results in the formation of FeC_2O_4 up to a temperature of 230 °C. FeC_2O_4 further dissociates into Fe_3O_4 above 230 °C temperature together with gaseous CO and CO_2 . Crystallization of magnetite is accompanied by the decomposition of FeC_2O_4 to iron carbide (Fe_3C) with CO gas above 360 °C. Iron carbide dissociates into Fe and C in the 415 – 535 °C temperature range. In the final stage of reaction, magnetite is reduced to wüstite (FeO) in the presence of CO above 535 °C (Hermanek et al., 2006). Therefore, the decomposition atmosphere is critical for producing desired phases after thermal decomposition. A series of experiments were conducted in the temperature range of 300 – 500 °C for 1 h to identify optimal decomposition conditions. XRD spectrum of decomposition product at different conditions is shown in Fig. 6 (a). The XRD of the sample heated at 600 °C shows the dehydrated ferrous oxalate (FeC_2O_4) phase. Maghemite ($\gamma\text{-}Fe_2O_3$) phase was detected in the 400 °C sample, while magnetite was the primary phase found above 450 °C.

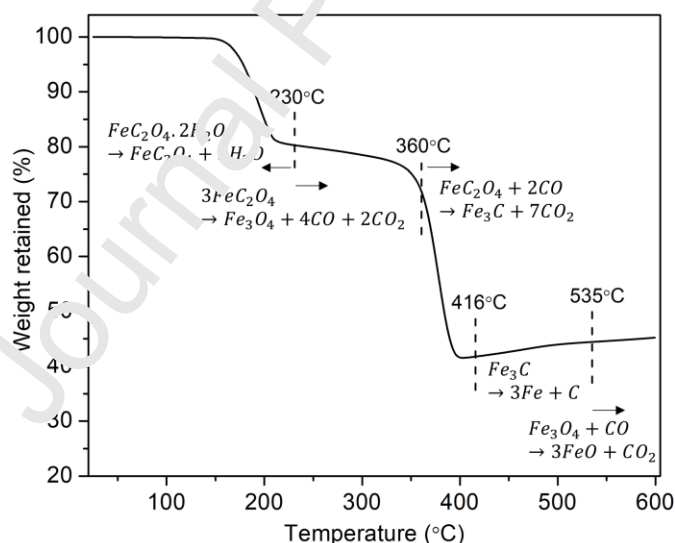


Fig. 5. Thermogravimetric analysis of ferrous oxalate precipitate.

Furthermore, Mössbauer spectroscopy was carried out to determine the quantitative fraction of different Fe phases. The Mössbauer spectra shown in Fig. 6 (b) correspond to different heating conditions, and the stick diagrams show the various phases found in the fitting. The assignment of Fe_3O_4 is based on the isomer shift value. Quantitative analysis (statistical uncertainties of $\pm$

1%) of different phases from Mössbauer data shows that the sample heated at 400 °C shows the presence of maghemite (87 %) as a major phase along with magnetite (13 %). The poor crystallization at low temperature and fine particle size resulted in the formation of maghemite. The sample heated at 450 °C for 1 h consists of 92 % magnetite and 8 % cementite. The cementite content was reduced to about 2 % after heating at 500 °C for 1 h, while magnetite content went up to 98 %.

Vibratory sample magnetometry (VSM) analysis (Fig. 6 (c)) was performed to measure the magnetic properties of the magnetite powder obtained at 500 °C, 1 h decomposition condition. The saturation magnetization of magnetite powder was determined as 80.8 emu/g, while the coercivity was 177 Oe. The high magnetic saturation value shows that the product is highly magnetic and qualifies as a high-grade magnetite product. Furthermore, the average particle size of the magnetite powder was about 16.04 microns determined using laser diffraction particle analyzer.

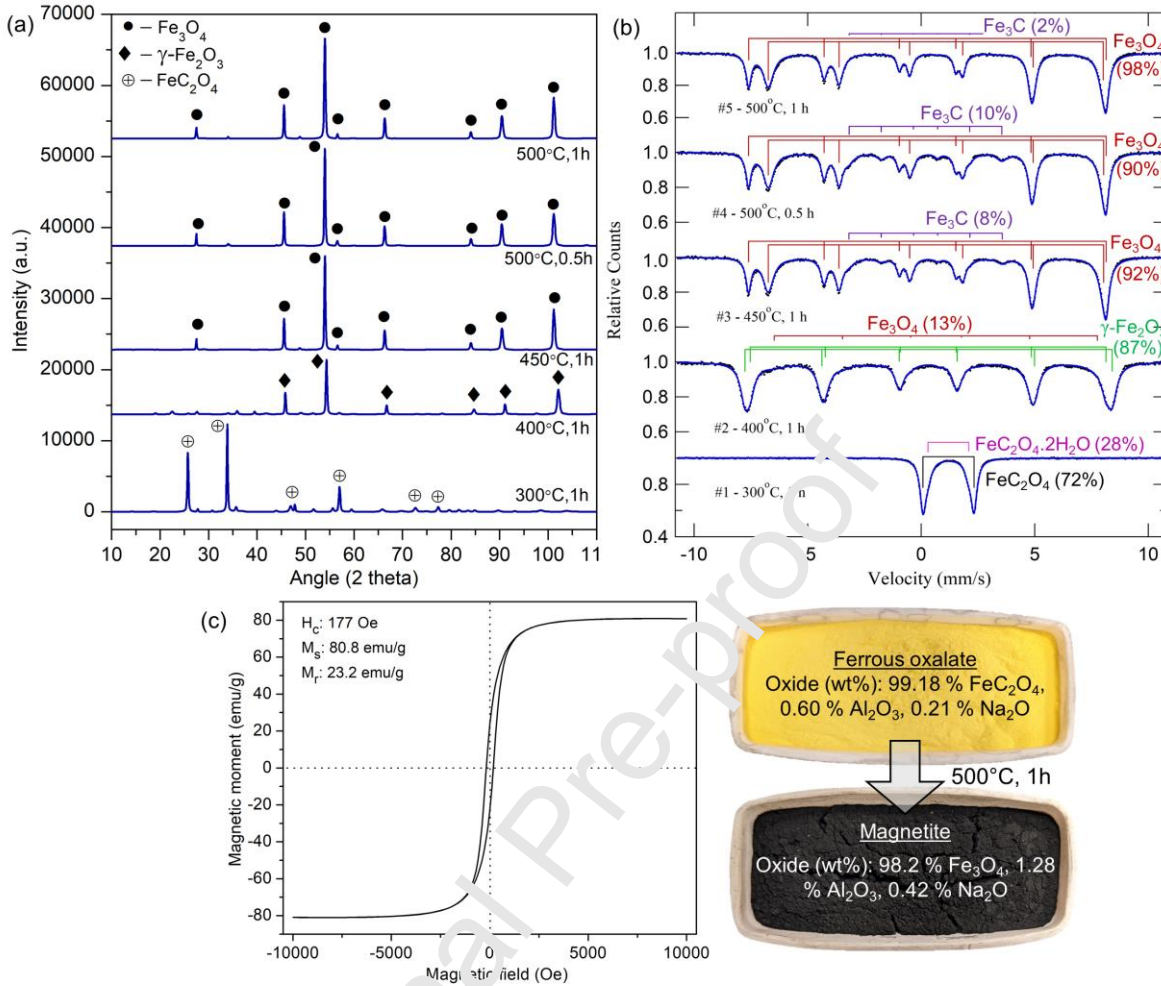


Fig. 6. Characterization of thermal decomposition of ferrous oxalate to magnetite at different temperatures: (a) XRD spectra, (b) Mössbauer spectra, (c) VSM analysis and chemical composition of magnetite at 500 °C, 1 h condition.

3.4. Sulfation baking and hydrolysis for titania recovery

The sulfuric acid leaching process is commercially adopted to process ilmenite ore for Ti recovery. The method includes digestion of ilmenite in 16.7 – 18.4 M sulfuric acid solution, iron crystallization, reduction and Ti hydrolysis to recover hydrated TiO_2 (Han et al., 1987; Liang et al., 2005). The typical processing temperature is in the range of 100 – 200 °C using 13 – 14 M sulfuric acid. The process is successful in the dissociation and dissolution of ilmenite (FeTiO_3) phase; however, TiO_2 phases, including rutile and anatase, behave inert (Dubenko et al., 2020). There are a few studies related to the roasting of high Ti slag with sulfuric acid at high temperature (200 – 500 °C) for Ti dissolution from TiO_2 phase (Sui and Zhai, 2014; Sui et al.,

2015). The studies state that the mass transfer between solid and sulfuric acid increases with an increase in temperature, thereby accelerating the reaction kinetics. The inert nature of TiO_2 phase during sulfuric acid leaching is due to the underlying crystal structure consisting of TiO_6 octahedra, in which each Ti ion is in coordination with six oxygen ions located in the octahedral system. The crystal structure consists of a densely packed oxygen ion plane parallel to the quadruple axis of rutile crystal like a spinel structure and is rigid (Dubenko et al., 2020). The breakage of -Ti-O-Ti- bond induces deformation in the crystal lattice due to the difference in ionic radii of SO_4^{2-} (0.258 nm) and O^{2-} (0.163nm). The large positive charge of Ti(IV) and its relatively large radii than other metal ions (such as Fe, Al) increase the activation energy of the substitution reaction of oxygen ions with other ligands (SO_4^{2-}). Therefore, high temperature is required to meet the additional energy requirement for TiO_2 phase dissociation.

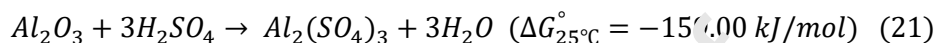
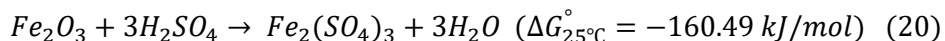
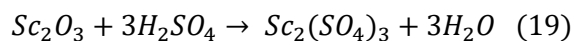
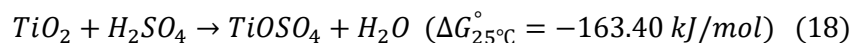
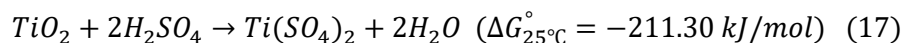
Sulfation baking is a function of the decomposition behavior of sulfuric acid at high temperatures and its reactivity. Sulfuric acid decomposes to H_2O and SO_3 predominantly in the temperature range of 127 – 427 °C. Some amount of gaseous sulfuric acid is also obtained. The second stage of decomposition involves endothermic reduction of SO_3 to SO_2 and is observed at a temperature of more than 750 °C (Schwartz et al., 2000). The main advantage of sulfation baking over direct leaching includes reduced acid demand, fast reaction kinetics and a high reaction rate.

In the context of bauxite residue, sulfation baking is mainly explored, focusing on Sc dissolution. The sulfation baking route involves roasting (120 – 200 °C, 2 – 24 h) of bauxite residue with sulfuric acid to generate metal sulfates and further decomposition of sulfates (except Sc) at high temperatures (600 – 800 °C) and water leaching to dissolve Sc (Agrawal and Dhawan, 2021c; Alkan et al., 2018; Ebra et al., 2016b). The main advantage of sulfation baking and decomposition is better selectivity for Sc dissolution than other metal ions such as Fe, Al, and Ti due to their decomposition at high temperatures. However, the process is not economically viable due to the very low concentration of Sc and high acid requirement due to the presence of other metal ions. Furthermore, Fe, Al, and Ti are neglected in the final residue and does not justify the complete recycling potential. In the present work, recovery of Ti and Sc was attempted after the recovery of major elements, including Fe, Al, and Si. It is worthwhile to mention that Ti and Sc were concentrated in the residue up to 4-fold after recovery of other elements. The residue after leaching with HCl and oxalic acid consists of approx. 10.3 % Si, 15.1

% Ti, 8.9 % Fe, 13.8 % Al and 0.0048 % Sc. Separation and recovery of major components before Ti and Sc recovery presents better selectivity, high reaction rate and reduced acid demand for downstream processing.

The underlying chemical reactions and standard Gibbs free energy for the reaction of different metal oxides present in bauxite residue with sulfuric acid are shown in Eq (17-21). The thermodynamic data shows that the reaction is thermodynamically favored where TiO_2 forms both $\text{Ti}(\text{SO}_4)_2$ and TiOSO_4 phases, with $\text{Ti}(\text{SO}_4)_2$ being more thermodynamically stable. Gibbs free energy for reaction of Sc is not presented due to the unavailability of $\text{Sc}_2(\text{SO}_4)_3$ in the database of FactSage 8.0/ HSC Chemistry 5.1 software. The stoichiometric calculations based on Eq (17-21) show that the required sulfuric acid dosage is 1.1 mL per gram of solid residue for complete reaction. During the experiments, sulfuric acid was added at an excess of 15 % (1.3 mL sulfuric acid per gram solid), considering the decomposition and loss of sulfuric acid at high temperatures. Experimental trials were conducted in the temperature range of 150 – 400 °C for 2 h duration. The sulfated sample was further dissolved in 0.5 M sulfuric acid at 65 °C for 90 min under continuous stirring. Dissolution of Ti requires a pH value less than 1 to prevent hydrolysis and precipitation of Ti as hydrated TiO_2 ; therefore, leaching in mildly acidic conditions was preferred (Hixson and Plechner, 1933). The dissolution of different elements and weight loss during heating are shown in Fig. 7 (a). Weight loss data shows that the weight loss increased gradually up to 300 °C (total weight loss of 34.5%) and further saturated. Rapid weight loss in the lower temperature range corresponds to the loss of water of hydration of sulfuric acid, and decomposition of sulfuric acid to SO_3 and H_2O . The Ti and Sc dissolution increased with an increase in baking temperature to 250 °C, with the highest dissolution of 89.1 % Ti and 66.1 % Sc at 250 °C. Whereas dissolution of Fe and Al was in the range of 80 – 90 % at all the temperature conditions. Maximum Sc dissolution of 73.9 % was obtained at 400 °C; however, there was no significant increase compared to 250 °C condition (66.1 % dissolution). Therefore, a sulfation temperature of 250 °C was considered optimal. The XRD spectra of the sulfated sample and leach residue are shown in Fig. 7 (b). The XRD micrograph of the sulfated sample confirms Ti, Al, and Fe sulfate formed during sulfation after dissociation of rutile, anatase and boehmite phases. The metal sulfates were further dissolved during mild acid leaching, and the final residue consists mainly of the quartz phase. Chemical analysis of residue obtained at different sulfation temperatures is presented in Fig. 7 (c). The chemical analysis of residue

obtained at 250 °C shows that Si (17.4 %) is the major component, along with 3.9 % Ti, 2.5 % Fe, and 2.8 % Al which can be used as a filler material in construction. Furthermore, the leach liquor obtained after filtration was subjected to hydrolysis to recover dissolved Ti values.



Hydrolysis of titanium sulfate solution for TiO_2 recovery is widely employed in the industrial processing of ilmenite ore (Grzmil et al., 2008; Hixson and Plehner, 1933). The typical leach liquor obtained after sulfuric acid leaching of ilmenite and cooling crystallization of excess Fe under vacuum consist of Fe to Ti mass ratio of 0.7 (Zheng et al., 2015). The leach liquor obtained after sulfation baking and leaching at optimized conditions comprised of 12311.01 ppm Ti, 7189.18 ppm Fe, and 7210.11 ppm Al. The low Fe/Ti ratio of 0.57 in the leach liquor eliminates the Fe crystallization requirement and can be directly processed to recover Ti. As per the Pourbaix diagram, Fe in its ferrous oxidation state (Fe^{2+}) is soluble in a broad pH range from highly acidic to a mild alkaline solution, whereas ferric ion (Fe^{3+}) is soluble only in the acidic range with oxidizing conditions ($Eh > 0.7 \text{ V}$) (Monhemius, 2017). Outside these boundary conditions, Fe is insoluble and precipitates as $Fe(OH)_3$ and $Fe(OH)_2$ in acidic and alkaline conditions, respectively. To selectively recover Ti from sulfate leach solution, Fe(III) was first reduced to Fe(II) using Fe filings to prevent coprecipitation with Ti. The hydrolysis experiments without Fe reduction caused Fe precipitation and contaminated the TiO_2 product; therefore, reduction of Fe(III) was necessary. The XRD spectra and chemical composition of hydrated TiO_2 precipitate shown in Fig. 7 (d) depict the effective separation of Ti from the sulfated leach liquor and recovery of pure TiO_2 product. The total recovery of Ti from leach liquor was more than 96 %, with the final solution consisting of 55.10 ppm Ti, 9080.00 ppm Fe, 7190.20 ppm Al and 4.1 ppm Sc.

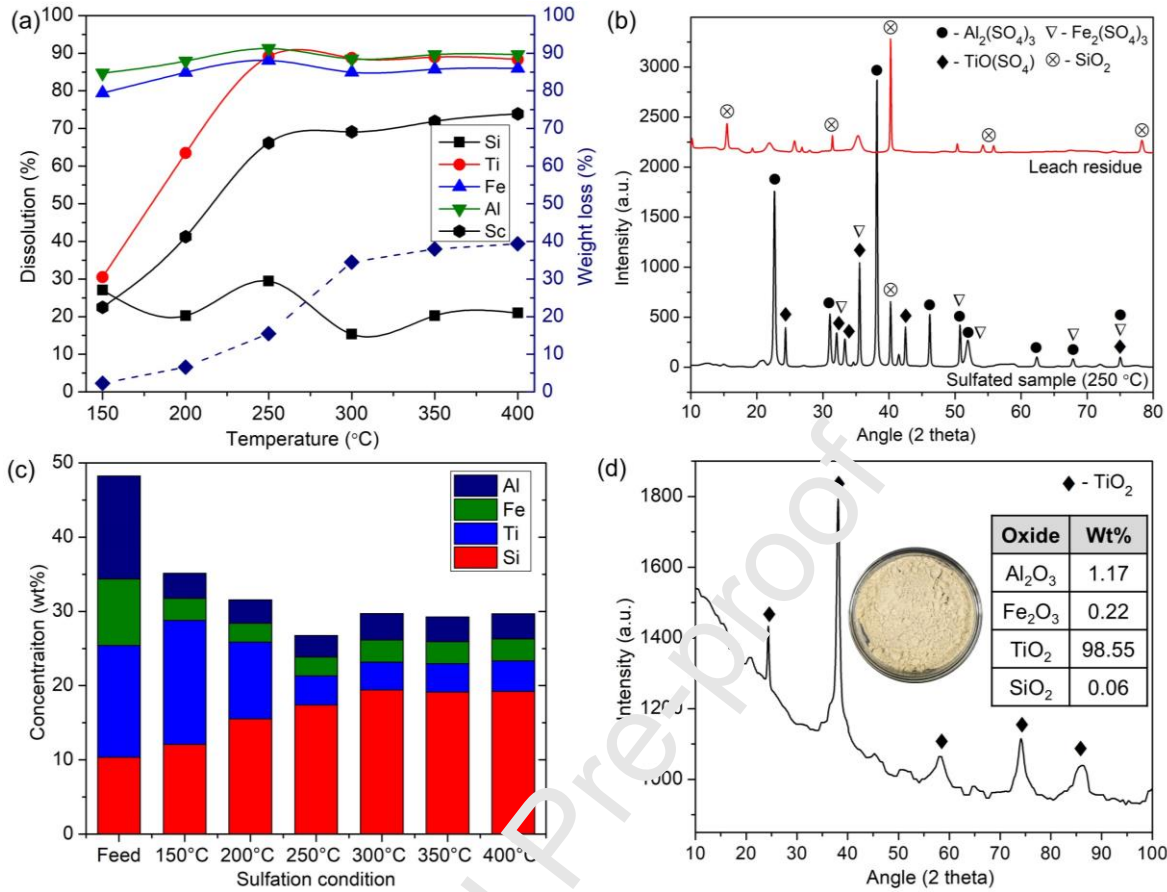


Fig. 7. (a) Dissolution (%) of different elements during sulfation-leaching at different baking temperatures, (b) XRD spectra of sulfated sample and leach residue, (c) Chemical composition of residue at different temperatures, (d) XRD spectrum and chemical analysis of titania product.

3.5. Recovery of critical elements (Sc, V)

Bauxite residue consists of multiple critical elements such as Sc, Ga and V with a concentration equivalent to mineral ores and can be considered a potential feedstock. Direct recovery of these elements is technically feasible but not favored economically due to low concentration (0.001 – 0.012 % RE, 0.001 – 0.011 % Ga, 0.03 – 0.23 % V) (Borra et al., 2016a; Li et al., 2021). Therefore, the concentration needs to be upgraded prior to recovering these elements. Furthermore, subsequent recovery of base metals (Fe, Ti) and critical elements (V, Sc) from bauxite residue will bolster the process economics and provide a comprehensive utilization opportunity. The behavior of Sc and V at different treatment and potential recovery stages in the proposed flowsheet is shown in Fig. 8.

The concentration of V was upgraded from 0.1074 % to 0.1534 % with only 2.5 % V dissolving during HCl leaching. Furthermore, 77.9 % of V was leached along with Fe during leaching with oxalic acid. The photochemical reduction of oxalate leach liquor separated Fe as ferrous oxalate while V remained dissolved in the solution. The solution obtained after precipitation consists of about 173.4 ppm V along with 108.1 ppm Si, 1266.1 ppm Fe, and 15113.2 ppm Al. Based on the literature, solvent extraction using Cyanex 923, and Aliquat 336 is successful in selective recovery of V from acid leach solution containing Al as major impurities (Liu et al., 2020; Wang et al., 2009).

The Sc values were upgraded from 0.0016 % to 0.0048 % in the residue obtained after leaching with oxalic acid. Approx. 66.2 % of Sc was dissolved during sulfation and reported to the final solution after Ti recovery. The concentration of Sc in the final solution was approx. 4.1 ppm and is consistent with the concentration of red mud leachate for Sc recovery processes in literature (Ochsenkühn-Petropoulou et al., 2002). Solvent extraction with the ionic liquid betainium bis(trifluoromethylsulfonyl)imide and adsorption on functionalized chitosan–silica hybrid materials are reported in the literature for recovery of Sc from similar leach liquors of bauxite residue (Onghena et al., 2017; Roosen et al., 2016).

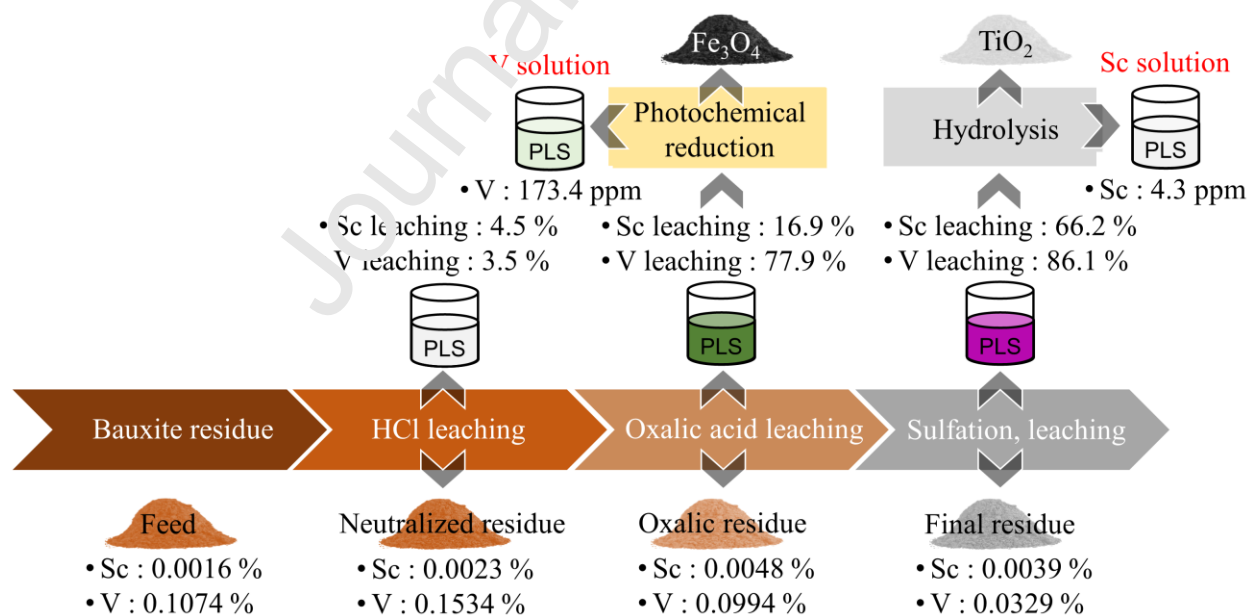


Fig. 8. Concentration and dissolution value of Sc and V at different stages of treatment.

3.6. Overall flowsheet and economic analysis

A complete flowsheet (Fig. 9) for comprehensive recycling of bauxite residue is proposed based on the research work carried out. The chemical composition of the key products presented in Fig. 9 is shown in Table 2. The major elements (Fe, Al, Ti, Si, Ca) associated in bauxite residue are recovered as high purity magnetite, alumina, titania, silica and calcium carbonate. Based on the material balance, it was found that processing one ton of bauxite residue through the proposed flowsheet will result in the recovery of 254 kg magnetite, 53 kg alumina, 62 kg titanium dioxide, 110 kg silica, and 23 kg calcium carbonate. While critical elements including Sc and V are recovered into the solution containing approx. 173.39 ppm V and 4.1 ppm Sc yielding 1200.0 g V_2O_5 and 10.9 g Sc_2O_3 , respectively, after final recovery through solvent extraction/ ion exchange.

A preliminary reagent cost analysis was carried out to assess the economic feasibility of the process. The cost of chemical reagents and marketable products was obtained from online sources such as Alibaba.com. The cost of HCl (37 %), oxalic acid (99 %), H_2SO_4 (98 %), NH_4OH (35 %) and Fe powder (98 %) was considered as \$130.0-160.0/ton, \$400-450/ton, \$80-120/ton, \$150-200/ton, and \$350-400/ton respectively. Whereas, the cost of magnetite, alumina, calcium carbonate, silica, titanium dioxide, vanadium pentoxide, and scandium oxide were considered as \$3000-5000/ton, \$1000-3000/ton, \$150-250/ton, \$10-15/ton, \$2000-5000/ton, \$40000-80000/ton, and \$550000-750000/ton respectively. As per the cost analysis, it was found that approx. +\$252.71 to +\$969.92 profit margin is made per ton of bauxite residue processed through the proposed process. However, it is important to mention that this does not consider the capital and operating expenses. Detailed life cycle assessment analysis is required to assess the economic feasibility of the process. Based on preliminary cost assessment the ranking of different marketable products with high profit margin is magnetite > titanium dioxide > alumina > vanadium pentoxide > scandium dioxide > calcium carbonate > silica. Sc and V oxide are the most critical raw materials within bauxite residue; however, the low concentration of these elements yields less product at the expense of expensive reagents; therefore, recovery of these elements as a byproduct of the base metal recovery process will favor the process economics.

A pictorial representation of the quantity of reagents required and different products generated per ton of bauxite residue is shown in Fig. 10. High purity magnetite possesses application in magnetic resonance imaging, targeted drug delivery systems, photo magnetics, and black

pigment material. Titania is mainly used as white pigment and photocatalyst. Titania can be further processed to produce Ti metal with a wide range of applications in alloys used in the engine, rotor, hydraulic system, compressor blades and nacelle. Alumina is widely utilized in manufacturing high-quality ceramics and can be electrolytically reduced to produce Al metal. Sc is mainly used in Sc-Al alloy for the aerospace industry and is considered a critical raw material for advanced manufacturing. V is used in flow batteries, catalysts, tool steel, and alloys for nuclear reactors.

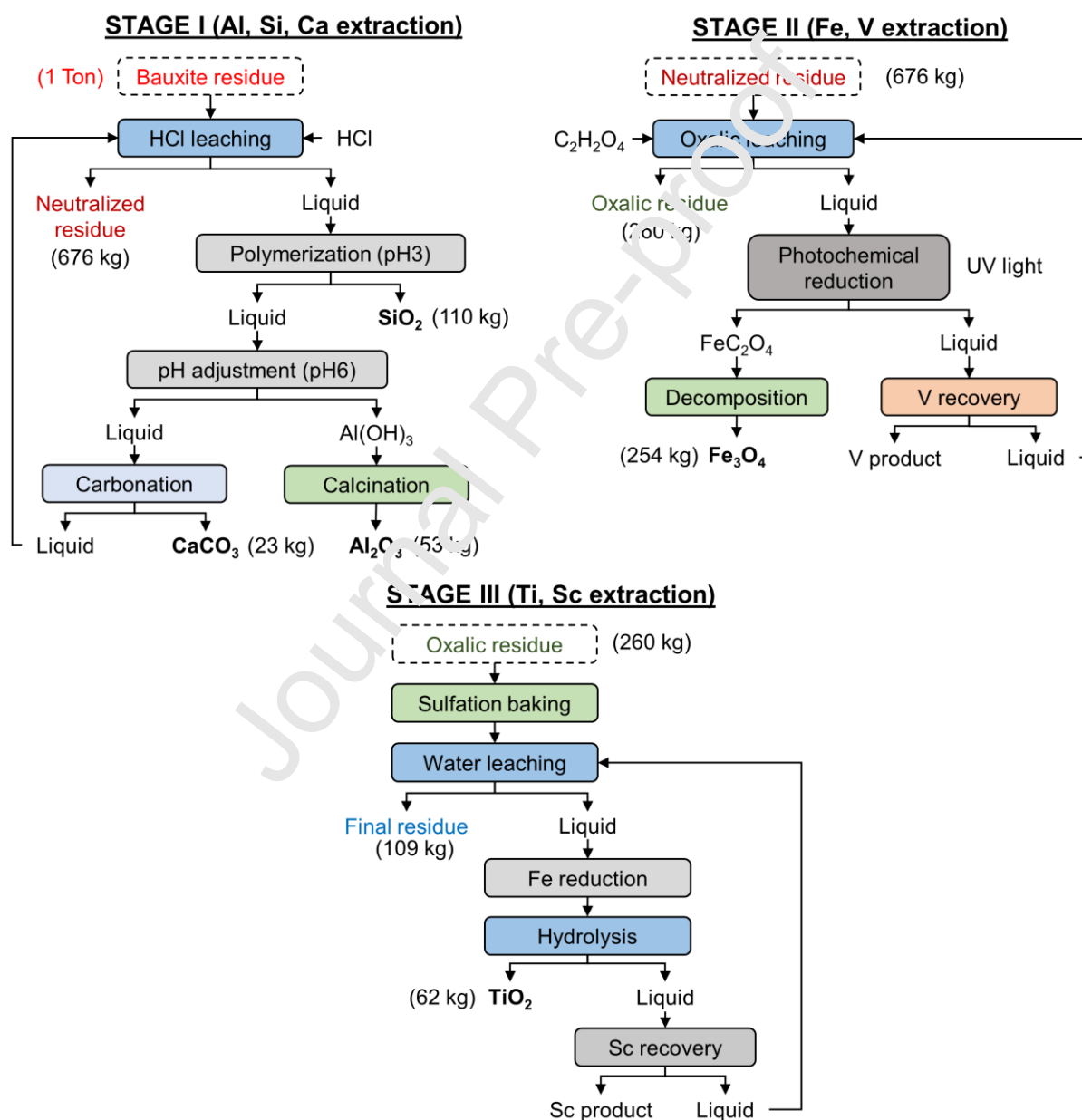


Fig. 9. Experimental flowsheet and material balance for 1 MT bauxite residue.

Table 2. Chemical composition of different samples presented in the flowsheet.

Sample	Quantity	Elt	CaO	SiO ₂	TiO ₂	Na ₂ O	Fe ₂ O ₃	Al ₂ O ₃	V ^X	Sc ^X
SiO ₂	110 kg	%	6.13*	49.67	-	16.70*	-	27.50 ⁺	-	-
Al ₂ O ₃	53 kg	%	0.21	0.79	-	0.55	-	98.45	-	-
CaCO ₃	23kg	%	98.01 ⁼	-	-	1.99	-	-	-	-
Fe ₃ O ₄	254 kg	%	0.01	-	-	0.42	98.22	1.28	-	-
TiO ₂	62 kg	%	-	0.06	98.55	-	0.22	1.17	-	-
Residue	109 kg	%	0.01	70.53	12.29	0.01	6.86	10.32	0.0329	0.0039
HCl waste	7692 L	ppm [#]	51.00*	1.23	-	8510.11*	-	7.92*	-	-
V solution	6760 L	ppm [#]	659.00	108.11	1579.42	332.55	1266.12	15113.21	173.39	0.11
Sc solution	2600 L	ppm [#]	-	-	55.10	-	9000.00	7190.20	-	4.1

*(chloride), ⁺(hydroxide), [#](ion in solution), ⁼(Carbonate)

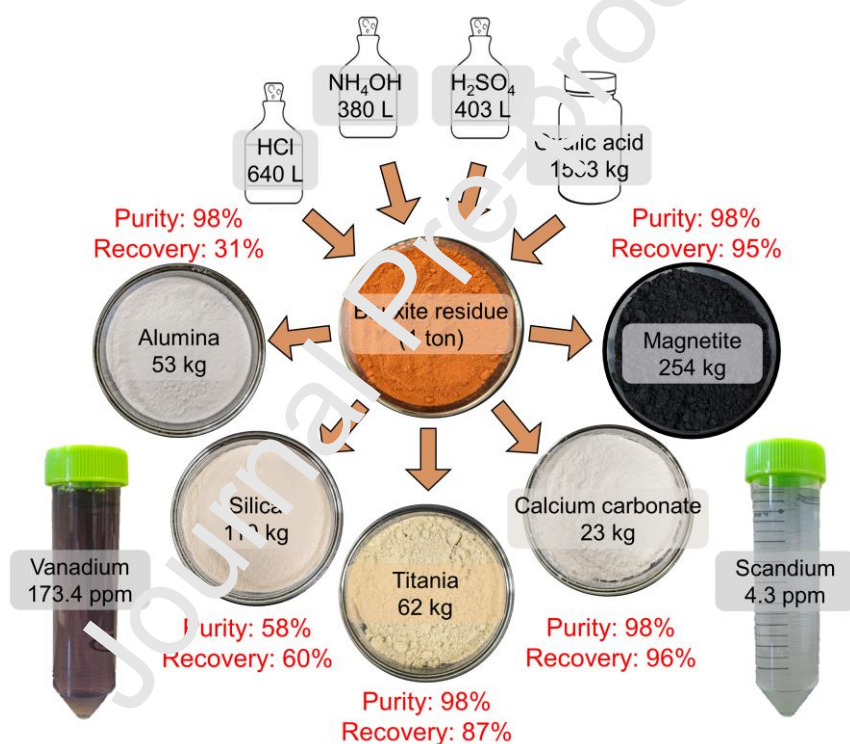


Fig. 10. Sample photographs of products generated and required reagents for the proposed process.

Conclusions

Based on the results presented in this study, the hydrometallurgy-based processing flowsheet was found superior to other processing options in terms of purity and yield of different products. The research findings indicate that the major fraction of bauxite residue (Fe, Ti, Al, Si, Ca) can be

recovered along with critical elements (V, Sc) through the proposed hydrometallurgical process flowsheet. The processing requires hydrochloric acid, sulfuric acid, oxalic acid, and ammonium hydroxide as chemical additives and are widely available on industrial scale. Furthermore, it results in the recovery of major elements of bauxite residue in the form of magnetite (98 % purity, 95 % recovery), alumina (98 % purity, 31 % recovery), titania (98 % purity, 87 % recovery), silica (58 % purity 60 % recovery), and calcium carbonate (98 % purity, 96 % recovery). Furthermore, a liquid stream of dissolved V and Sc is generated to recover critical elements. The proposed flowsheet is sustainable in recycling waste solution in the process, which results in regeneration of leaching reagent and drastically reduces acid demand and waste volume. Preliminary cost analysis shows a positive outlook with value generation of +\$252.71 to +\$969.92 per ton of bauxite residue and contributes to process development for comprehensive utilization of bauxite residue on an industrial scale.

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CRedit author statement

Himanshu Tanvar: Conceptualization, Investigation, Formal analysis, Writing - Original Draft;

Brajendra Mishra: Conceptualization, Validation, Writing - Review & Editing, Supervision

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: